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## Evaluated kinetic and photochemical data for atmospheric chemistry: Part 1 ? gas phase reactions of Ox, HOx, NOx and SOx species

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**Evaluated kinetic and  
photochemical data  
for atmospheric  
chemistry**

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# Evaluated kinetic and photochemical data for atmospheric chemistry: Part 1 – gas phase reactions of $O_x$ , $HO_x$ , $NO_x$ and $SO_x$ species

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## Abstract

This article, the first in the series, presents kinetic and photochemical data evaluated by the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. It covers the gas phase and photochemical reactions of O<sub>x</sub>, HO<sub>x</sub>, NO<sub>x</sub> and SO<sub>x</sub> species, which were last published in 1997, and were updated on the IUPAC website in late 2001. The article consists of a summary sheet, containing the recommended kinetic parameters for the evaluated reactions, and five appendices containing the data sheets, which provide information upon which the recommendations are made.

## 1. Introduction

In the mid 1970s it was appreciated that there was a need for the establishment of an international panel to produce a set of critically evaluated rate parameters for reactions of interest for atmospheric chemistry. To this end the CODATA Task Group on Chemical Kinetics, under the auspices of the International Council of Scientific Unions (ICSU), was constituted in 1977, and its aim was to produce an evaluation of relevant, available kinetic and photochemical data. The first evaluation by this international committee was published in J. Phys. Chem. Ref. Data in 1980 (Baulch et al., 1980), followed by Supplements in 1982 (Baulch et al., 1982) and 1984 (Baulch et al., 1984). In 1986 the IUPAC Subcommittee on Data Evaluation superseded the original CODATA Task Group for Atmospheric Chemistry, and the Subcommittee has continued its data evaluation program with Supplements published in 1989 (Atkinson et al., 1989), 1992 (Atkinson et al., 1992), 1997 (Atkinson et al., 1997a), 1997 (Atkinson et al., 1997b), 1999 (Atkinson et al., 1999), and 2000 (Atkinson et al., 2000). Following the last of these reports, Supplement VIII (Atkinson et al., 2000), the evaluation has continued to be updated and published on the worldwide web (<http://www.iupac-kinetic.ch.cam.ac.uk/>). The IUPAC website hosts an interactive database with a search facility and implemented hyperlinks between the summary table and the data sheets, both of which can be downloaded as

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individual PDF files. In order to further enhance the accessibility of this updated material to the scientific community, it is proposed to publish the evaluation as a series of articles in *Atmospheric Chemistry and Physics*. This will provide free online access and interactive comment on the database content at the ACPD (Discussion) stage, and ultimately hard copy in the form of a printed special issue of the ACP journal.

## 2. Summary of recommended rate coefficients

The ordering of families in the Summary Table is O<sub>x</sub>, HO<sub>x</sub>, NO<sub>x</sub> and SO<sub>x</sub>. Chemical reactions are listed as first reactant (usually an atom or radical) + second reactant (usually a molecule). The reaction ordering within a family is based on where the first reactant lies in the following ranking: 1) atoms (H, O, F, S, Cl, Br, I); 2) radicals a) HO, HO<sub>2</sub>, NH<sub>2</sub>, NO, NO<sub>2</sub>; b) inorganic sulphur radicals; c) organic radicals (C<sub>x</sub>H<sub>y</sub>, C<sub>x</sub>H<sub>y</sub>O, C<sub>x</sub>H<sub>y</sub>O<sub>2</sub>): and 3) closed shell molecules.

Photochemical reactions are listed at the end of each family section.

**Table 1. Summary of recommended rate coefficients**

Reaction	$k_{298}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/K^a$
<b>O<sub>x</sub> Reactions - based on data sheets in Appendix 1</b>					
O + O <sub>2</sub> + M → O <sub>3</sub> + M	6.0 × 10 <sup>-34</sup> [O <sub>2</sub> ]	(k <sub>0</sub> ) ±0.05	6.0 × 10 <sup>-34</sup> (T/300) <sup>-2.6</sup> [O <sub>2</sub> ]	100-300	Δn = ±0.5
	5.6 × 10 <sup>-34</sup> [N <sub>2</sub> ]	(k <sub>0</sub> ) ±0.05	5.6 × 10 <sup>-34</sup> (T/300) <sup>-2.6</sup> [N <sub>2</sub> ]	100-300	Δn = ±0.5
O + O <sub>3</sub> → 2 O <sub>2</sub>	8.0 × 10 <sup>-15</sup>	±0.08	8.0 × 10 <sup>-12</sup> exp(-2060/T)	200-400	±200
O( <sup>1</sup> D) + O <sub>2</sub> → O( <sup>3</sup> P) + O <sub>2</sub>	4.0 × 10 <sup>-11</sup>	±0.05	3.2 × 10 <sup>-11</sup> exp(67/T)	200-350	±100

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Reaction	$k_{298}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$\Delta \log k_{298}^a$	Temp. dependence of $k$ /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp. range/K	$\Delta(E/R)/K^a$
$O(^1D) + O_3 \rightarrow O_2 + 2 O(^3P)$	$1.2 \times 10^{-10}$	$\pm 0.1$			
$\rightarrow 2 O_2(^3\Sigma_g^-)$	$1.2 \times 10^{-10}$	$\pm 0.1$	$2.4 \times 10^{-10}$	100-400	$\Delta \log k = \pm 0.05$
$O_2 + O_3 \rightarrow O + 2 O_2$	See data sheet				
$O_2(^3\Sigma_g^-, v) + M \rightarrow O_2(^3\Sigma_g^-, v') + M$	See data sheet				
$O_2(^1\Delta_g) + M \rightarrow O_2(^3\Sigma_g^-) + M$	$1.6 \times 10^{-18}$ $\leq 1.4 \times 10^{-19}$ $5 \times 10^{-18}$ $\leq 2 \times 10^{-20}$	(M = O <sub>2</sub> ) $\pm 0.2$ (M = N <sub>2</sub> ) $\pm 0.3$ (M = H <sub>2</sub> O) $\pm 0.3$ (M = CO <sub>2</sub> ) $\pm 0.3$	$3.0 \times 10^{-18} \exp(-200/T)$	100-450	$\pm 200$
$O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$	$3.8 \times 10^{-15}$	$\pm 0.10$	$5.2 \times 10^{-11} \exp(-2840/T)$	280-360	$\pm 500$
$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^3\Sigma_g^-) + M$	$4.1 \times 10^{-17}$	(M = O <sub>2</sub> ) $\pm 0.3$			
$\rightarrow O_2(^1\Delta_g) + M$	$2.1 \times 10^{-15}$ $8.0 \times 10^{-14}$ $4.6 \times 10^{-12}$ $4.1 \times 10^{-13}$	(M = N <sub>2</sub> ) $\pm 0.10$ (M = O(^3P)) $\pm 0.3$ (M = H <sub>2</sub> O) $\pm 0.3$ (M = CO <sub>2</sub> ) $\pm 0.10$	$2.1 \times 10^{-15}$	200-350	$\pm 200$
$O_2(^1\Sigma_g^+) + O_3 \rightarrow 2O_2 + O$	See data sheet		$4.1 \times 10^{-13}$	245-360	$\pm 200$
$\rightarrow O_2(^1\Delta_g) + O_3$	$2.2 \times 10^{-11}$	$\pm 0.06$	$2.2 \times 10^{-11}$	295-360	$\pm 300$
$\rightarrow O_2(^3\Sigma_g^-) + O_3$					
$O_2 + hv \rightarrow$ products	See data sheet				
$O_3 + hv \rightarrow$ products	See data sheet				

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Reaction	$k_{298}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/K^a$
<b><i>HO<sub>x</sub> Reactions - based on data sheets in Appendix 2</i></b>					
H + HO <sub>2</sub> → H <sub>2</sub> + O <sub>2</sub>	$5.6 \times 10^{-12}$	±0.5	$5.6 \times 10^{-12}$	245-300	$\Delta \log k = \pm 0.5$
→ 2 HO	$7.2 \times 10^{-11}$	±0.1	$7.2 \times 10^{-11}$	245-300	$\Delta \log k = \pm 0.1$
→ H <sub>2</sub> O + O	$2.4 \times 10^{-12}$	±0.5	$2.4 \times 10^{-12}$	245-300	$\Delta \log k = \pm 0.5$
H + O <sub>2</sub> + M → HO <sub>2</sub> + M	$5.4 \times 10^{-32}[\text{N}_2]$	( $k_o$ ) ±0.1	$5.4 \times 10^{-32}(T/300)^{-1.8}[\text{N}_2]$	200-600	$\Delta n = \pm 0.6$
	$7.5 \times 10^{-11}$	( $k_\infty$ ) ±0.3	$9.5 \times 10^{-11} \exp(T/300)^{0.44}$	200-2000	$\Delta n = \pm 0.6$
	$F_c = 0.50$	$\Delta F_c = \pm 0.15$	$F_c = 0.5$	200-2000	
O + HO → O <sub>2</sub> + H	$3.5 \times 10^{-11}$	±0.1	$2.4 \times 10^{-11} \exp(110/T)$	150-500	±100
O + HO <sub>2</sub> → HO + O <sub>2</sub>	$5.8 \times 10^{-11}$	±0.08	$2.7 \times 10^{-11} \exp(224/T)$	220-400	±100
O + H <sub>2</sub> O <sub>2</sub> → HO + HO <sub>2</sub>	$1.7 \times 10^{-15}$	±0.3	$1.4 \times 10^{-12} \exp(-2000/T)$	280-390	±1000
O( <sup>1</sup> D) + H <sub>2</sub> → HO + H	$1.1 \times 10^{-10}$	±0.1	$1.1 \times 10^{-10}$	200-350	±100
O( <sup>1</sup> D) + H <sub>2</sub> O → 2 HO	$2.2 \times 10^{-10}$	±0.1	$2.2 \times 10^{-10}$	200-350	±100
HO + H <sub>2</sub> → H <sub>2</sub> O + H	$6.7 \times 10^{-15}$	±0.1	$7.7 \times 10^{-12} \exp(-2100/T)$	200-450	±200
HO + HO → H <sub>2</sub> O + O	$1.48 \times 10^{-12}$	±0.15	$6.2 \times 10^{-14} (T/298)^{2.6} \exp(945/T)$	200-350	±250
HO + HO + M → H <sub>2</sub> O <sub>2</sub> + M	$6.9 \times 10^{-31}[\text{N}_2]$	( $k_o$ ) ±0.1	$6.9 \times 10^{-31} (T/300)^{-0.8}[\text{N}_2]$	200-400	$\Delta n = \pm 0.5$
	$2.6 \times 10^{-11}$	( $k_\infty$ ) ±0.2	$2.6 \times 10^{-11}$	200-400	$\Delta \log k_\infty = \pm 0.2$
	$F_c = 0.50 \pm 0.05$	±0.05	$F_c = 0.50 \pm 0.05$	200-400	
HO + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	$1.1 \times 10^{-10}$	±0.1	$4.8 \times 10^{-11} \exp(250/T)$	250-400	±200
HO + H <sub>2</sub> O <sub>2</sub> → H <sub>2</sub> O + HO <sub>2</sub>	$1.7 \times 10^{-12}$	±0.1	$2.9 \times 10^{-12} \exp(-160/T)$	240-460	±100
HO + O <sub>3</sub> → HO <sub>2</sub> + O <sub>2</sub>	$7.3 \times 10^{-14}$	±0.15	$1.7 \times 10^{-12} \exp(-940/T)$	220-450	±300
HO <sub>2</sub> + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	$1.6 \times 10^{-12}$	±0.15	$2.2 \times 10^{-13} \exp(600/T)$	230-420	±200
HO <sub>2</sub> + HO <sub>2</sub> + M → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub> + M	$5.2 \times 10^{-32}[\text{N}_2]$	±0.15	$1.9 \times 10^{-33} [\text{N}_2] \exp(980/T)$	230-420	±300

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Reaction	$k_{298}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/K^a$
	$4.5 \times 10^{-32} [\text{O}_2]$ See data sheet for effect of H <sub>2</sub> O	$\pm 0.15$			
HO <sub>2</sub> + O <sub>3</sub> → HO + 2 O <sub>2</sub>	$2.0 \times 10^{-15}$	$\pm 0.2$	$2.03 \times 10^{-16} (T/300)^{4.57} \exp(693/T)$	250-340	+500/-100
H <sub>2</sub> O + hν → HO + H	See data sheet				
H <sub>2</sub> O <sub>2</sub> + hν → 2 HO	See data sheet				
<b>NO<sub>x</sub> Reactions - based on data sheets in Appendix 3</b>					
O + NO + M → NO <sub>2</sub> + M	$1.0 \times 10^{-31} [\text{N}_2]$ $3.0 \times 10^{-11}$ $F_c = 0.85$	$(k_o) \pm 0.1$ $(k_\infty) \pm 0.3$	$1.0 \times 10^{-31} (T/300)^{-1.6} [\text{N}_2]$ $3.0 \times 10^{-11} (T/300)^{0.3}$ $F_c = 0.85$	200-300 200-300 200-300	$\Delta n = \pm 0.3$ $\Delta n = \pm 0.3$
O + NO <sub>2</sub> → O <sub>2</sub> + NO	$1.0 \times 10^{-11}$	$\pm 0.06$	$5.5 \times 10^{-12} \exp(188/T)$	220-420	$\pm 80$
O + NO <sub>2</sub> + M → NO <sub>3</sub> + M	$1.3 \times 10^{-31} [\text{N}_2]$ $2.3 \times 10^{-11}$ $F_c = 0.6$	$(k_o) \pm 0.30$ $(k_\infty) \pm 0.2$	$1.3 \times 10^{-31} (T/300)^{-1.5} [\text{N}_2]$ $2.3 \times 10^{-11} (T/300)^{0.24}$ $F_c = 0.6$	200-400 200-400 200-400	$\Delta n = \pm 1$
O + NO <sub>3</sub> → O <sub>2</sub> + NO <sub>2</sub>	$1.7 \times 10^{-11}$	$\pm 0.3$			
O( <sup>1</sup> D) + N <sub>2</sub> + M → N <sub>2</sub> O + M	$2.8 \times 10^{-36} [\text{N}_2]$	$(k_o) \pm 0.5$			
O( <sup>1</sup> D) + N <sub>2</sub> → O( <sup>3</sup> P) + N <sub>2</sub>	$2.6 \times 10^{-11}$	$\pm 0.1$	$1.8 \times 10^{-11} \exp(107/T)$	100-350	$\pm 100$
O( <sup>1</sup> D) + N <sub>2</sub> O → N <sub>2</sub> + O <sub>2</sub>	$4.4 \times 10^{-11}$	$\pm 0.1$	$4.4 \times 10^{-11}$	200-350	$\pm 100$
→ 2 NO	$7.2 \times 10^{-11}$	$\pm 0.1$	$7.2 \times 10^{-11}$	200-350	$\pm 100$
→ O( <sup>3</sup> P) + N <sub>2</sub> O	$< 1.0 \times 10^{-12}$		$< 1.0 \times 10^{-12}$	200-350	
HO + NH <sub>3</sub> → H <sub>2</sub> O + NH <sub>2</sub>	$1.6 \times 10^{-13}$	$\pm 0.1$	$3.5 \times 10^{-12} \exp(-925/T)$	230-450	$\pm 200$
HO + HONO → H <sub>2</sub> O + NO <sub>2</sub>	$6.0 \times 10^{-12}$	$\pm 0.15$	$2.5 \times 10^{-12} \exp(260/T)$	290-380	$\pm 260$
HO + HONO <sub>2</sub> → H <sub>2</sub> O + NO <sub>3</sub>	$1.5 \times 10^{-13}$	(1 bar) $\pm 0.1$	See data sheet		

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HO + HO <sub>2</sub> NO <sub>2</sub> → products	4.7 × 10 <sup>-12</sup>	±0.2	1.9 × 10 <sup>-12</sup> exp(270/T)	240-340	±500
HO + NO + M → HONO + M	7.4 × 10 <sup>-31</sup> [N <sub>2</sub> ] 3.3 × 10 <sup>-11</sup> $F_c = 0.81$	( $k_o$ ) ±0.10 ( $k_\infty$ ) ±0.2	7.4 × 10 <sup>-31</sup> (T/300) <sup>-2.4</sup> [N <sub>2</sub> ] 3.3 × 10 <sup>-11</sup> (T/300) <sup>-0.3</sup> $F_c = \exp(-T/1420)$	200-400 200-400 250-400	$\Delta n = \pm 0.5$ $\Delta \log k_\infty = \pm 0.2$
HO + NO <sub>2</sub> + M → HONO <sub>2</sub> + M	3.3 × 10 <sup>-30</sup> [N <sub>2</sub> ] 1.2 × 10 <sup>-11</sup> $F_c = 0.4$	( $k_o$ ) ±0.1 ( $k_\infty$ ) ±0.3	3.3 × 10 <sup>-30</sup> (T/300) <sup>-3.0</sup> [N <sub>2</sub> ] 4.1 × 10 <sup>-11</sup> $F_c = 0.4$	200-300 200-400 250-400	$\Delta n = \pm 0.5$ $\Delta n = \pm 0.5$
HO + NO <sub>3</sub> → HO <sub>2</sub> + NO <sub>2</sub>	2.0 × 10 <sup>-11</sup>	±0.3			
HO <sub>2</sub> + NO → HO + NO <sub>2</sub>	8.8 × 10 <sup>-12</sup>	±0.1	3.6 × 10 <sup>-12</sup> exp(270/T)	200-400	±100
HO <sub>2</sub> + NO <sub>2</sub> + M → HO <sub>2</sub> NO <sub>2</sub> + M	1.8 × 10 <sup>-31</sup> [N <sub>2</sub> ] 4.7 × 10 <sup>-12</sup> $F_c = 0.6$	( $k_o$ ) ±0.10 ( $k_\infty$ ) ±0.2	1.8 × 10 <sup>-31</sup> (T/300) <sup>-3.2</sup> [N <sub>2</sub> ] 4.7 × 10 <sup>-12</sup> $F_c = 0.6$	220-360 220-360	$\Delta n = \pm 1$ $\Delta n = \pm 1$
HO <sub>2</sub> NO <sub>2</sub> + M → HO <sub>2</sub> + NO <sub>2</sub> + M	1.3 × 10 <sup>-20</sup> [N <sub>2</sub> ] 0.25 $F_c = 0.6$	( $k_o/s^{-1}$ ) ±0.3 ( $k_\infty/s^{-1}$ ) ±0.5	4.1 × 10 <sup>-5</sup> exp(-10650/T)[N <sub>2</sub> ] 4.8 × 10 <sup>-15</sup> exp(-11170/T) $F_c = 0.6$	260-300 260-300 260-300	±500 ±500
HO <sub>2</sub> + NO <sub>3</sub> → products	4.0 × 10 <sup>-12</sup>	±0.2			
NH <sub>2</sub> + O <sub>2</sub> → products	<6 × 10 <sup>-21</sup>				
NH <sub>2</sub> + O <sub>3</sub> → products	1.7 × 10 <sup>-13</sup>	±0.5	4.9 × 10 <sup>-12</sup> exp(-1000/T)	250-380	±500
NH <sub>2</sub> + NO → products	1.6 × 10 <sup>-11</sup>	±0.2	1.6 × 10 <sup>-11</sup> (T/298) <sup>-1.4</sup>	210-500	$\Delta n = \pm 0.5$
NH <sub>2</sub> + NO <sub>2</sub> → products	2.0 × 10 <sup>-11</sup>	±0.2	2.0 × 10 <sup>-11</sup> (T/298) <sup>-1.3</sup>	250-500	$\Delta n = \pm 0.7$
2NO + O <sub>2</sub> → 2 NO <sub>2</sub>	2.0 × 10 <sup>-38</sup> (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	±0.1	3.3 × 10 <sup>-39</sup> exp(530/T)	270-600	±400
NO + O <sub>3</sub> → NO <sub>2</sub> + O <sub>2</sub>	1.8 × 10 <sup>-14</sup>	±0.08	1.4 × 10 <sup>-12</sup> exp(-1310/T)	195-308	±200
NO + NO <sub>2</sub> + M → N <sub>2</sub> O <sub>3</sub> + M	3.1 × 10 <sup>-34</sup> [N <sub>2</sub> ]	( $k_o$ ) ±0.3	3.1 × 10 <sup>-34</sup> (T/300) <sup>-7.7</sup> [N <sub>2</sub> ]	200-300	$\Delta n = \pm 1$

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**Evaluated kinetic and  
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for atmospheric  
chemistry**

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Reaction	$k_{298}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/K^a$
	$7.9 \times 10^{-12}$ $F_c = 0.6$	$(k_\infty)$ $\pm 0.3$	$7.9 \times 10^{-12} (T/300)^{1.4}$	200-300	$\Delta n = \pm 0.5$
$\text{N}_2\text{O}_3 + \text{M} \rightarrow \text{NO} + \text{NO}_2 + \text{M}$	$1.6 \times 10^{-14} [\text{N}_2]$	$(k_0/s^{-1})$ $\pm 0.4$	$1.9 \times 10^{-7} (T/300)^{-8.7} \exp(4880/T) [\text{N}_2]$	225-300	$\pm 200$ $\Delta n = \pm 1$
	$3.6 \times 10^8$ $F_c = 0.6$	$(k_\infty/s^{-1})$ $\pm 0.3$	$4.7 \times 10^{15} (T/300)^{0.4} \exp(-4880/T)$	225-300	$\pm 100$ $\Delta n = \pm 1$
$\text{NO} + \text{NO}_3 \rightarrow 2 \text{NO}_2$	$2.6 \times 10^{-11}$	$\pm 0.1$	$1.8 \times 10^{-11} \exp(110/T)$	220-420	$\pm 100$
$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	$3.5 \times 10^{-17}$	$\pm 0.06$	$1.4 \times 10^{-13} \exp(-2470/T)$	230-360	$\pm 150$
$\text{NO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_4 + \text{M}$	$1.4 \times 10^{-33} [\text{N}_2]$ $1.0 \times 10^{-12}$ $F_c = 0.40$	$(k_0)$ $\pm 0.3$ $(k_\infty)$ $\pm 0.3$	$1.4 \times 10^{-33} (T/300)^{-3.8} [\text{N}_2]$ $1.0 \times 10^{-12}$	300-500 250-300	$\Delta n = \pm 1$ $\Delta \log k = \pm 0.3$
$\text{N}_2\text{O}_4 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_2 + \text{M}$	$6.1 \times 10^{-15} [\text{N}_2]$ $4.4 \times 10^6$ $F_c = 0.40$	$(k_0/s^{-1})$ $\pm 0.3$ $(k_\infty/s^{-1})$ $\pm 0.4$	$1.3 \times 10^{-5} (T/300)^{-3.8} \exp(-6400/T) [\text{N}_2]$ $1.15 \times 10^{16} \exp(-6460/T)$	300-500 250-300	$\pm 500$ $\pm 500$
$\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$	$3.6 \times 10^{-30} [\text{N}_2]$ $1.9 \times 10^{-12}$ $F_c = 0.35$	$(k_0)$ $\pm 0.10$ $(k_\infty)$ $\pm 0.2$	$3.6 \times 10^{-30} (T/300)^{-4.1} [\text{N}_2]$ $1.9 \times 10^{-12} (T/300)^{0.2}$ $F_c = 0.35$	200-300 200-400 200-400	$\Delta n = \pm 0.5$ $\Delta n = \pm 0.6$
$\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$	$1.2 \times 10^{-19} [\text{N}_2]$ $6.9 \times 10^{-2}$ $F_c = 0.35$	$(k_0/s^{-1})$ $\pm 0.2$ $(k_\infty/s^{-1})$ $\pm 0.3$	$1.3 \times 10^{-3} (T/300)^{-3.5} \exp(-11000/T) [\text{N}_2]$ $9.7 \times 10^{14} (T/300)^{0.1} \exp(-11080/T)$ $F_c = 0.35$	200-400 200-300 200-300	$\Delta n = \pm 0.5$ $\Delta n = \pm 0.2$
$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$	$2.5 \times 10^{-22}$				
$\text{N}_2\text{O}_5 + 2\text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{H}_2\text{O}$	$1.8 \times 10^{-39} (\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1})$				

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Reaction	$k_{298}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/K^a$
HONO + $h\nu$ → products	see data sheet				
HONO <sub>2</sub> + $h\nu$ → products	see data sheet				
HO <sub>2</sub> NO <sub>2</sub> + $h\nu$ → products	see data sheet				
NO <sub>2</sub> + $h\nu$ → products	see data sheet				
NO <sub>3</sub> + $h\nu$ → products	see data sheet				
N <sub>2</sub> O + $h\nu$ → products	see data sheet				
N <sub>2</sub> O <sub>5</sub> + $h\nu$ → products	see data sheet				

### SO<sub>x</sub> Reactions - based on data sheets in Appendix 4

O + CS → CO + S	2.1 × 10 <sup>-11</sup>	±0.1	2.7 × 10 <sup>-10</sup> exp(-760/T)	150-300	±250
O + CH <sub>3</sub> SCH <sub>3</sub> → CH <sub>3</sub> SO + CH <sub>3</sub>	5.0 × 10 <sup>-11</sup>	±0.1	1.3 × 10 <sup>-11</sup> exp(409/T)	270-560	±100
O + CS <sub>2</sub> → products	3.7 × 10 <sup>-12</sup>	±0.2	3.3 × 10 <sup>-11</sup> exp(-650/T)	210-500	±100
O + CH <sub>3</sub> SSCH <sub>3</sub> → CH <sub>3</sub> SO + CH <sub>3</sub> S	1.5 × 10 <sup>-10</sup>	±0.3	6.5 × 10 <sup>-11</sup> exp(250/T)	290-570	±100
O + OCS → SO + CO	1.2 × 10 <sup>-14</sup>	±0.2	1.6 × 10 <sup>-11</sup> exp(-2150/T)	230-500	±150
O + SO <sub>2</sub> + M → SO <sub>3</sub> + M	1.4 × 10 <sup>-33</sup> [N <sub>2</sub> ]	( <i>k<sub>o</sub></i> ) ±0.3	4.0 × 10 <sup>-32</sup> exp(-1000/T)[N <sub>2</sub> ]	200-400	±200
S + O <sub>2</sub> → SO + O	2.1 × 10 <sup>-12</sup>	±0.2	2.1 × 10 <sup>-12</sup>	250-430	±200
S + O <sub>3</sub> → SO + O <sub>2</sub>	1.2 × 10 <sup>-11</sup>	±0.3			
Cl + H <sub>2</sub> S → HCl + HS	7.4 × 10 <sup>-11</sup>	±0.1	3.7 × 10 <sup>-11</sup> exp(208/T)	200-430	±100
Cl + OCS → SCl + CO	<1.0 × 10 <sup>-16</sup>				
Cl + CS <sub>2</sub> → products	≤ 4 × 10 <sup>-15</sup>	(1 bar air)			
Cl + CH <sub>3</sub> SH → products	2.0 × 10 <sup>-10</sup>	±0.1	1.2 × 10 <sup>-10</sup> exp(150/T)	190-430	±100
Cl + CH <sub>3</sub> SCH <sub>3</sub> → products	3.3 × 10 <sup>-10</sup>	(1 bar N <sub>2</sub> ) ±0.15			
HO + H <sub>2</sub> S → H <sub>2</sub> O + HS	4.7 × 10 <sup>-12</sup>	±0.08	6.1 × 10 <sup>-12</sup> exp(-80/T)	220-520	±80
HO + SO <sub>2</sub> + M → HOSO <sub>2</sub> + M	4.5 × 10 <sup>-31</sup> [N <sub>2</sub> ]	( <i>k<sub>o</sub></i> ) ±0.3	4.5 × 10 <sup>-31</sup> (T/300) <sup>-3.9</sup> [N <sub>2</sub> ]	200-300	Δ <i>n</i> = ±1

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Reaction	$k_{298}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$		$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/K^a$
	$1.3 \times 10^{-12}$	$(k_\infty)$	$\pm 0.3$	$1.3 \times 10^{-12} (T/300)^{-0.7}$	200-300	$\Delta \log k = \pm 0.3$
	$F_c = 0.525$					
$\text{HOSO}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3$	$4.3 \times 10^{-13}$		$\pm 0.10$	$1.3 \times 10^{-12} \exp(-330/T)$	290-420	$\pm 200$
$\text{HO} + \text{OCS} \rightarrow \text{products}$	$2.0 \times 10^{-15}$		$\pm 0.3$	$1.1 \times 10^{-13} \exp(-1200/T)$	250-500	$\pm 500$
$\text{HO} + \text{CS}_2 + \text{M} \rightarrow \text{HOCS}_2 + \text{M}$	$8 \times 10^{-31} [\text{N}_2]$	$(k_o)$	$\pm 0.5$	$8 \times 10^{-31} [\text{N}_2]$	250-320	$\Delta \log k = \pm 0.5$
	$8 \times 10^{-12}$	$(k_\infty)$	$\pm 0.5$	$8 \times 10^{-12}$	250-300	$\Delta \log k = \pm 0.5$
	$F_c = 0.8$					
$\text{HO} + \text{CS}_2 \rightarrow \text{HS} + \text{OCS}$	$< 2 \times 10^{-15}$					
$\text{HOCS}_2 + \text{M} \rightarrow \text{HO} + \text{CS}_2 + \text{M}$	$4.8 \times 10^{-14} [\text{N}_2]$	$(k_o/s^{-1})$	$\pm 0.5$	$1.6 \times 10^{-6} \exp(-5160/T) [\text{N}_2]$	250-300	$\pm 500$
	$4.8 \times 10^5$	$(k_\infty/s^{-1})$	$\pm 0.5$	$1.6 \times 10^{13} \exp(-5160/T)$	250-300	$\pm 500$
	$F_c = 0.8$					
$\text{HOCS}_2 + \text{O}_2 \rightarrow \text{products}$	$2.8 \times 10^{-14}$		$\pm 0.15$	$2.8 \times 10^{-14}$	240-350	$\Delta \log k = \pm 0.15$
$\text{HO} + \text{CH}_3\text{SH} \rightarrow \text{products}$	$3.3 \times 10^{-11}$		$\pm 0.10$	$9.9 \times 10^{-12} \exp(356/T)$	240-430	$\pm 100$
$\text{HO} + \text{CH}_3\text{SCH}_3 \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{SCH}_3$	$4.8 \times 10^{-12}$		$\pm 0.10$	$1.13 \times 10^{-11} \exp(-253/T)$	240-400	$\pm 150$
$\quad \rightarrow \text{CH}_3\text{S}(\text{OH})\text{CH}_3$	$1.7 \times 10^{-12}$	(1 bar air)	$\pm 0.30$	$1.0 \times 10^{-39} [\text{O}_2] \exp(5820/T) /$ $\{1 + 5.0 \times 10^{-30} [\text{O}_2] \exp(6280/T)\}$	240-360	$\pm 150$
$\text{HO} + \text{CH}_3\text{SSCH}_3 \rightarrow \text{products}$	$2.3 \times 10^{-10}$		$\pm 0.10$	$7.0 \times 10^{-11} \exp(350/T)$	250-370	$\pm 200$
$\text{HO}_2 + \text{H}_2\text{S} \rightarrow \text{products}$	$< 3 \times 10^{-15}$					
$\text{HO}_2 + \text{SO}_2 \rightarrow \text{products}$	$< 1 \times 10^{-18}$					
$\text{HO}_2 + \text{CH}_3\text{SH} \rightarrow \text{products}$	$< 4 \times 10^{-15}$					
$\text{HO}_2 + \text{CH}_3\text{SCH}_3 \rightarrow \text{products}$	$< 5 \times 10^{-15}$					
$\text{NO}_3 + \text{H}_2\text{S} \rightarrow \text{products}$	$< 1 \times 10^{-15}$					
$\text{NO}_3 + \text{CS}_2 \rightarrow \text{products}$	$< 4 \times 10^{-16}$					
$\text{NO}_3 + \text{OCS} \rightarrow \text{products}$	$< 1 \times 10^{-16}$					

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$\text{NO}_3 + \text{SO}_2 \rightarrow \text{products}$	$<1 \times 10^{-19}$				
$\text{NO}_3 + \text{CH}_3\text{SH} \rightarrow \text{products}$	$9.2 \times 10^{-13}$	$\pm 0.15$	$9.2 \times 10^{-13}$	250-370	$\pm 400$
$\text{NO}_3 + \text{CH}_3\text{SCH}_3 \rightarrow \text{CH}_3\text{SCH}_2 + \text{HNO}_3$	$1.1 \times 10^{-12}$	$\pm 0.15$	$1.9 \times 10^{-13} \exp(520/T)$	250-380	$\pm 200$
$\text{NO}_3 + \text{CH}_3\text{SSCH}_3 \rightarrow \text{products}$	$7 \times 10^{-13}$	$\pm 0.3$	$7 \times 10^{-13}$	300-380	$\pm 500$
$\text{HS} + \text{O}_2 \rightarrow \text{products}$	$<4 \times 10^{-19}$				
$\text{HS} + \text{O}_3 \rightarrow \text{HSO} + \text{O}_2$	$3.7 \times 10^{-12}$	$\pm 0.2$	$9.5 \times 10^{-12} \exp(-280/T)$	290-440	$\pm 250$
$\text{HS} + \text{NO} + \text{M} \rightarrow \text{HSNO} + \text{M}$	$2.4 \times 10^{-31} [\text{N}_2]$ $2.7 \times 10^{-11}$ $F_c = 0.6$	$(k_0) \pm 0.3$ $(k_\infty) \pm 0.5$	$2.4 \times 10^{-31} (T/300)^{-2.5} [\text{N}_2]$ $2.7 \times 10^{-11}$	250-300 250-300	$\Delta n = \pm 1$ $\Delta \log k = \pm 0.5$
$\text{HS} + \text{NO}_2 \rightarrow \text{HSO} + \text{NO}$	$6.7 \times 10^{-11}$	$\pm 0.3$	$2.9 \times 10^{-11} \exp(240/T)$	220-420	$\pm 100$
$\text{HSO} + \text{O}_2 \rightarrow \text{products}$	$\leq 2.0 \times 10^{-17}$				
$\text{HSO} + \text{O}_3 \rightarrow \text{products}$	$1.1 \times 10^{-13}$	$\pm 0.2$			
$\text{HSO} + \text{NO} \rightarrow \text{products}$	$<1.0 \times 10^{-15}$				
$\text{HSO} + \text{NO}_2 \rightarrow \text{products}$	$9.6 \times 10^{-12}$	$\pm 0.3$			
$\text{HSO}_2 + \text{O}_2 \rightarrow \text{products}$	$3.0 \times 10^{-13}$	$\pm 0.8$			
$\text{SO} + \text{O}_2 \rightarrow \text{SO}_2 + \text{O}$	$7.6 \times 10^{-17}$	$\pm 0.15$	$1.6 \times 10^{-13} \exp(-2280/T)$	230-420	$\pm 500$
$\text{SO} + \text{O}_3 \rightarrow \text{SO}_2 + \text{O}_2$	$8.9 \times 10^{-14}$	$\pm 0.1$	$4.5 \times 10^{-12} \exp(-1170/T)$	230-420	$\pm 150$
$\text{SO} + \text{NO}_2 \rightarrow \text{SO}_2 + \text{NO}$	$1.4 \times 10^{-11}$	$\pm 0.1$	$1.4 \times 10^{-11}$	210-360	$\pm 100$
$\text{SO}_3 (+ \text{H}_2\text{O}) \rightarrow \text{H}_2\text{SO}_4$	$5.7 \times 10^4 \text{ s}^{-1}$ (at 50% relative humidity)				
$\text{SO}_3 + \text{NH}_3 \rightarrow \text{products}$	$2.0 \times 10^{-11}$ (1 bar)	$\pm 0.2$			
$\text{CS} + \text{O}_2 \rightarrow \text{products}$	$2.9 \times 10^{-19}$	$\pm 0.6$			
$\text{CS} + \text{O}_3 \rightarrow \text{OCS} + \text{O}_2$	$3.0 \times 10^{-16}$	$\pm 0.5$			
$\text{CS} + \text{NO}_2 \rightarrow \text{OCS} + \text{NO}$	$7.6 \times 10^{-17}$	$\pm 0.5$			

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CH <sub>2</sub> SH + O <sub>2</sub> → products	6.6 × 10 <sup>-12</sup>	±0.3			
CH <sub>2</sub> SH + O <sub>3</sub> → products	3.5 × 10 <sup>-11</sup>	±0.3			
CH <sub>2</sub> SH + NO → products	1.5 × 10 <sup>-11</sup>	±0.3			
CH <sub>2</sub> SH + NO <sub>2</sub> → products	4.4 × 10 <sup>-11</sup>	±0.5			
CH <sub>3</sub> S + O <sub>2</sub> + M → CH <sub>3</sub> SOO + M	see data sheet				
CH <sub>3</sub> SOO + M → CH <sub>3</sub> S + O <sub>2</sub> + M	see data sheet				
CH <sub>3</sub> S + O <sub>3</sub> → products	4.9 × 10 <sup>-12</sup>	±0.2	1.15 × 10 <sup>-12</sup> exp(432/T)	259-381	±100
CH <sub>3</sub> S + NO + M → CH <sub>3</sub> SNO + M	3.3 × 10 <sup>-29</sup> [N <sub>2</sub> ]	( <i>k<sub>o</sub></i> ) ±0.3	3.3 × 10 <sup>-29</sup> (T/300) <sup>-4</sup> [N <sub>2</sub> ]	290-450	Δ <i>n</i> = ±2
	4 × 10 <sup>-11</sup>	( <i>k<sub>∞</sub></i> ) ±0.5	4 × 10 <sup>-11</sup>	290-450	Δlog <i>k</i> = ±0.5
	<i>F<sub>c</sub></i> = 0.54		<i>F<sub>c</sub></i> = 0.54		
CH <sub>3</sub> S + NO <sub>2</sub> → CH <sub>3</sub> SO + NO	6.0 × 10 <sup>-11</sup>	±0.15	3.0 × 10 <sup>-11</sup> exp(210/T)	240-350	±200
CH <sub>3</sub> SO + O <sub>3</sub> → products	6.0 × 10 <sup>-13</sup>	±0.3			
CH <sub>3</sub> SO + NO <sub>2</sub> → products	1.2 × 10 <sup>-11</sup>	±0.2			
CH <sub>3</sub> SOO + O <sub>3</sub> → products	<8 × 10 <sup>-13</sup>	(227 K)			
CH <sub>3</sub> SOO + NO → products			1.1 × 10 <sup>-11</sup>	227-256	Δlog <i>k</i> = ±0.3
CH <sub>3</sub> SOO + NO <sub>2</sub> → products			2.2 × 10 <sup>-11</sup>	227-246	Δlog <i>k</i> = ±0.3
CH <sub>3</sub> SO <sub>2</sub> + NO <sub>2</sub> → products	≤1 × 10 <sup>-15</sup>				
CH <sub>3</sub> SCH <sub>2</sub> + O <sub>2</sub> → CH <sub>3</sub> SCH <sub>2</sub> O <sub>2</sub>	5.7 × 10 <sup>-12</sup>	(1 bar) ±0.4			
CH <sub>3</sub> SCH <sub>2</sub> O <sub>2</sub> + NO → CH <sub>3</sub> SCH <sub>2</sub> O + NO <sub>2</sub>	1.2 × 10 <sup>-11</sup>	±0.2	4.9 × 10 <sup>-12</sup> exp(260/T)	260-400	±300
CH <sub>3</sub> SCH <sub>2</sub> O <sub>2</sub> + NO <sub>2</sub> + M → CH <sub>3</sub> SCH <sub>2</sub> O <sub>2</sub> NO <sub>2</sub> + M	9 × 10 <sup>-12</sup>	(1 bar) ±0.5			
CH <sub>3</sub> SCH <sub>2</sub> O <sub>2</sub> + CH <sub>3</sub> SCH <sub>2</sub> O <sub>2</sub> → 2CH <sub>3</sub> SCH <sub>2</sub> O + O <sub>2</sub>	1.0 × 10 <sup>-11</sup>	±0.3			
CH <sub>3</sub> SS + O <sub>3</sub> → products	4.6 × 10 <sup>-13</sup>	±0.3			
CH <sub>3</sub> SS + NO <sub>2</sub> → products	1.8 × 10 <sup>-11</sup>	±0.3			

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$\text{CH}_3\text{SSO} + \text{NO}_2 \rightarrow \text{products}$	$4.5 \times 10^{-12}$	$\pm 0.3$			
$\text{O}_3 + \text{CH}_3\text{SCH}_3 \rightarrow \text{products}$	$< 1 \times 10^{-18}$				
$\text{ClO} + \text{CH}_3\text{SCH}_3 \rightarrow \text{products}$	$9 \times 10^{-15}$	$\pm 0.5$			
$\text{BrO} + \text{CH}_3\text{SCH}_3 \rightarrow \text{products}$	$4.4 \times 10^{-13}$	$\pm 0.3$			
$\text{IO} + \text{CH}_3\text{SCH}_3 \rightarrow \text{products}$	$1.3 \times 10^{-14}$	$\pm 0.2$			

**Data for the following Photochemical Reactions**

$\text{OCS} + h\nu \rightarrow \text{products}$	See data sheet
$\text{CS}_2 + h\nu \rightarrow \text{products}$	See data sheet
$\text{CH}_3\text{SSCH}_3 + h\nu \rightarrow \text{products}$	See data sheet
$\text{CH}_3\text{SNO} + h\nu \rightarrow \text{products}$	See data sheet

<sup>a</sup>The cited uncertainty is an expanded uncertainty corresponding approximately to a 95% confidence limit.

**3. Guide to the data sheets**

The data sheets are principally of two types: (i) those for individual thermal reactions and (ii) those for the individual photochemical reactions.

5 **3.1. Thermal reactions**

The data sheets begin with a statement of the reactions including all pathways which are considered feasible. This is followed by the corresponding enthalpy changes at 298 K, calculated from the enthalpies of formation summarized in the Thermodynamics Data summary.

10 The available kinetic data on the reactions are summarized under two headings: (i) Absolute Rate Coefficients, and (ii) Relative Rate Coefficients. Under these headings,

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we include new data which have been published since the last published IUPAC evaluation as well as the data used in deriving the preferred values. Under both of the headings above, the data are presented as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in a temperature dependent form over a stated temperature range. For bimolecular reactions, the temperature dependence is usually expressed in the normal Arrhenius form,  $k = A \exp(B/T)$ , where  $B = E/R$ . For a few bimolecular reactions, we have listed temperature dependences in the alternative form,  $k = A'T^n$  or  $CT^n \exp(D/T)$ , where the original authors have found this to give a better fit to the data. For pressure dependent combination and dissociation reactions, the non-Arrhenius temperature dependence is used. This is discussed more fully in a subsequent section of this Introduction.

Single temperature data are presented as such and wherever possible the rate coefficient at, or close to, 298 K is quoted directly as measured by the original authors. This means that the listed rate coefficient at 298 K may differ slightly from that calculated from the Arrhenius parameters determined by the same authors. Rate coefficients at 298 K marked with an asterisk indicate that the value was calculated by extrapolation of a measured temperature range which did not include 298 K. The tables of data are supplemented by a series of comments summarizing the experimental details. The following list of abbreviations, relating to experimental techniques, is used in the Techniques and Comments sections:

A - absorption

AS - absorption spectroscopy

CCD - charge coupled detector

CIMS - chemical ionization mass spectroscopy/spectrometric

CL - chemiluminescence

CRDS - cavity ring-down spectroscopy

DF - discharge flow

EPR - electron paramagnetic resonance

F - flow system

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FP - flash photolysis

FTIR - Fourier transform infrared

FTS - Fourier transform spectroscopy

GC - gas chromatography/gas chromatographic

5 HPLC - high-performance liquid chromatography

IR - infrared

LIF - laser induced fluorescence

LMR - laser magnetic resonance

LP - laser photolysis

10 MM - molecular modulation

MS - mass spectrometry/mass spectrometric

P - steady state photolysis

PLP - pulsed laser photolysis

PR - pulse radiolysis

15 RA - resonance absorption

RF - resonance fluorescence

RR - relative rate

S - static system

20 TDLS - tunable diode laser spectroscopy

UV - ultraviolet

UVA - ultraviolet absorption

VUVA - vacuum ultraviolet absorption

For measurements of relative rate coefficients, wherever possible the comments contain the actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient given in the table may be different from that reported by the original author owing to a different choice of rate coefficient of the reference reaction. Whenever possible the reference rate data are those preferred in the present evaluation.

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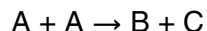
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The preferred rate coefficients are presented (i) at a temperature of 298 K and (ii) in temperature dependent form over a stated temperature range. This is followed by a statement of the uncertainty limits in  $\log k$  at 298 K and the uncertainty limits either in  $(E/R)$  or in  $n$ , for the mean temperature in the range. Some comments on the assignment of uncertainties are given later in this introduction.

The “Comments on Preferred Values” describe how the selection was made and give any other relevant information. The extent of the comments depends upon the present state of our knowledge of the particular reaction in question. The data sheets are concluded with a list of the relevant references.

### 3.2. Conventions concerning rate coefficients

All of the reactions in the table are elementary processes. Thus the rate expression is derived from a statement of the reaction, e.g.



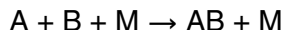
$$-\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A]^2.$$

Note that the stoichiometric coefficient for A, i.e. 2, appears in the denominator before the rate of change of [A] (which is equal to  $2k[A]^2$ ) and as a power on the righthand side.

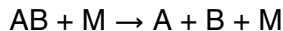
Representations of  $k$  as a function of temperature characterize simple “direct” bimolecular reactions. Sometimes it is found that  $k$  also depends on the pressure and the nature of the bath gas. This may be an indication of complex formation during the course of the bimolecular reaction, which is always the case in combination reactions. In the following sections the representations of  $k$  which are adopted in these cases are explained.

### 3.3. Treatment of combination and dissociation reactions

Unlike simple bimolecular reactions such as those considered in Sect. 1.2, combination reactions



5 and the reverse dissociation reactions



are composed of sequences of different types of physical and chemical elementary processes. Their rate coefficients reflect the more complicated sequential mechanism and depend on the temperature,  $T$ , and the nature and concentration of the third body,  $[M]$ . In this evaluation, the combination reactions are described by a formal second-order rate law:

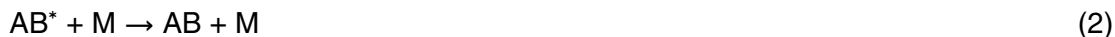
$$\frac{d[AB]}{dt} = k[A][B]$$

while dissociation reactions are described by a formal first-order rate law:

$$\frac{-d[AB]}{dt} = k[AB]$$

15 In both cases,  $k$  depends on the temperature and on  $[M]$ .

In order to rationalize the representations of the rate coefficients used in this evaluation, we first consider the Lindemann-Hinshelwood reaction scheme. The combination reactions follow an elementary mechanism of the form,



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while the dissociation reactions are characterized by:



5 Assuming quasi-stationary concentrations for the highly excited unstable species  $AB^*$  (i.e. that  $d[AB^*]/dt \sim 0$ ), it follows that the rate coefficient for the combination reaction is given by:

$$k = k_1 \left( \frac{k_2[M]}{k_{-1} + k_2[M]} \right)$$

while that for the dissociation reaction is given by:

$$10 \quad k = k_{-2}[M] \left( \frac{k_{-1}}{k_{-1} + k_2[M]} \right)$$

In these equations the expressions before the parentheses represent the rate coefficients of the process initiating the reaction, whereas the expressions within the parentheses denote the fraction of reaction events which, after initiation, complete the reaction to products.

15 In the low pressure limit ( $[M] \rightarrow 0$ ) the rate coefficients are proportional to  $[M]$ ; in the high pressure limit ( $[M] \rightarrow \infty$ ) they are independent of  $[M]$ . It is useful to express  $k$  in terms of the limiting low pressure and high pressure rate coefficients,

$$k_0 = \lim_{[M] \rightarrow 0} k([M]) \quad \text{and,} \quad k_\infty = \lim_{[M] \rightarrow \infty} k([M])$$

respectively. From this convention, the Lindemann-Hinshelwood equation is obtained

$$20 \quad k = \frac{k_0 k_\infty}{k_0 + k_\infty}$$

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It follows that for combination reactions,  $k_0 = k_1 k_2 [M] / k_{-1}$  and  $k_\infty = k_1$ , while for dissociation reactions,  $k_0 = k_{-2} [M]$  and  $k_\infty = k_{-1} k_{-2} / k_2$ . Since detailed balancing applies, the ratio of the rate coefficients for combination and dissociation at a fixed  $T$  and  $[M]$  is given by the equilibrium constant  $K_c = k_1 k_2 / k_{-1} k_{-2}$ .

Starting from the high-pressure limit, the rate coefficients fall-off with decreasing third body concentration  $[M]$  and the corresponding representation of  $k$  as a function of  $[M]$  is termed the “falloff curve” of the reaction. In practice, the above -Hinshelwood expressions do not suffice to characterize the falloff curves completely. Because of the multistep character of the collisional deactivation ( $k_2[M]$ ) and activation ( $k_{-2}[M]$ ) processes, and energy- and angular momentum-dependencies of the association ( $k_1$ ) and dissociation ( $k_{-1}$ ) steps, as well as other phenomena, the falloff expressions have to be modified. This can be done by including a broadening factor  $F$  to the Lindemann-Hinshelwood expression (Troe, 1979):

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty} F = k_0 \left( \frac{1}{1 + \frac{k_0}{k_\infty}} \right) F = k_\infty \left( \frac{\frac{k_0}{k_\infty}}{1 + \frac{k_0}{k_\infty}} \right) F$$

The broadening factor  $F$  depends on the ratio  $k_0/k_\infty$ , which is proportional to  $[M]$ , and can be used as a measure of “reduced pressure”. The first factors on the right-hand side represent the Lindemann-Hinshelwood expression and the additional broadening factor  $F$ , at not too high temperatures, is approximately given by (Troe, 1979):

$$\log F \cong \frac{\log F_c}{1 + [\log(k_0/k_\infty)/N]^2}$$

where  $\log = \log_{10}$  and  $N = [0.75 - 1.27 \log F_c]$ . In this way the three quantities  $k_0$ ,  $k_\infty$ , and  $F_c$  characterise the falloff curve for the present application.

The given approximate expression for the broadening factor  $F$  was obtained from statistical unimolecular rate theory in its simplest form (Troe, 1979). More rigorous representations require detailed information on the potential energy surfaces and on

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the collisional energy transfer step of the reaction. If this information is not available, one may assume typical behaviour and rely on the theoretical analysis given by Cobos and Troe (2003). For  $T = 200\text{--}300\text{ K}$  and the collider  $M = \text{N}_2$  (with a collision efficiency  $\beta_c \approx 0.3$ ), this treatment predicts  $F_c \approx 0.49, 0.44, 0.39,$  and  $0.35$ , if the reactants A and B in total have  $r = 3, 4, 5,$  or  $6$  rotational degrees of freedom, respectively (e.g. for the reaction  $\text{HO} + \text{NO}_2$ , one would have  $r = 5$  and hence  $F_c \approx 0.39$ ). It is also predicted that  $F_c$ , for the present applications, should be nearly temperature independent. Finally, more rigorous expressions for the broadening factors  $F$  are given in Cobos and Troe (2003) which, in general do not differ from the above formula by more than about 10 percent. Since the special properties of each reaction system may lead to some deviations from the given values of  $F_c$ , these should only be used for a first orientation. Larger deviations of experimentally fitted  $F_c$ -values from the given “standard values”, however, may be an indication for inadequate falloff extrapolations to  $k_0$  and  $k_\infty$ . In this case, the apparent values for  $F_c, k_0,$  and  $k_\infty$  obtained by fitting still can provide a satisfactory representation of the considered experimental data, in spite of the fact that inadequate values of  $k_0$  and  $k_\infty$  are obtained by extrapolation.

If a given falloff curve is fitted in different ways, changes in  $F_c$  require changes in the limiting  $k_0$  and  $k_\infty$  values. For the purpose of this evaluation, this is irrelevant if the preferred  $k_0$  and  $k_\infty$  are used consistently together with the preferred  $F_c$  values. If the selected  $F_c$  value is too large, the values of  $k_0$  and  $k_\infty$  obtained by fitting the falloff expression to the experimental data are underestimated. If  $F_c$  is too small,  $k_0$  and  $k_\infty$  are overestimated. However uncertainties in  $F_c$  influence the fitted  $k_0$  and  $k_\infty$  in different ways. A simpler policy of fitting falloff was chosen by the NASA/JPL panel (Sander et al.(2003)) in putting  $F = 0.6$  and  $N = 1$ . This generally leads to different values of the fitted  $k_0$  and  $k_\infty$  and their temperature dependencies than derived here, although experimental data over the range of atmospheric interest can be generally be reproduced equally well. However the derived  $k_0$  and  $k_\infty$  may differ from the true limiting rate coefficients and thus should be interpreted by theory only with caution.

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In the present evaluation, we generally follow the experimentally fitted values for  $F_c$ ,  $k_0$ , and  $k_\infty$ , provided  $F_c$  does not differ too much from the values given above. If large deviations are encountered, the experimental data are re-evaluated using the given  $F_c$ -values given above.

Besides the energy-transfer mechanism, i.e. reactions (1), (-1), and (2), a second mechanism appears to be relevant for some reactions considered here. This is the radical-complex (or chaperon) mechanism



which, in the low pressure range, leads to

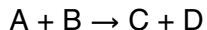
$$k_0 = (k_3/k_{-3})k_4[M].$$

For some tri- and tetra-atomic adducts AB, this value of  $k_0$  may exceed that from the energy-transfer mechanism and show stronger temperature dependencies. This mechanism may also influence high pressure experiments when  $k_0$  from the radical-complex mechanism exceeds  $k_\infty$  from the energy-transfer mechanism (Oum et al., 2003). In this case falloff over wide pressure ranges cannot be represented by contributions from the energy-transfer mechanism alone, in particular when measurements at pressures above about 10 bar are taken into consideration.

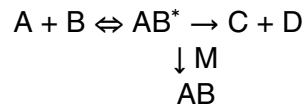
The dependence of  $k_0$  and  $k_\infty$  on the temperature  $T$  is represented in the form:  $k \propto T^{-n}$  except for cases with an established energy barrier in the potential. We have used this form of temperature dependence because it usually gives a better fit to the data over a wider range of temperature than does the Arrhenius expression. It should be emphasised that the chosen form of the temperature dependence is often only adequate over limited temperature ranges such as 200 – 300 K. Obviously, the relevant values of  $n$  are different for  $k_0$  and  $k_\infty$ . In this evaluation, values of  $k_0$  are given for selected examples of third bodies M, and if possible for M = N<sub>2</sub>, O<sub>2</sub> or air.

### 3.4. Treatment of complex-forming bimolecular reactions

Bimolecular reactions may follow the “direct” pathway



and/or involve complex formation,



5

We designate the rate coefficients of the individual steps as in Sect. 1.3, above:



Assuming quasi-stationary concentrations of  $AB^*$  (i.e.  $d[AB^*]/dt \sim 0$ ), a Lindemann-Hinshelwood type of analysis leads to,

$$\frac{d[AB]}{dt} = k_S[A][B]$$

$$\frac{d[C]}{dt} = k_D[A][B]$$

15 
$$\frac{d[A]}{dt} = (k_S + k_D)[A][B]$$

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where

$$k_S = k_1 \left( \frac{k_2}{k_{-1} + k_2 + k_3} \right)$$

$$k_D = k_1 \left( \frac{k_3}{k_{-1} + k_2 + k_3} \right)$$

Note that since  $k_2$  is proportional to  $[M]$ ,  $k_S$  and  $k_D$  are dependent on the nature and concentration of the third body M, in addition to their temperature dependence. In reality, as for the combination and dissociation reactions, the given expressions for  $k_S$  and  $k_D$  have to be extended by suitable broadening factors  $F$  in order to account for the multistep character of process (2) and the energy dependencies of processes (1), (-1) and (3). These broadening factors, however, differ from those for combination and dissociation reactions. For simplicity, they are ignored in this evaluation such that  $k_D$  at high pressure approaches

$$k_D \rightarrow k_1 k_3 / k_2$$

which is inversely proportional to  $[M]$ .  $k_D$  may also be expressed by

$$k_D \approx k_{D0} k_S / k_{S0}$$

where  $k_{D0}$  and  $k_{S0}$  are the respective limiting low-pressure rate coefficients for the formation of C + D or A + B at the considered  $[M]$ . When it is established that complex-formation is involved, this equation is used to characterize the increasing suppression of C + D formation with increasing  $[M]$ .

### 3.5. Photochemical reactions

The data sheets begin with a list of feasible primary photochemical transitions for wavelengths usually down to 170 nm, along with the corresponding enthalpy changes at 0 K

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where possible or alternatively at 298 K, calculated from the data in the Thermodynamic Data summary. Calculated threshold wavelengths corresponding to these enthalpy changes are also listed, bearing in mind that the values calculated from the enthalpy changes at 298 K are not true “threshold values”.

5 This is followed by tables which summarise the available experimental data for: (i) absorption cross-sections and (ii) quantum yields. These data are supplemented by a series of comments.

The next table lists the preferred absorption cross-section data and the preferred quantum yields at appropriate wavelength intervals. For absorption cross-sections the intervals are usually 1 nm, 5 nm or 10 nm. Any temperature dependence of the absorption cross-sections is also given where possible. The aim in presenting these preferred data is to provide a basis for calculating atmospheric photolysis rates. For absorption continua the temperature dependence is often represented by Sulzer-Wieland type expressions (Astholz et al., 1981). Alternately a simple empirical expression of the form:  $\log_{10}(\sigma_{T_1}/\sigma_{T_2}) = B(T_1 - T_2)$  is used.

15 The comments again describe how the preferred data were selected and include other relevant points. The photochemical data sheets are also concluded with a list of references.

### 3.6. Conventions concerning absorption cross-sections

20 These are presented in the data sheets as “absorption cross-sections per molecule, base e.” They are defined according to the equations

$$I/I_0 = \exp(-\sigma x[N]x/l),$$

$$\sigma = \{1/([N]x/l)\} \ln(I_0/I),$$

where  $I_0$  and  $I$  are the incident and transmitted light intensities,  $\sigma$  is the absorption cross-section per molecule (expressed in this paper in units of  $\text{cm}^2$ ),  $[N]$  is the number concentration of absorber (expressed in molecule  $\text{cm}^{-3}$ ), and  $l$  is the path length

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(expressed in cm). Other definitions and units are frequently quoted. The closely related quantities “absorption coefficient” and “extinction coefficient” are often used, but care must be taken to avoid confusion in their definition. It is always necessary to know the units of concentration and of path length and the type of logarithm (base e or base 10) corresponding to the definition. To convert an absorption cross-section to the equivalent Napierian (base e) absorption coefficient (expressed in  $\text{cm}^{-1}$ ) of a gas at a pressure of one standard atmosphere and temperature of 273 K, multiply the value of  $\sigma$  in  $\text{cm}^2$  by  $2.69 \times 10^{19}$ .

### 3.7. Assignment of uncertainties

Under the heading “reliability,” estimates have been made of the absolute accuracies of the preferred values of  $k$  at 298 K and of the preferred values of  $E/R$  over the quoted temperature range. The accuracy of the preferred rate coefficient at 298 K is quoted as the term  $\Delta \log k$ , where  $\Delta \log k = D$  and  $D$  is defined by the equation,  $\log_{10} k = C \pm D$ . This is equivalent to the statement that  $k$  is uncertain to a factor of  $F$ , where  $D = \log_{10} F$ . The accuracy of the preferred value of  $E/R$  is quoted as the term  $\Delta(E/R)$ , where  $\Delta(E/R) = G$  and  $G$  is defined by the equation  $E/R = H \pm G$ .  $D$  and  $G$  are expanded uncertainties corresponding approximately to a 95% confidence limit.

For second-order rate coefficients listed in this evaluation, an estimate of the uncertainty at any given temperature within the recommended temperature range may be obtained from the equation:

$$\Delta \log k(T) = \Delta \log k(298 \text{ K}) + 0.4343\{\Delta E/R(1/T - 1/298)\}$$

The assignment of these absolute uncertainties in  $k$  and  $E/R$  is a subjective assessment of the evaluators. They are not determined by a rigorous, statistical analysis of the database, which is generally too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the techniques, the difficulties of the experimental measurements, the potential for systematic errors, and the number of studies

conducted and their agreement or lack thereof. Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurement, i.e. the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 90% confidence limits, of  $\pm 10\%$  or less are frequently reported in the literature. Unfortunately, when evaluators come to compare data for the same reaction studied by more than one group of investigators and involving different techniques, the rate coefficients often differ by a factor of 2 or even more. This can only mean that one or more of the studies has involved large systematic uncertainty which is difficult to detect. This is hardly surprising since, unlike molecular reactions, it is not always possible to study atomic and free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise.

The arbitrary assignment of uncertainties made here is based mainly on our state of knowledge of a particular reaction which is dependent upon factors such as the number of independent investigations carried out and the number of different techniques used. On the whole, our assessment of uncertainty limits tends towards the cautious side. Thus, in the case where a rate coefficient has been measured by a single investigation using one particular technique and is unconfirmed by independent work, we suggest that minimum uncertainty limits of a factor of 2 are appropriate.

In contrast to the usual situation for the rate coefficients of thermal reactions, where intercomparison of results of a number of independent studies permits a realistic assessment of reliability, for many photochemical processes there is a scarcity of apparently reliable data. Thus, we do not feel justified at present in assigning uncertainty limits to the parameters reported for the photochemical reactions.

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## Appendix 1: O<sub>x</sub> reactions



$$\Delta H^\circ = -106.5 \text{ kJ} \cdot \text{mol}^{-1}$$

### Low-pressure rate coefficients

#### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$6.75 \times 10^{-35} [\text{O}_2] \times \exp[(635 \pm 18)/T]$	262-319	Arnold and Comes, 1979 <sup>1</sup>	FP-RA
$(5.69 \pm 0.40) \times 10^{-34} [\text{O}_2]$	298		
$1.82 \times 10^{-35} [\text{N}_2] \times \exp[(995 \pm 37)/T]$	262-309		
$(5.13 \pm 0.60) \times 10^{-34} [\text{N}_2]$	298		
$(6.9 \pm 1.0) \times 10^{-34} (T/300)^{-(1.25 \pm 0.2)} [\text{O}_2]$	219-368	Klais et al, 1980 <sup>2</sup>	FP-RF
$(6.2 \pm 0.9) \times 10^{-34} (T/300)^{-(2.0 \pm 0.5)} [\text{N}_2]$	219-368		
$(5.69 \pm 0.34) \times 10^{-34} (T/300)^{-(2.37 \pm 0.37)} [\text{O}_2]$	227-353	Lin and Leu, 1982 <sup>3</sup>	FP-RF
$(5.70 \pm 0.19) \times 10^{-34} (T/300)^{-(2.62 \pm 0.18)} [\text{N}_2]$	218-366		
$5.5 \times 10^{-34} (T/300)^{-2.6} [\text{N}_2]$	100-400	Hippler et al., 1990 <sup>4</sup>	PLP-UVA (a)
$5.2 \times 10^{-35} (T/1000)^{-1.3} [\text{N}_2]$	700-900		
$(6.5 \pm 1.1) \times 10^{-34} [\text{N}_2]$	296	Anderson et al., 1997 <sup>5</sup>	(b)

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## Comments

(a) The O<sub>3</sub> product was monitored by UV absorption at 265 nm. Data for  $T > 400$  K are based on dissociation experiments. The reaction is suggested to follow the energy transfer mechanism at high temperatures. The strong temperature dependence observed for low temperatures suggests that a radical-complex mechanism dominates.

(b) Steady-state photolysis of O<sub>2</sub> near 200 Torr monitoring O<sub>3</sub> absorption at 254 nm and following isotopic compositions by molecular beam mass spectrometric sampling. Isotope effects with <sup>16</sup>O and <sup>18</sup>O resolved.

## Preferred Values

$k_o = 5.6 \times 10^{-34} (T/300)^{-2.6} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 100–300 K.

$k_o = 6.0 \times 10^{-34} (T/300)^{-2.6} [\text{O}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 100–300 K.

### Reliability

$\Delta \log k_o = \pm 0.05$  at 298 K.

$\Delta n = \pm 0.5$ .

### Comments on Preferred Values

The preferred values at 300 K are averages of the data from references 1–4, the temperature coefficients are taken from reference 4. The experiments from reference 4 under low temperature and high pressure conditions indicate anomalous falloff behaviour different from the formalism described for the energy transfer mechanism in the

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Introduction. These effects are not relevant for atmospheric conditions as such, and they are not included in this evaluation.

## References

<sup>1</sup>I. Arnold and F. J. Comes, Chem. Phys. 42, 231, 1979.

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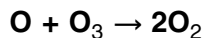
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$$\Delta H^\circ = -391.9 \text{ kJ}\cdot\text{mol}^{-1}$$

### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.1 \times 10^{-11} \exp(-2155/T)$	269-409	McCrum and Kaufman, 1972 <sup>1</sup>	(a)
$2.0 \times 10^{-11} \exp(-2280/T)$	220-353	Davis et al., 1973 <sup>2</sup>	PLP-RF
$8.3 \times 10^{-15}$	298	West et al., 1978 <sup>3</sup>	PLP-RF
$2.12 \times 10^{-11} \exp(-2337/T)$	262-335	Arnold and Comes, 1979 <sup>4</sup>	FP-RA
$5.6 \times 10^{-12} \exp(-1959/T)$	220-377	Wine et al., 1983 <sup>5</sup>	PLP-RF
$8.26 \times 10^{-15}$	297		

### Comments

10 (a) Flow system used with O(<sup>3</sup>P) atoms being produced by the pyrolysis of O<sub>3</sub>.

### Preferred Values

$k = 8.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

15  $k = 8.0 \times 10^{-12} \exp(-2060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-400 K.

### Reliability

$\Delta \log k = \pm 0.08$  at 298 K.

20  $\Delta(E/R) = \pm 200 \text{ K}$ .

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The study of Wine et al.<sup>5</sup> yields values of  $k$  in close agreement with those from other studies, over the whole temperature range covered. Our preferred values are based on the least-squares expression obtained by Wine et al.<sup>5</sup> from a fit of their data plus those of McCrumb and Kaufman,<sup>1</sup> Davis et al.,<sup>2</sup> West et al.<sup>3</sup> and Arnold and Comes.<sup>4</sup> Computed rate constants<sup>6</sup> using variational transition state theory are in satisfactory agreement with the experimental results.

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<sup>2</sup>D. D. Davis, W. Wong, and J. Lephardt, Chem. Phys. Lett., 22, 273, 1973.

<sup>3</sup>G. A. West, R. E. Weston, Jr., and G. W. Flynn, Chem. Phys. Lett., 56, 429, 1978.

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$$\Delta H^\circ (1) = -32.8 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ (2) = -95.4 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ (3) = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.9 \times 10^{-11} \exp[(67 \pm 11)/T]$	104-354	Streit et al., 1976 <sup>1</sup>	(a)
$3.6 \times 10^{-11}$	298		
$(4.2 \pm 0.2) \times 10^{-11}$	295	Amimoto et al., 1979 <sup>2</sup>	PLP-RA (b)
$(4.0 \pm 0.6) \times 10^{-11}$	298	Brock and Watson, 1979 <sup>3</sup>	PLP-RF (b)
<i>Branching Ratios</i>			
$k_1/k = 0.77 \pm 0.2$	300	Lee and Slanger, 1978 <sup>4</sup>	(c)
$k_2/k \leq 0.05$	300	Gauthier and Snelling, 1971 <sup>5</sup>	(d)

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## Comments

- (a) O(<sup>1</sup>D) atoms were produced by flash photolysis of O<sub>3</sub> and detected by O(<sup>1</sup>D) → O(<sup>3</sup>P) emission at 630 nm.
- (b) O(<sup>3</sup>P) atom product detected by resonance absorption<sup>2</sup> or resonance fluorescence.<sup>3</sup>
- 5 (c) O(<sup>1</sup>D) atoms detected by O(<sup>1</sup>D) → O(<sup>3</sup>P) emission at 630 nm. O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) was monitored from the O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) → O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) (1-1) and (0-0) band emission. O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) is only formed in the *v* = 0 and 1 levels, with *k*(1)/*k*(0) = 0.7.
- (d) O(<sup>1</sup>D) atom production by the photolysis of O<sub>3</sub>.

## Preferred Values

10  $k = 4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.  
 $k = 3.2 \times 10^{-11} \exp(67/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-350 K.  
 $k_1/k = 0.8$  at 298 K.  
 $k_2/k \leq 0.05$  at 298 K.

## Reliability

15  $\Delta \log k = \pm 0.05$  at 298 K.  
 $\Delta(E/R) = \pm 100 \text{ K}$ .  
20  $\Delta(k_1/k) = \pm 0.1$  at 298 K.

## Comments on Preferred Values

25 The preferred 298 K rate coefficient is the average of the results from Streit et al.,<sup>1</sup> Amimoto et al.<sup>2</sup> and Brock and Watson.<sup>3</sup> The temperature dependence is that measured by Streit et al.<sup>1</sup> The branching ratios of Lee and Slanger<sup>3</sup> and Gauthier and Snelling<sup>4</sup> are recommended.

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- <sup>3</sup>J. C. Brock and R. T. Watson, Reported at the NATO Advanced Study Institute on Atmospheric Ozone, Portugal (1979). See also G. K. Moortgat, in Report. No. FAA-EE.80-20, 1980.
- <sup>4</sup>L. C. Lee and T. Slanger, J. Chem. Phys., 69, 4053, 1978.
- <sup>5</sup>M. Gauthier and D. R. Snelling, J. Chem. Phys., 54, 4317, 1971.

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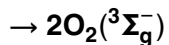
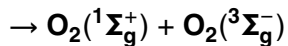
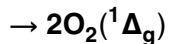
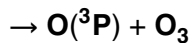
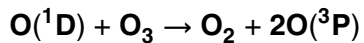
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$$\Delta H^\circ = -83.2 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ = -393.0 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ = -424.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ = -581.6 \text{ kJ}\cdot\text{mol}^{-1}$$

(1)

(2)

(3)

(4)

(5)

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**Rate coefficient data ( $k = k_1 + k_2 + k_3 + k_4 + k_5$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.4 \pm 0.5) \times 10^{-10}$	103-393	Streit et al., 1976 <sup>1</sup>	(a)
$(2.5 \pm 0.5) \times 10^{-10}$	300	Amimoto et al., 1978 <sup>2</sup> ; 1980 <sup>3</sup>	PLP-RA (b)
$(2.28 \pm 0.23) \times 10^{-10}$	298	Wine and Ravishankara, 1981 <sup>4</sup>	PLP-RF (b)
$(2.5 \pm 0.2) \times 10^{-10}$	298	Greenblatt and Wiesenfeld, 1983 <sup>5</sup>	PLP-RF (b)
<i>Branching Ratios</i>			
$k_1/(k_3 + k_4 + k_5) = 1$	~298	Davenport et al., 1972 <sup>6</sup>	FP-RF (b)
$k_1/k = 0.53$	298	Cobos et al., 1983 <sup>7</sup>	(c)
$k_5/k = 0.47$			

**Comments**

(a) O(<sup>1</sup>D) atoms produced by flash photolysis of O<sub>3</sub> in a flow system and detected by emission at 630 nm.

(b) The product O(<sup>3</sup>P) atoms were detected by resonance absorption<sup>2,3</sup> or resonance fluorescence.<sup>4,5</sup>

(c) Steady-state photolysis of pure O<sub>3</sub> and O<sub>3</sub>-inert gas mixtures. Ozone removal was monitored manometrically at high pressures and spectrophotometrically at lower pressures. The quantum yield of O<sub>3</sub> removal was interpreted in terms of a complex reaction scheme.

**Preferred Values**

$k = 2.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 100-400 K.



$k_1/k = k_5/k = 0.5$  at 298 K.

### Reliability

- 5  $\Delta \log k = \pm 0.05$  over the temperature range 100-400 K.  
 $\Delta k_1/k = \Delta k_5/k = \pm 0.1$  at 298 K.

### Comments on Preferred Values

- 10 The recommendation for the rate coefficient is based on the data of Streit et al.,<sup>1</sup> Amimoto et al.,<sup>2,3</sup> Wine and Ravishankara<sup>4</sup> and Greenblatt and Wiesenfeld.<sup>5</sup> The branching ratios are based on these studies plus the work of Davenport et al.<sup>6</sup> and Cobos et al.<sup>7</sup>

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- 15 <sup>1</sup>G. E. Streit, C. J. Howard, A. L. Schmeltekopf, J. A. Davidson, and H. I. Schiff, J. Chem. Phys., 65, 4761, 1976; J. A. Davidson, C. M. Sadowski, H. I. Schiff, G. E. Streit, C. J. Howard, D. A. Jennings, and A. L. Schmeltekopf, J. Chem. Phys., 64, 57, 1976.  
<sup>2</sup>S. T. Amimoto, A. P. Force, and J. R. Wiesenfeld, Chem. Phys. Lett., 60, 40, 1978.  
<sup>3</sup>S. T. Amimoto, A. P. Force, J. R. Wiesenfeld, and R. H. Young, J. Chem. Phys., 73,  
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<sup>5</sup>G. D. Greenblatt and J. R. Wiesenfeld, J. Chem. Phys., 789, 4924, 1983.  
<sup>6</sup>J. Davenport, B. Ridley, H. I. Schiff, and K. H. Welge, J. Chem. Soc. Faraday Disc.,  
53, 230, 1972.  
<sup>7</sup>C. Cobos, E. Castellano, and H. J. Schumacher, J. Photochem., 21, 291, 1983.  
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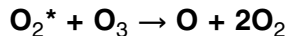
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## Comments

5 Arnold and Comes<sup>1,2</sup> have studied this reaction of vibrationally excited oxygen molecules in the ground electronic state with ozone and they report a rate coefficient of  $2.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. The vibrationally excited oxygen molecules were produced in the reaction of  $\text{O}(^1\text{D})$  atoms with  $\text{O}_3$  following the UV photolysis of ozone. This is the only reported study of this rate coefficient, and we make no recommendation. For  
10 further discussion the reader is referred to the review by Steinfeld et al.<sup>3</sup>

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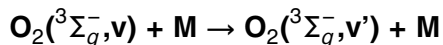
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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	M	$\nu$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>					
$(4.7 \pm 0.3) \times 10^{-15}$	O <sub>2</sub>	19	295	Price et al., 1993 <sup>1</sup>	(a)
$(3.2 \pm 0.3) \times 10^{-15}$		20			
$(5.8 \pm 1.2) \times 10^{-15}$		21			
$(5.4 \pm 0.8) \times 10^{-14}$		22			
$(1.2 \pm 0.4) \times 10^{-14}$		23			
$(0.84 \pm 0.04) \times 10^{-14}$		24			
$(1.8 \pm 0.05) \times 10^{-14}$	25				
$(4.7 \pm 0.2) \times 10^{-14}$	O <sub>2</sub>	26			
$(2.3 \pm 0.1) \times 10^{-14}$		19	460		
$(3.1 \pm 0.08) \times 10^{-14}$		20			
$(2.2 \pm 0.9) \times 10^{-14}$		21			
$(3.7 \pm 0.3) \times 10^{-14}$		22			
$(4.1 \pm 0.6) \times 10^{-14}$		23			
$(6.9 \pm 0.5) \times 10^{-14}$		24			
$(11.7 \pm 0.2) \times 10^{-14}$		25			
$(16.4 \pm 2) \times 10^{-14}$		26			

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	M	$\nu$	Temp./K	Reference	Technique/Comments
$>8.3 \times 10^{-14}$		27			
$>1.2 \times 10^{-11}$		28			
$6.5 \times 10^{-14}$	O <sub>2</sub>	8	300	Park and Slanger, 1994 <sup>2</sup>	(b)
$>1.3 \times 10^{-13}$	He	22			
$(1.53 \pm 0.25) \times 10^{-11}$	O <sub>3</sub>	22			
$2 \times 10^{-13}$	CO <sub>2</sub>	14			
$9 \times 10^{-14}$		22			

### Comments

(a) Vibrationally highly excited electronic ground state O<sub>2</sub> molecules were generated by stimulated emission pumping, and detected by LIF.

(b) Vibrationally highly excited electronic ground state O<sub>2</sub> molecules were formed by ozone photodissociation at 248 nm (Hartley band). The excited molecules were detected by LIF. Rate coefficients were evaluated using a cascade model, in which relaxation through single-quantum V-V and V-T steps was assumed.

### Preferred Values

See table.

### Reliability

$\Delta \log k = \pm 0.5$ .

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The results given from reference 1, and more results presented in graphical form from reference 2, appear consistent with each other.

5 **References**

<sup>1</sup>J. M. Price, J. A. Mack, C. A. Rogaski, and A. M. Wodtke, Chem. Phys., 175, 83, 1993.

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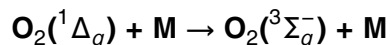
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$$\Delta H^\circ = -94.3 \text{ kJ}\cdot\text{mol}^{-1}$$

## 5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	M		Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>				
$(1.51 \pm 0.05) \times 10^{-18}$	O <sub>2</sub>	298	Borrell et al., 1977 <sup>1</sup>	DF-CL (a)
$(1.47 \pm 0.05) \times 10^{-18}$	O <sub>2</sub>	298	Leiss et al., 1978 <sup>2</sup>	(b)
$(1.65 \pm 0.07) \times 10^{-18}$	O <sub>2</sub>	298	Raja et al., 1986 <sup>3</sup>	DF-CL (a)
$3.15 \times 10^{-18} \exp(-205/T)$	O <sub>2</sub>	100-450	Billington and Borrell, 1986 <sup>4</sup>	DF-CL (a)
$1.57 \times 10^{-18}$		298		
$1.4 \times 10^{-19}$	N <sub>2</sub>	300	Collins et al., 1973 <sup>5</sup>	FP-VUVA (c)
$5.6 \times 10^{-18}$	H <sub>2</sub> O	298	Findlay and Snelling, 1971 <sup>6</sup>	(d)
$<1.5 \times 10^{-20}$	CO <sub>2</sub>	298		
$(4 \pm 1) \times 10^{-18}$	H <sub>2</sub> O	298	Becker et al., 1971 <sup>7</sup>	(e)

## Comments

- 10 (a) Discharge flow system. O<sub>2</sub>(<sup>1</sup>Δ) was monitored by dimol emission at 634 nm or from O<sub>2</sub>(<sup>1</sup>Σ) emission at 762 nm.
- (b) Large static reactor. O<sub>2</sub>(<sup>1</sup>Δ) was monitored by emission at 1.27 μm.
- (c) O<sub>2</sub>(<sup>1</sup>Δ) was detected by time-resolved absorption at 144 nm.
- (d) Flow system, with photolysis of C<sub>6</sub>H<sub>6</sub>-O<sub>2</sub> mixtures at 253.7 nm to produce O<sub>2</sub>(<sup>1</sup>Δ).  
 15 O<sub>2</sub>(<sup>1</sup>Δ) was measured by 1.27 μm emission.

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(e) As (b) but using dimol emission at 634 nm.

## Preferred Values

$k = 1.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $M = \text{O}_2$  at 298 K.

5  $k = 3.0 \times 10^{-18} \exp(-200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $M = \text{O}_2$  over the temperature range 100-450 K.

$k \leq 1.4 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $M = \text{N}_2$  at 298 K.

$k = 5 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $M = \text{H}_2\text{O}$  at 298 K.

$k \leq 2 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $M = \text{CO}_2$  at 298 K.

10

### Reliability

$\Delta \log k = \pm 0.2$  for  $M = \text{O}_2$  at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$  for  $M = \text{O}_2$ .

15  $\Delta \log k = \pm 0.3$  for  $M = \text{H}_2\text{O}$  at 298 K.

### Comments on Preferred Values

20 The preferred value for  $k(M = \text{O}_2)$  is based on the data of Borrell et al.,<sup>1</sup> Leiss et al.,<sup>2</sup> Raja et al.<sup>3</sup> and Billington and Borrell,<sup>4</sup> which also gives the temperature dependence adopted. For other quenching gases the recommendation for  $k(M = \text{N}_2)$  is based on the data of Collins et al.<sup>5</sup> for  $k(M = \text{H}_2\text{O})$  on the data of Findlay and Snelling<sup>6</sup> and Becker et al.,<sup>7</sup> and for  $k(M = \text{CO}_2)$  on the data of Leiss et al.<sup>2</sup> and Findlay and Snelling.<sup>6</sup>

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- <sup>5</sup>R. J. Collins, D. Husain, and R. J. Donovan, *J. Chem. Soc. Faraday Trans. 2*, 69, 145, 1973.
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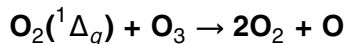
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$$\Delta H^\circ = 12.2 \text{ kJ}\cdot\text{mol}^{-1}$$

## 5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.5 \times 10^{-11} \exp(-2830/T)$	283-321	Findlay and Snelling, 1971 <sup>1</sup>	F-CL (a)
$3.4 \times 10^{-15}$	298		
$6.0 \times 10^{-11} \exp(-2850/T)$	296-360	Becker et al., 1972 <sup>2</sup>	S-CL (b)
$4.2 \times 10^{-15}$	298		

## Comments

10 (a)  $\text{O}_2(^1\Delta_g)$  produced by photolysis of  $\text{O}_3$  at 253.7 nm.

(b)  $\text{O}_2(^1\Delta_g)$  produced by a microwave discharge of  $\text{O}_2$  and flowed into the large static reaction vessel.

## Preferred Values

15  $k = 3.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 5.2 \times 10^{-11} \exp(-2840/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 280-360 K.

## Reliability

20  $\Delta \log k = \pm 0.10$  at 298 K.

$\Delta(E/R) = \pm 500 \text{ K}$ .

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The preferred values are mean values from the studies listed.<sup>1,2</sup> While the data of Clark et al.<sup>3</sup> are in good agreement with these studies<sup>1,2</sup> for the room temperature value, their temperature coefficient is substantially lower. In view of the consistency of the results from Findlay and Snelling<sup>1</sup> and Becker et al.,<sup>2</sup> which were obtained by two completely different techniques, we favour their temperature coefficient over that from reference 3.

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$$\Delta H^\circ(1) = -156.9 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(2) = -62.6 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	M	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>				
$(4.6 \pm 1) \times 10^{-17}$	O <sub>2</sub>	294	Thomas and Thrush, 1975 <sup>1</sup>	DF-CL
$4.6 \times 10^{-12}$	H <sub>2</sub> O	294		
$(4.0 \pm 0.4) \times 10^{-17}$	O <sub>2</sub>	298	Martin et al., 1976 <sup>2</sup>	FP-CL
$(2.2 \pm 0.1) \times 10^{-15}$	N <sub>2</sub>	298		
$(3.8 \pm 0.3) \times 10^{-17}$	O <sub>2</sub>	300	Lawton et al., 1977 <sup>3</sup>	FP-CL
$(2.5 \pm 0.2) \times 10^{-17}$	O <sub>2</sub>	298	Chatha et al., 1979 <sup>4</sup>	DF-CL
$(1.7 \pm 0.1) \times 10^{-15}$	N <sub>2</sub>	298		
$1.7 \times 10^{-15} \exp(48/T)$	N <sub>2</sub>	203-349	Kohse-Höinghaus and Stuhl, 1980 <sup>5</sup>	PLP (a)
$(8.0 \pm 2.0) \times 10^{-14}$	O	300	Slanger and Black, 1979 <sup>6</sup>	FP (a)
$4.4 \times 10^{-13}$	CO <sub>2</sub>	298	Filseth et al., 1970 <sup>7</sup>	FP (a)
$(3.0 \pm 0.5) \times 10^{-13}$	CO <sub>2</sub>	298	Noxon, 1970 <sup>8</sup>	FP (a)
$(4.1 \pm 0.3) \times 10^{-13}$	CO <sub>2</sub>	298	Davidson et al., 1972 <sup>9</sup>	FP (a)
$(4.53 \pm 0.29) \times 10^{-13}$	CO <sub>2</sub>	298	Avilés et al., 1980 <sup>10</sup>	PLP (a)

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	M	Temp./K	Reference	Technique/Comments
$(5.0 \pm 0.3) \times 10^{-13}$	CO <sub>2</sub>	298	Muller and Houston, 1981 <sup>11</sup>	PLP (a)
$(3.4 \pm 0.4) \times 10^{-13}$	CO <sub>2</sub>	293	Borrell et al., 1983 <sup>12</sup>	DF-CL
$(1.7 \pm 0.1) \times 10^{-15}$	N <sub>2</sub>	298	Choo and Leu, 1985 <sup>13</sup>	DF (a)(b)
$(4.6 \pm 0.5) \times 10^{-13}$	CO <sub>2</sub>	245-262		
$5.6 \times 10^{-17}$	O <sub>2</sub>	302	Knickerbein et al., 1987 <sup>14</sup>	PLP (a)
$(2.2 \pm 0.2) \times 10^{-15}$	N <sub>2</sub>	298	Wildt et al., 1988 <sup>15</sup>	PLP-CL (c)
$(2.4 \pm 0.4) \times 10^{-13}$	CO <sub>2</sub>	298		
$<1.0 \times 10^{-16}$	O <sub>2</sub>	298	Shi and Barker, 1990 <sup>16</sup>	PLP-CL (d)
$(2.32 \pm 0.14) \times 10^{-15}$	N <sub>2</sub>	298		
$(4.0 \pm 0.1) \times 10^{-13}$	CO <sub>2</sub>	298		
$(4.25 \pm 0.52) \times 10^{-17}$	O <sub>2</sub>	295	Kebabian and Freeman, 1997 <sup>17</sup>	(e)

## Comments

- 5 (a) Time-resolved emission from O<sub>2</sub>(<sup>1</sup>Σ) measured near 762 nm.
- (b) Negligible temperature dependence observed for quenching by CO<sub>2</sub> over the range 245-362 K, with  $E/R < \pm 200$  K.
- (c) Direct laser excitation of O<sub>2</sub>(<sup>1</sup>Σ) from O<sub>2</sub> by photolysis at 600-800 nm.
- (d) O<sub>2</sub>(<sup>1</sup>Σ) formed by the reaction O(<sup>1</sup>D) + O<sub>2</sub> → O(<sup>3</sup>P) + O<sub>2</sub>(<sup>1</sup>Σ).
- 10 (e) Fluorescence following broadband excitation in an integrating sphere.

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## Preferred Values

$k = 4.1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $M = \text{O}_2$  at 298 K.

$k = 2.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $M = \text{N}_2$  over the temperature range 200-350 K.

5  $k = 8.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $M = \text{O}(^3\text{P})$  at 298 K.

$k = 4.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $M = \text{H}_2\text{O}$  at 298 K.

$k = 4.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $M = \text{CO}_2$  over the temperature range 245-360 K.

### Reliability

10  $\Delta \log k = \pm 0.3$  for  $M = \text{O}_2, \text{O}(^3\text{P})$  and  $\text{H}_2\text{O}$  at 298 K.

$\Delta \log k = \pm 0.10$  for  $M = \text{N}_2, \text{CO}_2$  at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$  for  $M = \text{N}_2, \text{CO}_2$ .

### Comments on Preferred Values

15 The preferred value for  $k(M = \text{O}_2)$  is based on the data of Thomas and Thrush,<sup>1</sup> Martin et al.,<sup>2</sup> Lawton et al.,<sup>3</sup> Chatha et al.,<sup>4</sup> Knickelbein et al.<sup>14</sup> and Kebabian and Freeman.<sup>17</sup> For  $M = \text{N}_2$  the value is based on the data of Kohse-Höinghaus and Stuhl,<sup>5</sup> Martin et al.,<sup>2</sup> Chatha et al.,<sup>4</sup> Choo and Leu,<sup>13</sup> Wildt et al.<sup>15</sup> and Shi and Barker.<sup>16</sup> The value of Slinger and Black<sup>6</sup> is adopted for  $M = \text{O}(^3\text{P})$  and the value of Thomas and Thrush<sup>1</sup> for  $M = \text{H}_2\text{O}$ . For  $k(M = \text{CO}_2)$  the results of Choo and Leu,<sup>13</sup> Filseth et al.,<sup>7</sup> Noxon,<sup>8</sup> Davidson et al.,<sup>9</sup> Avilés et al.,<sup>10</sup> Muller and Houston,<sup>11</sup> Borrell et al.,<sup>12</sup> Wildt et al.<sup>15</sup> and Shi and Barker<sup>16</sup> are used.

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- <sup>15</sup>J. Wildt, G. Bednarek, E. H. Fink, and R. P. Wayne, *Chem. Phys.*, 122, 463, 1988.
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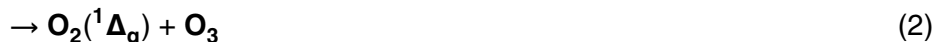
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$$\Delta H^\circ(1) = -50.4 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -62.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -156.9 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.5 \pm 0.5) \times 10^{-11}$	295	Gilpin et al., 1971 <sup>1</sup>	FP-CL (a)
$(2.3 \pm 0.5) \times 10^{-11}$	295	Snelling, 1974 <sup>2</sup>	FP (a)
$(2.2 \pm 0.2) \times 10^{-11}$	300	Slanger and Black, 1979 <sup>3</sup>	(a) (b)
$(1.8 \pm 0.2) \times 10^{-11}$	295	Amimoto and Wiesenfeld, 1980 <sup>4</sup>	FP-RA
$(2.2 \pm 0.3) \times 10^{-11}$	295-361	Choo and Leu, 1985 <sup>5</sup>	DF-CL (c)
$(1.96 \pm 0.09) \times 10^{-11}$	300	Shi and Barker, 1990 <sup>6</sup>	PLP-CL (d)
$(2.06 \pm 0.22) \times 10^{-11}$	300	Turnipseed et al., 1991 <sup>7</sup>	PLP-RF (e)

### Comments

(a)  $\text{O}_2(^1\Sigma_g^+)$  detected in emission.

(b) Flow system with  $\text{O}_2(^1\Sigma_g^+)$  being produced by the modulated photolysis of  $\text{O}_2$  at 147.0 nm to produce  $\text{O}(^1\text{D})$  atoms, followed by  $\text{O}(^1\text{D}) + \text{O}_2 \rightarrow \text{O}(^3\text{P}) + \text{O}_2(^1\Sigma_g^+)$ .

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(c) Negligible temperature dependence was observed, with  $E/R < \pm 300$  K.

(d)  $O_2(^1\Sigma_g^+)$  generated by the reaction  $O(^1D) + O_2 \rightarrow O + O_2(^1\Sigma_g^+)$ , with  $O(^1D)$  atoms being produced from 308 nm pulsed laser photolysis of  $O_3$ .

(e) Rate coefficient for global reaction of  $O_2(^1\Sigma_g^+)$  with  $O_3$  was derived by modeling the temporal behavior of  $O(^3P)$  and  $O(^1D)$  atoms.

### Preferred Values

$k = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 295–360 K.

$k_1 = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Reliability

$\Delta \log k = \pm 0.06$  at 298 K.

$\Delta \log k_1 = \pm 0.10$  at 298 K.

$\Delta(E/R) = \pm 300$  K.

### Comments on Preferred Values

The preferred value at 298 K is based on all of the studies cited in the table,<sup>1–7</sup> which show very good agreement at room temperature. The temperature independence reported in the study of Choo and Leu<sup>5</sup> is adopted in the evaluation. Channel (1) accounts for  $70 \pm 20\%$  of the total reaction.<sup>3,4</sup>

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## O<sub>2</sub> + hν → products

### Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
O <sub>2</sub> + hν → O( <sup>3</sup> P) + O( <sup>3</sup> P) (1)	494	242
→ O( <sup>3</sup> P) + O( <sup>1</sup> D) (2)	683	175
→ O( <sup>1</sup> D) + O( <sup>1</sup> D) (3)	873	137
→ O( <sup>3</sup> P) + O( <sup>1</sup> S) (4)	898	132

### Absorption cross-section data

Wavelength range/nm	Reference	Comment
230-280 nm	Oshima et al., 1995 <sup>1</sup>	(a)
240-270 nm	Yoshino et al., 1995 <sup>2</sup>	(b)
205-240 nm	Yoshino et al., 1988 <sup>3</sup>	(c)
242.2-244.2 nm	Slanger et al., 1996 <sup>4</sup>	(d)
240-275 nm	Yoshino et al., 1999 <sup>5</sup> ; 2000 <sup>6</sup>	(e)

### Quantum yield data

Measurement	λ/nm	Reference	Comment
φ[O( <sup>1</sup> D)]	130-175	Nee and Lee, 1997 <sup>7</sup>	(f)
φ[O( <sup>3</sup> P), O( <sup>1</sup> D)]	159	Lin et al., 1998 <sup>8</sup>	(g)
φ[O( <sup>1</sup> D)]	121.2-121.9	Lacoursière et al., 1999 <sup>9</sup>	(h)

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- 5 (a) The effect of pressurized foreign gases on the photoabsorption of O<sub>2</sub> in the Herzberg bands and Herzberg continuum (230-280 nm) was studied. The values of the cross-sections in O<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> mixtures under various pressures were in good agreement with the previous literature.
- (b) High resolution FT spectrometry (0.06 cm<sup>-1</sup>) was used to measure photoabsorption cross-sections of O<sub>2</sub> in the Herzberg I bands (240-270 nm). Precise band oscillator strengths of the (4,0)-(11,0) bands were obtained, which were significantly higher than previous experimental values.
- 10 (c) Analysis and combination of data of Cheung et al.<sup>10</sup> and Jenouvrier et al.<sup>11</sup>
- (d) Cavity ring down (CRD) spectroscopy of O<sub>2</sub> in the 40 950–41 300 cm<sup>-1</sup> region. Five new bands were observed in addition to many weak lines in the previously observed ( $A^3\Sigma_u^+ - X^3\Sigma_g^-$ ) 11-0 band. Intensities were given.
- 15 (e) FT spectroscopic absorption measurements of the Herzberg II ( $c'\Sigma_u^- - X^3\Sigma_g^-$ ) and Herzberg III ( $A'^3\Delta_u - X^3\Sigma_g^-$ ) bands at 295 K with resolution of 0.06 cm<sup>-1</sup>. Precise band oscillator strengths obtained by summing the cross sections of individual rotational lines.
- (f) O(<sup>1</sup>D) produced by O<sub>2</sub> photodissociation in the Schumann-Runge continuum and monitored by fluorescence from ( $b'\Sigma_g^+$ ) produced by O(<sup>1</sup>D) + O<sub>2</sub> reaction.  $\phi[\text{O}(\text{}^1\text{D})] = 1$  for  $139 < \lambda/\text{nm} < 175$ . At 130-139 nm,  $\phi < 1$ , arising from upper state crossing; at  $\lambda > 175$  nm  $\phi > 0$  due to rotational energy contribution.
- 20 (g) Photodissociation of O<sub>2</sub> at 157 nm by photofragmentation translational spectroscopy. Both energetically available channels (1) and (2) observed.

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(h) Tunable laser photolysis of O<sub>2</sub> at spectral resolution of 1 cm<sup>-1</sup> (1.5 × 10<sup>-3</sup> nm) O(<sup>1</sup>D) yield in the envelope of the H-Lyman α feature. Measurements monitored the emission from O<sub>2</sub> (*b* Σ<sub>g</sub><sup>+</sup>) at 762 nm produced by the quenching of O(<sup>1</sup>D) by O<sub>2</sub>.  $\phi$ (<sup>1</sup>D) was strongly wavelength dependent: 1.0 at 121.35 nm decreasing to a minimum of 0.48 near 121.62 nm. Strong temperature dependence found, the minimum yield at 121.62 nm was 0.28 at 84 K.

### Preferred Values

### Absorption cross-section of O<sub>2</sub> in the 205-240 nm region of the Herzberg continuum

$\lambda/\text{nm}$	$10^{24} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{24} \sigma/\text{cm}^2$
205	7.35	223	3.89
207	7.05	225	3.45
209	6.68	227	2.98
211	6.24	229	2.63
213	5.89	231	2.25
215	5.59	233	1.94
217	5.13	235	1.63
219	4.64	237	1.34
221	4.26	239	1.10
		240	1.01

### Quantum Yields

$\phi_1 = 1$  for  $242 > \lambda > 175$  nm  
 $\phi_2 = 1$  for  $175 > \lambda > 139$  nm

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$$\phi_2 = 0.44 \text{ for } \lambda = 121.6 \text{ nm}$$

### Comments on Preferred Values

5 The recommended absorption cross-section values for the Herzberg continuum are taken from the study of Yoshino et al.,<sup>3</sup> where values are tabulated for every nm from 205-240 nm. These values were derived from an analysis and combination of the data of Cheung et al.<sup>10</sup> and Jenouvrier et al.<sup>11</sup> These data are in agreement with the results of Johnston et al.,<sup>12</sup> and are consistent with the lower absorption cross-section values inferred from balloon-borne measurements of solar irradiance attenuation in the stratosphere by Frederick and Mentall,<sup>13</sup> Herman and Mentall<sup>14</sup> and Anderson and Hall.<sup>15</sup> Herzberg continuum cross-section values under the S-R bands (< 200 nm) have been determined more accurately by Yoshino et al.<sup>16</sup> and are significantly smaller than any previous values. The data from Oshima et al.,<sup>1</sup> Yoshino et al.,<sup>2</sup> Slanger et al.<sup>4</sup> and Yoshino et al.<sup>5,6</sup> relate to the Herzberg bound system in the region beyond the photodissociation threshold for O<sub>2</sub>, and do not affect the preferred cross-sections for the photolysis of atmospheric O<sub>2</sub>.

10 In the Schumann-Runge wavelength region (175-200 nm), a detailed analysis of the penetration of solar radiation requires absorption cross-section measurements with very high spectral resolution. Absorption cross-section values for the (0, 0)-(12, 0) S-R bands measured by the Harvard-Smithsonian group<sup>17-25</sup> are the first set of values which are independent of instrumental resolution. Band oscillator strengths for these bands have been determined by direct numerical integration of these absolute cross-section values. Minschwaner et al.<sup>26,27</sup> have fitted O<sub>2</sub> cross-sections for the frequency range 49 000-57 000 cm<sup>-1</sup> (175-204 nm) with temperature-dependent polynomial expressions for the temperature range 130-500 K using the latest laboratory spectroscopic data. This model provides an efficient and accurate means of determining S-R band absorption cross-sections at 0.5 cm<sup>-1</sup> resolution. These high resolution calculated values differ from the WMO<sup>28</sup> recommendations by up to 10-20% at some

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wavelengths. Mean-band parameterizations of O<sub>2</sub> absorption in the S-R bands for calculating UV transmission and photolysis rates have been presented by Murtagh<sup>29</sup> and by Nicolet and Kennes.<sup>30</sup>

The effect on ozone formation in the 214 nm photolysis of oxygen due to O<sub>2</sub> - O<sub>2</sub> collision pairs at high O<sub>2</sub> pressure and the effect of high N<sub>2</sub> pressure has been studied by Horowitz et al.<sup>31</sup> Greenblatt et al.<sup>32</sup> studied the absorption spectrum of O<sub>2</sub> and O<sub>2</sub> - O<sub>2</sub> collision pairs over the wavelength range 330-1140 nm for O<sub>2</sub> pressures from 1 to 55 bar at 298 K. Band centers, band widths, and absorption cross-sections were reported for the absorption features in this wavelength region.<sup>33</sup>

At  $\lambda < 242$  nm O<sub>2</sub> dissociates with unit quantum efficiency. Below the threshold for O(<sup>1</sup>D) production (reaction (2)) two ground state O atoms are produced, but above this wavelength both O(<sup>3</sup>P) and O(<sup>1</sup>D) are produced.<sup>8</sup> The work of Nee and Lee<sup>7</sup> showed that  $\phi(2) = 1$  in the range 175-139 nm based on measurement of O(<sup>1</sup>D) production. This work also confirmed that  $\phi(O^1D)$  showed sharp variations at shorter wavelengths as observed in earlier work by Lee et al.<sup>34</sup> who also reported a value of  $\phi(2) = 0.44 \pm 0.05$  for absorption of Lyman- $\alpha$  at 121.6 nm. A detailed study<sup>9</sup> of O(<sup>1</sup>D) production over the entire H Lyman- $\alpha$  profile using a tunable VUV laser source has confirmed that a strong wavelength dependence of O(<sup>1</sup>D) exists in this region.

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## O<sub>3</sub> + hν → products

### Primary Photochemical Transitions

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
O <sub>3</sub> + hν → O( <sup>3</sup> P) + O <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>-</sup> )	(1)	101	1180
→ O( <sup>3</sup> P) + O <sub>2</sub> ( <sup>1</sup> Δ <sub>g</sub> )	(2)	196	611
→ O( <sup>3</sup> P) + O <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	(3)	258	463
→ O( <sup>1</sup> D) + O <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>-</sup> )	(4)	291	411
→ O( <sup>1</sup> D) + O <sub>2</sub> ( <sup>1</sup> Δ <sub>g</sub> )	(5)	386	310
→ O( <sup>1</sup> D) + O <sub>2</sub> ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	(6)	448	267
→ 3 O( <sup>3</sup> P)	(7)	595	201

### Absorption Cross-section Data

Wavelength range/nm	Reference	Comment
245 - 350	Bass and Paur, 1985 <sup>1</sup>	(a)
185 - 350	Molina and Molina, 1986 <sup>2</sup>	(b)
253.7	Mauersberger et al., 1986 <sup>3</sup>	(c)
175 - 360	WMO, 1986 <sup>4</sup>	(d)
410 - 760	Burkholder and Talukdar, 1994 <sup>5</sup>	(e)
195 - 345	Malicet et al., 1995 <sup>6</sup>	(f)
350 - 830	Brion et al., 1998 <sup>7</sup>	(f)

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Measurement	$\lambda$ /nm	Reference	Comment
$\phi[\text{O}(^3\text{P})]$	275	Fairchild et al., 1978 <sup>8</sup>	(g)
$\phi[\text{O}(^3\text{P})]$	266	Sparks et al., 1995 <sup>9</sup>	(h)
$\phi[\text{O}(^1\text{D})]$	297.5 - 325	Brock and Watson, 1980 <sup>10</sup>	(i)
$\phi[\text{O}(^1\text{D})]$	266	Brock and Watson, 1980 <sup>11</sup>	(j)
$\phi[\text{O}(^1\text{D})]$	248	Wine and Ravishankara, 1982 <sup>12</sup>	(k)
$\phi[\text{O}(^1\text{D})]$	248, 308	Greenblatt and Wiesenfeld, 1983 <sup>13</sup>	(l)
$\phi[\text{O}(^1\text{D})]$	275 - 325	Trolier and Wiesenfeld, 1988 <sup>14</sup>	(m)
$\phi[\text{O}(^1\text{D})]$	222, 193	Turnipseed et al., 1991 <sup>15</sup>	(n)
$\phi[\text{O}(^1\text{D})]$	221 - 243	Cooper et al., 1993 <sup>16</sup>	(o)
$\phi[\text{O}_2(^1\Delta_g)]$	300 - 322	Ball and Hancock, 1995 <sup>17</sup>	(p)
$\phi[\text{O}_2(^1\Delta_g)]$	287 - 331	Ball et al., 1995 <sup>18</sup>	(q)
$\phi[\text{O}_2(^1\Delta_g)]$	300 - 322	Ball et al., 1995 <sup>19</sup>	(r)
$\phi[\text{O}(^1\text{D})]$	300 - 355	Armerding et al., 1995 <sup>20</sup>	(s)
$\phi[\text{O}(^1\text{D})]$	248	Amimoto et al., 1980 <sup>21</sup>	(t)
$\phi[\text{O}(^1\text{D}), \text{O}(^3\text{P})]$	308 - 326	Takahashi et al., 1996 <sup>22</sup>	(u)
$\phi[\text{O}(^1\text{D})]$	300 - 328	Ball et al., 1997 <sup>23</sup>	(v)
$\phi[\text{O}(^1\text{D})]$	308	Talukdar et al., 1997 <sup>24</sup>	(w)
$\phi[\text{O}(^1\text{D})]$	305 - 329	Takahashi et al., 1998 <sup>25</sup>	(x)
$\phi[\text{O}(^1\text{D})]$	289 - 329	Talukdar et al., 1998 <sup>26</sup>	(y)
$\phi[\text{O}(^1\text{D})]$	301 - 375	Bauer et al., 2000 <sup>27</sup>	(z)
$\phi[\text{O}(^1\text{D})]$	295 - 338	Smith et al., 2000 <sup>28</sup>	(aa)
$\phi[\text{O}(^1\text{D})]$	297 - 305	Taniguchi et al., 2000 <sup>29</sup>	(bb)

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- (a) Measured at 226–298 K with spectral resolution of 0.07 nm.
- (b) Measured at 200–300 K with spectral resolution of 0.025 nm. Relative values normalised to a value of  $1147 \times 10^{-20} \text{ cm}^2$  at the 253.65 nm mercury line.
- (c) Measured at 297 K and later (reference 7) at 195–351 K on the 253.65 nm mercury line.
- (d) Critical review of all published data. Recommended values given for standard spectral intervals from 175–360 nm for 203 and 273 K.
- (e) Measured with a diode array. Cross-sections independent of temperature.
- (f) Absolute cross sections for  $\text{O}_3$  absorption in the range 195–345 nm measured at high resolution ( $\Delta\lambda = 0.01\text{--}0.02$  nm) using a conventional absorption cell–monochromator combination, with ozone measured manometrically. The temperature dependence of the absorption in the Hartley and Huggins bands was also measured over the range 218–295 K. A small increase in  $\sigma$  with decreasing temperature (1.0% over the whole temperature range) was observed at  $\lambda = 253.65$  nm, near the maximum in the Hartley band; at 298 K,  $\sigma(253.65 \text{ nm}) = (113.05 \pm 1.1) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ . In the Huggins bands (300–345 nm) there is a larger temperature dependence (up to 50%), which increases progressively to longer wavelengths. In contrast to the Hartley band there is a decrease in  $\sigma$  with decreasing temperature. The second paper from this group presents absorption spectra measurements for the ozone molecule in the 350–830 nm region, including the Chappuis bands.
- (g) Photofragment spectroscopy of  $\text{O}_3$ : co-product is  $\text{O}_2(^3\Sigma^-)$ ;  $\phi(1) = 0.1$ .
- (h) High resolution photofragment spectroscopy giving  $\phi(1) = 0.1$ .

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- (i) Laser photolysis of  $O_3 - N_2O$  mixture: NO product of  $O(^1D)$  reaction with  $N_2O$  measured by chemiluminescence from  $NO_2$ .
- (j) Laser flash photolysis:  $O(^3P)$  by RF;  $\phi(1) = 0.12 \pm 0.02$  at 266 nm.
- (k) Laser flash photolysis:  $O(^3P)$  by RF;  $\phi(1) = 0.093 \pm 0.028$  at 248 nm.
- 5 (l) Laser photolysis at 248 nm and 308 nm:  $O(^3P)$  by RF;  $\phi[O(^1D)] = 0.94 \pm 0.01$  at 248 nm,  $\phi[O(^1D)] = 0.79 \pm 0.02$  at 308 nm.
- (m) Laser photolysis of  $O_3 - N_2O$  mixtures:  $O(^1D)$  quenching by  $CO_2$  monitored by infrared chemiluminescence from  $CO_2$ .
- 10 (n) Laser photolysis:  $O(^3P)$  by RF;  $\phi[O(^3P)] = 0.12 \pm 0.02$ ;  $\phi[O(^1D)] = 0.87$  at 222 nm.
- (o) Laser photolysis:  $O(^1D)$  detected by weak 630 nm fluorescence emission from  $O(^1D) \rightarrow O(^3P)$ . Relative  $\phi[O(^1D)]$  normalised to  $\phi[O(^1D)] = 0.87$  at 222 nm of Turnipseed et al.<sup>15</sup>
- 15 (p) Relative quantum yields of  $O_2(^1\Delta)$  from laser photolysis of  $O_3$  in the range  $300 < \lambda < 322$  nm measured by  $[2 + 1]$  resonance enhanced multiphoton ionisation (REMPI) at 227K. For  $\lambda > 309$  nm,  $\phi[O_2(^1\Delta)]$  at 227K falls more rapidly than observed at 298K (Ball et al.<sup>30</sup>) confirming that internal energy of  $O_3$  contributes to formation of  $O_2(^1\Delta)$ , just beyond the 310 nm threshold for spin allowed production of the two singlet products of channel (5). At  $\lambda > 320$  nm,  $\phi[O_2(^1\Delta)]$  was approximately equal at the two temperatures, and substantially larger than the then current measurements of  $\phi(O^1D)$  suggesting a spin forbidden channel for  $O_2(^1\Delta)$  production, e.g. channel (2), with  $\phi(2) = 0.1$  at 320 nm.
- 20 (q) Kinetic energies of the  $O_2(^1\Delta)$  fragment of  $O_3$  photolysis in the range 287.57 and 331.52 nm measured by time-of-flight mass spectrometry. Between 308 and 318

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nm dissociation is dominated by the spin allowed dissociation channel (5). At longer wavelengths, photofragments with higher kinetic energies are produced, consistent with the occurrence of the spin forbidden process, channel (2).

(r) Data for  $\phi[\text{O}_2(^1\Delta)]$  temperature dependence reported in earlier publications<sup>17,18,30</sup> were compared with earlier data for  $\phi[\text{O}(^1\text{D})]$ . At 300–309 nm there is no temperature dependence of the yield of either photo-product. In the fall-off region, 307–319 nm, there is good agreement between the measured yields of  $\text{O}_2(^1\Delta)$  and modelling calculations by Michelson et al.<sup>31</sup> which take into account dissociation of internally excited ozone molecules for the formation of  $\text{O}(^1\text{D})$ .

(s)  $\phi[\text{O}(^1\text{D})]$  in the wavelength range 300–330 nm and at 355 nm determined indirectly by observation of the LIF of OH produced by the reaction of photofragment  $\text{O}(^1\text{D})$  with  $\text{H}_2\text{O}$ .  $\phi[\text{O}(^1\text{D})]$  was determined to be unity at 302.5 nm decreasing to 0.6 at 310 nm with a characteristic 'saddle' point at 315 nm and with a long wavelength tail extending to a threshold between 331 and 333 nm. No  $\text{O}(^1\text{D})$  was detected at 355 nm.

(t) Laser flash photolysis:  $\text{O}(^3\text{P})$  by RA;  $\phi(1) = 0.15 \pm 0.02$  at 248 nm.

(u) The photo fragment yields spectra of  $\text{O}(^1\text{D})$  and  $\text{O}(^3\text{P})$  produced in the photodissociation of  $\text{O}_3$  in the Huggins band system over the range 308–326 nm were determined using vacuum ultraviolet LIF. The  $\text{O}(^3\text{P})$  yield exhibited vibrational structure as in the absorption spectrum in the Huggins band, whilst  $\text{O}(^1\text{D})$  showed a smooth dependence on wavelength. The quantum yield of  $\text{O}(^1\text{D})$  was calculated assuming  $\phi[\text{O}(^1\text{D}) + \text{O}(^3\text{P})] = 1$ . Using the absorption spectrum of Molina and Molina,<sup>2</sup>  $\phi[\text{O}(^1\text{D})]$  showed a distinct 'tail' for the region beyond the threshold for channel (5) at 310 nm, as had been reported in some previous studies (Brock and Watson<sup>10</sup>; Trolier and Wiesenfeld<sup>14</sup>), and in the co-product from the spin allowed channel (5),  $\text{O}_2(^1\Delta)$ , reported by Ball and co-workers.<sup>17–19,30</sup> The 'tail'

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in  $\phi[\text{O}(^1\text{D})]$  in the wavelength range 310–321 nm is attributed to hot band excitation of the repulsive limb of the excited state ( $^1\text{B}_2$  or  $^2\text{A}_1$ ) correlating with the singlet products. The non-zero formation of  $\text{O}(^1\text{D})$  at  $\lambda > 321$  nm was tentatively attributed to the spin forbidden process producing  $\text{O}(^1\text{D}) + \text{O}_2(^3\Sigma_g^-)$ .

(v) Relative quantum yields of  $\text{O}(^1\text{D})$  determined by REMPI detection of  $\text{O}(^1\text{D})$  following laser photolysis of  $\text{O}_3$  between 300 and 328 nm. Results confirm the tail in the quantum yield extending to wavelengths beyond the thermodynamic threshold at 310 nm, which is attributed to the occurrence of both spin allowed and spin forbidden processes. Absolute quantum yields were obtained by normalisation to a constant value of  $\phi = 0.95$  in the range 300–305 nm as recommended by NASA<sup>33</sup>.

(w) Temperature dependence of quantum yields of  $\text{O}(^1\text{D})$  following laser photolysis of  $\text{O}_3$  at 308 nm and 248 nm between 200–320 K.  $\text{O}(^1\text{D})$  determined indirectly by 1) conversion to  $\text{O}(^3\text{P})$  followed by RF detection; 2) conversion to OH/OD, followed by LIF detection. At 308 nm,  $\phi[\text{O}(^1\text{D})]$  decreased very slightly with temperature from 0.79 at 298 K to 0.73 at 200 K, whilst at 248 nm  $\phi[\text{O}(^1\text{D})]$  was independent of temperature.

(x) Wavelength and temperature dependence of quantum yields of  $\text{O}(^1\text{D})$  following laser photolysis of  $\text{O}_3$  between 305–329 nm and at 295 and 227 K. The photofragment yield spectra of  $\text{O}(^1\text{D})$  and  $\text{O}(^3\text{P})$  were determined using vacuum ultraviolet LIF and converted to absolute quantum yields by matching to the  $\text{O}_3$  absorption spectrum of Malicet et al.<sup>6</sup> at the two temperatures and assuming  $\phi[\text{O}(^1\text{D}) + \text{O}(^3\text{P})] = 1$ . Doppler profiles of nascent  $\text{O}(^1\text{D})$  were measured, providing information on the dissociation processes. The results are consistent with a dominant hot band contribution at  $310 < \lambda < 321$  nm, and with occurrence of the spin forbidden process at  $\lambda > 318$  nm producing  $\text{O}(^1\text{D}) + \text{O}_2(^3\Sigma_g^-)$  with  $\phi = 0.08$ .

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- (y) Temperature and wavelength dependence of quantum yields of  $O(^1D)$  following laser photolysis of  $O_3$  between 289 - 329 nm at 203–320 K.  $O(^1D)$  determined indirectly by 1) conversion to  $O(^3P)$  followed by RF detection; 2) conversion to OH/OD followed by LIF detection. Absolute values of  $\phi[O(^1D)]$  were based on a value of  $\phi = 0.79$  at 308 nm, and temperature independent values of  $\phi = 0.89 \pm 0.02$  at  $289 < \lambda < 305$  nm and  $\phi = 0.06$  for the spin forbidden process at  $\lambda > 318$  nm.
- (z) Relative quantum yields for  $O(^1D)$  between 305 and 375 nm at 298 and 273 K.  $O(^1D)$  measured indirectly via LIF detection of vibrationally excited OH produced in  $O(^1D) + H_2$  reaction. Use of blue shifted LIF gave high detection sensitivity and eliminated probe laser interference. Significant temperature dependent  $O(^1D)$  quantum yield at  $\lambda = 310$ –325 nm confirmed. Between 325 and 375 nm a temperature independent quantum yield of  $\phi = 0.064 \pm 0.006$  observed, which is assigned to the spin forbidden channel (4). This study supersedes and extends earlier work by this group published by Silvente et al.<sup>32</sup> which reached similar conclusions.
- (aa) Quantum yields for  $O(^1D)$  from broadband photolysis of ozone in wavelength range 295–338 nm and temperatures 226 – 298 K.  $O(^1D)$  detected by CIMS and absolute quantum yields were based on a value of  $\phi = 0.79$  at 308 nm. At  $\lambda = 312$ –324 nm the  $O(^1D)$  quantum yield was temperature dependent. Between 328 and 338 nm a temperature independent quantum yield of  $\phi \sim 0.12$  was observed, which is assigned to the spin forbidden channel (4).
- (bb) Wavelength dependence of quantum yields of  $O(^1D)$  following laser photolysis of  $O_3$  between 297–316 nm and at 295 K. The photofragment yield spectra of  $O(^1D)$  and  $O(^3P)$  were determined using vacuum ultraviolet LIF. The photofragment yield spectra of  $O(^3P)$  were used to determine quantum yields of  $O(^1D)$  between 297–305 nm, which were almost independent of photolysis wavelength in this range

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( $\phi = 0.89$ ).

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## Ozone absorption cross-sections averaged over spectral intervals

int #	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	int #	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$10^{20} \sigma/\text{cm}^2$
			273 K		273 K	203 K
1	175.4-177.0	81.1	31	238.1-241.0	797	797
2	178.6	79.9	32	243.9	900	900
3	180.2	78.6	33	246.9	1000	1000
4	181.8	76.3	34	250.1	1080	1085
5	183.5	72.9	35	253.2	1130	1140
6	185.2	68.8	36	256.4	1150	1160
7	186.9	62.2	37	259.7	1120	1130
8	188.7	57.6	38	263.2	1060	1060
9	190.5	52.6	39	266.7	965	959
10	192.3	47.6	40	270.3	834	831
11	194.2	42.8	41	274.0	692	689
12	196.1	38.3	42	277.8	542	535
13	198.0	34.7	43	281.7	402	391
14	200.0	32.3	44	285.7	277	267
15	202.0	31.4	45	289.9	179	173
16	204.1	32.6	46	294.1	109	104
17	206.2	36.4	47	298.5	62.4	58.5
18	208.3	43.4	48	303.0	34.3	31.6
19	210.5	54.2	49	307.7	18.5	16.6
20	212.8	69.9	50	312.5	9.80	8.67

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int #	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	int #	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$10^{20} \sigma/\text{cm}^2$
			273 K		273 K	203 K
21	215.0	92	51	317.5	5.00	4.33
22	217.4	119	52	322.5	2.49	2.09
23	219.8	155	53	327.5	1.20	0.937
24	222.2	199	54	332.5	0.617	0.471
25	224.7	256	55	337.5	0.274	0.198
26	227.3	323	56	342.5	0.117	0.077
27	229.9	400	57	347.5	0.059	0.017
28	232.6	483	58	352.5	0.027	–
29	235.3	579	59	357.5	0.011	–
30	238.1	686	60	362.5	0.005	–

$\sigma = (1143 \pm 15) \times 10^{-20} \text{cm}^2 \text{ molecule}^{-1}$  at 253.7 nm at 298 K

$\sigma = (1154 \pm 15) \times 10^{-20} \text{cm}^2 \text{ molecule}^{-1}$  at 253.7 nm at 220 K

5 **Ozone absorption cross-sections in the visible spectral region \***

$\lambda/\text{nm}$	$10^{23} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{23} \sigma/\text{cm}^2$
410	1.2	560	394
420	2.2	580	459
440	11.2	600	511
460	32.8	620	400
480	68.4	640	296
500	122	660	209
520	182	680	136
540	291	700	91

$\sigma$  is independent of temperature in the region 410–700 nm.

\* Values are for specific wavelengths given; they are not averaged over wavelength ranges.

5 **Quantum Yields for O(<sup>1</sup>D) production from O<sub>3</sub> photolysis at 298 K**

Wavelength/nm	$\phi[\text{O}(\text{}^1\text{D})]$	Wavelength/nm	$\phi[\text{O}(\text{}^1\text{D})]$
305	0.900	317	0.222
306	0.884	318	0.206
307	0.862	319	0.187
308	0.793	320	0.166
309	0.671	321	0.146
310	0.523	322	0.128
311	0.394	323	0.113
312	0.310	324	0.101
313	0.265	325	0.092
314	0.246	326	0.086
315	0.239	327	0.082
316	0.233	328	0.080

220 <  $\lambda/\text{nm}$  < 305:  $\phi[\text{O}(\text{}^1\text{D})] = 0.90$ ;  $\phi[\text{O}(\text{}^3\text{P})] = 0.10$

330 <  $\lambda/\text{nm}$  < 370:  $\phi[\text{O}(\text{}^1\text{D})] = 0.080$ ;  $\phi[\text{O}(\text{}^3\text{P})] = 0.92$

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## Temperature dependence of Quantum Yields for O(<sup>1</sup>D) production from O<sub>3</sub> photolysis

For 306 < λ/nm < 328 and 200 < T/K < 320:

$$\phi(\lambda, T) = \left\{ \frac{q_1}{q_1 + q_2} \right\} \times A_1 \times \exp \left\{ - \left( \frac{X_1 - \lambda}{\omega_1} \right)^4 \right\} + \left\{ \frac{q_2}{q_1 + q_2} \right\} \times A_2 \times \left\{ \frac{T}{300} \right\}^2 \exp \left\{ - \left( \frac{X_2 - \lambda}{\omega_2} \right)^2 \right\} + A_3 \times \left\{ \frac{T}{300} \right\}^{1.5} \exp \left\{ - \left( \frac{X_3 - \lambda}{\omega_3} \right)^2 \right\} + c$$

where  $q_i = \exp \left( - \frac{\nu_i}{RT} \right)$

$A_1 = 0.8036$ ;  $A_2 = 8.9061$ ;  $A_3 = 0.1192$ ;  $X_1 = 304.225$ ;  $X_2 = 314.957$ ;  $X_3 = 310.737$ ;  
 $\omega_1 = 5.576$ ;  $\omega_2 = 6.601$ ;  $\omega_3 = 2.187$ ;  $\nu_1 = 0$ ;  $\nu_2 = 825.518$ ;  $c = 0.0765$ ;

We recommend this expression for use in the wavelength and temperature range given above. It should not be used outside this range.  $\phi[\text{O}(\text{}^1\text{D})]$  is independent of temperature in the range 220 < λ/nm < 305 and 330 < λ/nm < 370.

### Comments on Preferred Values

#### Absorption cross-sections

The recommended absorption cross-section values at 273 K for the wavelength range 175–362 nm are averaged values for the standard spectral intervals used in atmospheric modelling calculations. These values have been adopted from earlier evaluations (NASA 1994,<sup>33</sup> IUPAC 1996<sup>34</sup>) which accepted the values tabulated in the WMO 1986 review,<sup>4</sup> except for the region 185–225 nm where the values were taken from the

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study of Molina and Molina.<sup>2</sup> Recommended values at 203 K in the Huggins bands are also taken from the WMO 1986 review and are based on the data of Bass and Paur.<sup>1</sup>

The new work of Malicet et al.<sup>6</sup> provides detailed data on the absolute absorption cross sections of ozone and their temperature dependence (218–295 K) over the wavelength range 195–345 nm. The measurements are at sufficient resolution to resolve the vibrational structure in the Huggins bands. The data are generally in excellent agreement with earlier measurements, although there are small differences in detail in specific regions of the spectrum. At wavelengths below 240 nm the cross-sections are identical with those of Molina and Molina,<sup>2</sup> confirming the basis of the recommended values in this range. In the range 240–335 nm the new data are between 1.5% and 3.0% lower than those of Molina and Molina<sup>2</sup> but about 1.5% higher than those of Yoshino et al.<sup>35</sup> The new data are very close to the data of Bass and Paur<sup>1</sup> up to 310 nm. In the Huggins bands ( $\lambda > 310$  nm), shifts of +0.05 nm in the vibrational structure are apparent in the Bass and Paur data,<sup>1</sup> which may be due to error in the wavelength calibration. This gives rise to small but significant differences in the individual cross-sections and their temperature dependence. Nevertheless the small differences do not influence the averaged cross-sections sufficiently to warrant revision of the recommended values for calculation of the atmospheric photoabsorption rates of ozone in the Huggins bands. For cross-sections at high resolution, the data of Malicet et al.<sup>6</sup> which are available in digital form from the authors, is recommended.

Malicet et al.<sup>6</sup> observed a weak temperature dependence near the maximum in the Hartley band, leading to an increase of approximately 1% in  $\sigma$  between 295 and 218 K, in agreement with earlier work of Molina and Molina<sup>2</sup> and Barnes and Mauersberger.<sup>36</sup> The values recommended for the cross section at 253.7 nm have been obtained by averaging the data of Daumont et al.,<sup>36</sup> Malicet et al.,<sup>6</sup> Hearn,<sup>37</sup> Molina and Molina<sup>2</sup> and Mauersberger et al.<sup>3,36</sup> The new recommendation is slightly lower than previously given on the basis of the last three studies.

Ozone cross sections in the Chappius bands (450–750 nm), which are independent of temperature, are taken from Burkholder and Talukdar.<sup>5</sup> The values reported by Brion

et al.<sup>7</sup> are in good agreement.

### Quantum Yields

5 A wealth of data from studies cited in the table for the quantum yield for O(<sup>1</sup>D) production and its co-product, O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>), in the spin allowed dissociation channel (5), give clear evidence for substantially enhanced dissociation into electronically excited products beyond the threshold at 310 nm. This is attributed to the contribution of vibrational energy contained in ground state O<sub>3</sub> molecules. Recent measurements also show that  
10 significant O(<sup>1</sup>D) production occurs at λ = 320–370 nm which is attributed to the spin forbidden channel (4). The new data up to 1997 were considered in IUPAC (Supplement VI),<sup>6</sup> where a complete revision in the recommended quantum yields for O(<sup>1</sup>D) production at 298 K was made, which included the ‘tail’ in φ[O(<sup>1</sup>D)] at wavelengths beyond 312 nm (see Fig. 1). The recommended values for φ[O(<sup>1</sup>D)] covering the range  
15 300–335 nm at 298 K, were obtained by taking a smooth curve through the mean of the experimental values reported by Brock and Watson,<sup>10</sup> Trolier and Wiesenfeld,<sup>14</sup> Armerding et al.,<sup>20</sup> Takahashi et al.<sup>22</sup> and Silvente et al.<sup>32</sup> (for λ > 325 nm only). In the absence of direct measurements of φ[O(<sup>1</sup>D)] at other temperatures, no recommendation was made for the temperature dependence. The ‘tail’, was partly attributed to the  
20 involvement of vibrationally excited ozone, implying a fall off in φ[O(<sup>1</sup>D)] with temperature in the important region between 308–320 nm. This has now been confirmed in several studies.

Since 1997 there have been six new studies<sup>23–28</sup> in which φ[O(<sup>1</sup>D)] was determined, the data now covering a range of temperature from 200 to 320 K and wavelength from  
25 289 to 375 nm. The results of these studies at 298 K are plotted, together with the earlier data cited above, in Fig. 1. The studies are all in good agreement and support O(<sup>1</sup>D) production beyond the threshold at 310 nm. Recently, a rigorous evaluation of the data has been conducted by a group involving the principal investigators of these recent studies (Matsumi et al.<sup>39</sup>) The group had access to all experimental data and were

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able to harmonise and renormalise the quantum yield values to eliminate systematic errors. The  $O_3$  absorption spectrum of Malicet et al.<sup>6</sup> was used in the renormalisation.

The recommendations for the  $\phi[O(^1D)]$  were derived using the following procedures. First  $\phi[O(^1D)]$  at 308 nm and 298 K was set at 0.79. This was based on the measurements of Greenblatt and Wiesenfeld,<sup>13</sup> Talukdar et al.<sup>24</sup> and Takahashi et al.<sup>22,25</sup> A wavelength dependence of  $\phi[O(^1D)]$  at 298 K between 306 and 328 nm was derived by averaging the renormalised data from Brock and Watson,<sup>10</sup> Troler and Wiesenfeld,<sup>14</sup> Armerding et al.,<sup>20</sup> Takahashi et al.,<sup>22</sup> Ball et al.,<sup>23</sup> Talukdar et al.,<sup>24,26</sup> Bauer et al.<sup>27</sup> and Smith et al.<sup>28</sup>

The recent studies of Talukdar et al.,<sup>26</sup> Taniguchi et al.<sup>29</sup> and Smith et al.<sup>28</sup> show  $\phi[O(^1D)]$  values in the range 290–305 nm of around 0.90. The renormalised values of Troler and Wiesenfeld,<sup>14</sup> Armerding et al.,<sup>20</sup> Takahashi et al.,<sup>22</sup> Ball et al.,<sup>23</sup> also showed values in this region. Matsumi et al.<sup>39</sup> therefore recommended a value of  $\phi[O(^1D)] = 0.90 \pm 0.09$  for  $290 < \lambda < 305$  nm. We adopt these recommendations as our preferred values at 298 K, which are listed in the Table.

There are several studies (Brock and Watson,<sup>11</sup> Amimoto et al.,<sup>21</sup> Wine and Ravishankara,<sup>13</sup> Greenblatt and Wiesenfeld,<sup>13</sup> Turnipseed et al.,<sup>15</sup> Cooper et al.,<sup>16</sup> Talukdar et al.<sup>26</sup>) which show that, in the wavelength range 222–275 nm,  $\phi[O(^1D)]$  is between 0.85 and 0.90 without significant variation. Fairchild et al.<sup>8</sup> and Sparks et al.<sup>9</sup> report significant  $O(^3P)$  production in the Hartley Band at 275 and 266 nm. We therefore recommend a value of  $\phi[O(^1D)] = 0.90 \pm 0.05$  and  $\phi[O(^3P)] = 0.10 \pm 0.05$  for the entire range  $220 < \lambda < 305$  nm.

Recent data on the temperature dependence of  $\phi[O(^1D)]$  (Takahashi et al.,<sup>25</sup> Talukdar et al.,<sup>26</sup> Bauer et al.,<sup>27</sup> Smith et al.<sup>28</sup>) confirms that the yield is temperature dependent at wavelengths  $> 308$  nm, as indicated by earlier indirect measurements of Lin and DeMore<sup>40</sup> (275–320 nm) at 233 K and Kuis et al.<sup>41</sup> (313 nm) in the range 221–293 K, and measurements of Ball et al.<sup>17,18,19</sup> of  $\phi[O_2(^1\Delta_g)]$  at 298 K and 227 K. However the recent observations show that at all temperatures,  $\phi[O(^1D)]$  and  $\phi[O_2(^1\Delta_g)]$  decline to a limiting value of  $\sim 0.1$ . Evidence from the time-of-flight experiments of Ball et al.<sup>18</sup> and

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the Doppler profiles of nascent  $O(^1D)$ ] (Takahashi et al.,<sup>42,25</sup> Denzer et al.<sup>43</sup>) strongly points to a contribution from the spin forbidden channel (2). O’Keeffe et al.<sup>44</sup> have observed nascent  $O_2(b^1\Sigma_g)$  photofragments from  $O_3$  photodissociation between 335 and 352 nm, indicating a contribution from channel (3) in this region. These channels involve ground state  $O_3$  and are, therefore, unlikely to be temperature dependent.

Experiments show that at wavelengths below 305 nm,  $\phi[O(^1D)]$  is invariant with temperature. At 308 nm, Matsumi et al.<sup>39</sup> recommend the following expression based on the recent data:<sup>25–28</sup>

$$\phi(308\text{nm}, T) = 6.10 \times 10^{-4} T + 0.608$$

Matsumi et al.<sup>39</sup> have fitted the renormalised quantum yield data of Brock and Watson,<sup>10</sup> Trolier and Wiesenfeld,<sup>14</sup> Armerding et al.,<sup>20</sup> Takahashi et al.,<sup>22,25</sup> Ball et al.,<sup>23</sup> Talukdar et al.,<sup>24,26</sup> Bauer et al.<sup>27</sup> and Smith et al.<sup>28</sup> for  $306 < \lambda/\text{nm} < 328$  and  $200 < T/\text{K} < 320$  with an expression using three Gaussian terms and a constant term representing the spin- forbidden channel(4). Figure 2 shows the quantum yields calculated with this expression at 203, 298 and 320 K, together with selected experimental data. This expression, which is given in the preferred values above, is recommended for use in the wavelength and temperature range given above. It should not be used outside this range.

In the Chappius bands, dissociation to ground state products via reaction (1) is generally assumed to occur with a quantum yield of 1. Recent theoretical calculations<sup>43</sup> lend support for this.

Two field studies in which chemical actinometer measurements of  $J(O^1D)$  have been compared with values calculated from simultaneously measured actinic flux spectra have been reported recently by Mueller et al.<sup>45</sup> and by Shetter et al.<sup>46</sup> Both support the existence of the long wavelength tail in  $\phi(O^1D)$  in atmospheric photolysis rates.



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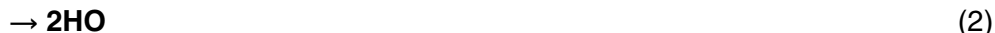
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$$\Delta H^\circ(1) = -232.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -156.2 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -225.2 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(7.4 \pm 1.2) \times 10^{-11}$	245-300	Sridharan et al., 1982 <sup>1</sup>	DF-RF
$(8.7 \pm 1.5) \times 10^{-11}$	245-300	Keyser, 1986 <sup>2</sup>	DF-RF
<i>Branching Ratios</i>			
$k_1/k = 0.08 \pm 0.04$	245-300	Keyser, 1986 <sup>2</sup>	
$k_2/k = 0.90 \pm 0.04$			
$k_3/k = 0.02 \pm 0.04$			

### Preferred Values

$k = 8.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 245–300 K.

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$k_1 = 5.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 245–300 K.

$k_2 = 7.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 245–300 K.

5  $k_3 = 2.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 245–300 K.

*Reliability*

10  $\Delta \log k = \pm 0.1$  over the temperature range 245–300 K.

$\Delta(E/R) = \pm 200 \text{ K}$ .

$\Delta \log k_1 = \pm 0.5$  over the temperature range 245–300 K.

$\Delta \log k_2 = \pm 0.1$  over the temperature range 245–300 K.

$\Delta \log k_3 = \pm 0.5$  over the temperature range 245–300 K.

15

*Comments on Preferred Values*

The study of Keyser<sup>2</sup> is the most detailed to date. Several species were monitored and the possible effects of side reactions were carefully analyzed. Values obtained for the overall rate coefficient and the branching ratios agree with the values obtained by Sridharan et al.,<sup>1</sup> who used a similar technique. The recommended values for  $k$  and the branching ratios are the means of the values from these two studies.<sup>1,2</sup> In both cases,<sup>1,2</sup>  $k_1/k$  was not measured directly but obtained by difference. A direct measurement of this branching ratio is desirable.

20

The yield of  $\text{O}_2(^1\Sigma)$  has been measured by Hislop and Wayne,<sup>3</sup> Keyser et al.<sup>4</sup> and Michelangeli et al.,<sup>5</sup> who report values of  $(2.8 \pm 1.3) \times 10^{-4}$ ,  $< 8 \times 10^{-3}$  and  $< 2.1 \times 10^{-2}$ , respectively.

25

Keyser<sup>2</sup> observed no effect of temperature on the rate coefficient  $k$  over the small range studied. This suggests that the value of  $k_2 = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 349 K obtained by Pagsberg et al.<sup>6</sup> is too low or there is a substantial negative temper-

ature coefficient. We provisionally recommend  $E/R = 0$  but only over the temperature range 245-300 K.

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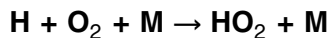
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$$\Delta H^\circ = -203.4 \text{ kJ}\cdot\text{mol}^{-1}$$

## 5 Low-pressure rate coefficients

### Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.33 \times 10^{-32} (T/298)^{-1.77} [\text{N}_2]$	226-298	Kurylo, 1972 <sup>1</sup>	FP-RF
$(5.46 \pm 0.7) \times 10^{-32} (T/298)^{-1.50} [\text{N}_2]$	220-298	Wong and Davis, 1974 <sup>2</sup>	FP-RF
$6.5 \times 10^{-32} [\text{N}_2]$	298	Cobos et al., 1985 <sup>3</sup>	PLP-UVA (a)
$6.2 \times 10^{-32} (T/300)^{-1.66} [\text{N}_2]$	298-639	Hsu et al., 1989 <sup>4</sup>	DF-RF
$2.9 \times 10^{-33} \exp[(825 \pm 130)/T] [\text{N}_2]$	298-580	Carleton et al., 1993 <sup>5</sup>	PLP-LIF/RA
$4.6 \times 10^{-32} [\text{N}_2]$	298		
$3.9 \times 10^{-32} \exp[(600 \pm 1050)/T] [\text{H}_2\text{O}]$	575-750		

### Comments

- 10 (a) Measurements of the falloff curve between 1 and 200 bar, with determination of  $k_0$ ,  $k_\infty$ , and  $F_c$ .

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## Preferred Values

$k_0 = 5.4 \times 10^{-32} (T/300)^{-1.8} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-600 K.

### 5 *Reliability*

$\Delta \log k_0 = \pm 0.1$  at 298 K.

$\Delta n = \pm 0.6$ .

### 10 *Comments on Preferred Values*

The preferred values are an average of the results from refs. 1-5. There is a single study of the full falloff curve<sup>3</sup> which leads to  $k_\infty = 7.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and a broadening factor of  $F_c = 0.55 \pm 0.15$  at 298 K. Theoretical modeling<sup>6,7</sup> using an ab initio potential energy surface gives  $k_\infty = 9.5 \times 10^{-11} (T/300)^{0.44} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $F_c = 0.5$  over the range 200-2000 K.

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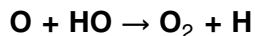
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$$\Delta H^\circ = -68.4 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.35 \times 10^{-11} (T/300)^{-0.36}$	221-499	Lewis and Watson, 1980 <sup>1</sup>	DF-RF (a)
$3.84 \times 10^{-11} (T/300)^{-0.5}$	250-500	Howard and Smith, 1981 <sup>2</sup>	DF/FP-RF
$3.52 \times 10^{-11}$	298	Temps, 1983 <sup>3</sup>	DF-LMR
$3.1 \times 10^{-11}$	298	Brune et al., 1983 <sup>4</sup>	DF-LMR/RA/RF
$4.1 \times 10^{-11} (T/300)^{-0.6}$	158-294	Smith and Stewart, 1994 <sup>5</sup>	DF/PLP-RF
<i>Relative Rate Coefficients</i>			
$3.4 \times 10^{-11}$	298	Keyser, 1983 <sup>6</sup>	DF-RF (b)

### Comments

(a) "Best-fit" values for 300 K from this work are preferred.

(b) Measurements relative to the reaction  $\text{O} + \text{HO}_2 \rightarrow \text{HO} + \text{O}_2$  evaluated with  $k(\text{O} + \text{HO}_2) = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

### Preferred Values

$k = 3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 2.4 \times 10^{-11} \exp(110/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 150-500 K.

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## Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

5  $\Delta(E/R) = \pm 100$  K.

## Comments on Preferred Values

10 The recommended temperature dependence is based on a least-squares fit of the data of Lewis and Watson<sup>1</sup> and Howard and Smith,<sup>2</sup> which are in close agreement. The preferred value for 300 K is the average of data obtained near 300 K in refs. 1-5. The reaction has also been the subject of numerous theoretical studies; see Miller and Klippenstein<sup>7</sup> or Troe and Ushakov<sup>8</sup>.

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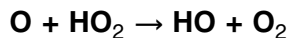
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$$\Delta H^\circ = -225.6 \text{ kJ}\cdot\text{mol}^{-1}$$

## 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.1 \times 10^{-11} \exp(200 \pm 28/T)$	229-372	Keyser, 1982 <sup>1</sup>	DF-RF
$(6.1 \pm 0.4) \times 10^{-11}$	299		
$(5.4 \pm 0.9) \times 10^{-11}$	296	Sridharan et al., 1982 <sup>2</sup>	DF-RF
$(6.2 \pm 1.1) \times 10^{-11}$	298	Ravishankara et al., 1983 <sup>3</sup>	PLP-RF
$(5.2 \pm 0.8) \times 10^{-11}$	300	Brune et al., 1983 <sup>4</sup>	DF-RF
$2.91 \times 10^{-11} \exp[(228 \pm 75)/T]$	266-391	Nicovich and Wine, 1987 <sup>5</sup>	PLP-RF
$(6.30 \pm 0.91) \times 10^{-11}$	298		

## Preferred Values

$k = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 2.7 \times 10^{-11} \exp(224/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220-400 K.

## Reliability

$\Delta \log k = \pm 0.08$  at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$ .

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The recommended rate coefficient at 298 K is the mean of those obtained in the studies of Keyser,<sup>1</sup> Sridharan et al.,<sup>2</sup> Ravishankara et al.,<sup>3</sup> Brune et al.,<sup>4</sup> and Nicovich and Wine,<sup>5</sup> all of which are in excellent agreement. The temperature coefficient is the mean of the values obtained by Keyser<sup>1</sup> and Nicovich and Wine,<sup>5</sup> with the pre-exponential factor being based on this value of  $E/R$  and the recommended value of  $k$  at 298 K.

In the two most recent studies of the reaction mechanism, Keyser et al.<sup>6</sup> have shown that the yield of  $O_2(^1\Sigma)$  from the reaction is  $< 1 \times 10^{-2}$  per  $HO_2$  radical removed and Sridharan et al.<sup>7</sup> have shown, in an  $^{18}O$  labelling experiment, that the reaction proceeds via formation of an  $HO_2-^{18}O$  intermediate which dissociates to HO and  $^{18}OO$  by rupture of an O-O bond rather than via a four center intermediate yielding  $H^{18}O + OO$ .

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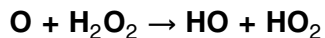
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$$\Delta H^\circ = -60.1 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.75 \times 10^{-12} \exp[-(2125 \pm 261)/T]$	283-368	Davis et al., 1974 <sup>1</sup>	FP-RF
$2.1 \times 10^{-15}$	298		
$1.13 \times 10^{-12} \exp[-(2000 \pm 160)/T]$	298-386	Wine et al., 1983 <sup>2</sup>	FP-RF
$(1.45 \pm 0.29) \times 10^{-15}$	298		

### Preferred Values

$k = 1.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.4 \times 10^{-12} \exp(-2000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 280-390 K.

### Reliability

$\Delta \log k = \pm 0.3$  at 298 K.

$\Delta(E/R) = \pm 1000 \text{ K}$ .

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The preferred values are based on the results of Davis et al.<sup>1</sup> and Wine et al.<sup>2</sup> These two studies are in agreement with regard to the temperature coefficient of the rate coefficient, but the absolute values of  $k$  differ by a factor of 2 throughout the range. In both cases the pre-exponential factor obtained is low compared with other atom-molecule reactions. To obtain the preferred values the temperature coefficient is accepted and the pre-exponential factor adjusted to obtain agreement with the recommended value of  $k$  at 298 K, which is the mean of the values found in the two studies.

Roscoe<sup>3</sup> has discussed earlier work on this reaction, which was invalidated by secondary reactions affecting the measurements.

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$$\Delta H^\circ(1) = -182.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(2) = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.9 \pm 3) \times 10^{-11}$	204-352	Davidson et al., 1976 <sup>1</sup> , 1977 <sup>2</sup>	(a)
$(1.18 \pm 0.12) \times 10^{-10}$	297	Wine and Ravishankara, 1981 <sup>3</sup>	PLP-RF (b)
$(1.0 \pm 0.1) \times 10^{-10}$	298	Force and Wiesenfeld, 1981 <sup>4</sup>	(c)
$(1.2 \pm 0.1) \times 10^{-10}$	298	Talukdar and Ravishankara, 1996 <sup>5</sup>	PLP-RF (d)

### 10 Comments

(a) Pulsed laser photolysis of  $\text{O}_3$  at 266 nm, with  $\text{O}(^1\text{D})$  atoms being monitored by time-resolved emission at 630 nm.

(b)  $\text{O}(^3\text{P})$  atoms were monitored by time-resolved resonance fluorescence.

(c) Pulsed laser photolysis of  $\text{O}_3$  at 248 nm. H and  $\text{O}(^3\text{P})$  atoms were monitored by  
15 time-resolved absorption spectroscopy.

(d)  $\text{O}(^3\text{P})$  and H atom products were monitored by resonance fluorescence.

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## Preferred Values

$k = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 200–350 K.

### 5 *Reliability*

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta(E/R) = \pm 100$  K.

### 10 *Comments on Preferred Values*

The recommended value is the mean of the values of Davidson et al.,<sup>1,2</sup> Wine and Ravishankara,<sup>3</sup> Force and Wiesenfeld<sup>4</sup> and Talukdar and Ravishankara,<sup>5</sup> all of which are in excellent agreement. Channel (1) appears to be the dominant pathway (>95%)<sup>6</sup> for the reaction.

Absolute rate constants and isotopic branching ratios have recently been reported<sup>6</sup> for the reaction of O(<sup>1</sup>D) with HD. The  $k$  values were insignificantly different from the recommendation for H<sub>2</sub>, with a branching ratio OH/OD =  $1.35 \pm 0.20$ .<sup>7</sup>

## References

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$$\Delta H^\circ(1) = -120.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -197.1 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.3 \pm 0.4) \times 10^{-10}$	253-353	Streit et al., 1976 <sup>1</sup>	PLP (a)
$(1.95 \pm 0.3) \times 10^{-10}$	295	Amimoto et al., 1979 <sup>2</sup>	PLP-RA (b)
$(2.6 \pm 0.5) \times 10^{-10}$	300	Lee and Slanger, 1979 <sup>3</sup>	PLP (c)
$k_1 = (2.02 \pm 0.41) \times 10^{-10}$	298	Gericke and Comes, 1981 <sup>4</sup>	PLP-RA
$(1.95 \pm 0.2) \times 10^{-10}$	298	Wine and Ravishankara, 1981 <sup>5</sup>	PLP-RF (d)
<i>Branching Ratios</i>			
$k_2/k = 0.01_{(-0.01)}^{(+0.005)}$	298	Zellner et al., 1980 <sup>6</sup>	FP-RA (e)
$k_3/k = 0.049 \pm 0.032$	298 ± 2	Wine and Ravishankara, 1982 <sup>7</sup>	PLP-RF (d)
$k_2/k = 0.006_{(-0.006)}^{(+0.007)}$	298	Glinski and Birks, 1985 <sup>8</sup>	(f)

### Comments

(a) O(<sup>1</sup>D) atoms were monitored by time-resolved emission from the O(<sup>1</sup>D) → O(<sup>3</sup>P) transition at 630 nm.

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(b) O(<sup>3</sup>P) atoms were measured by resonance absorption.

(c) O(<sup>1</sup>D) atoms were measured by emission at 630 nm and, indirectly, by O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup> → <sup>3</sup>Σ<sub>g</sub><sup>-</sup>) emission at 720 nm.

(d) O(<sup>3</sup>P) atom formation was monitored by RF.

5 (e) The H<sub>2</sub> yield was measured by GC, together with the OH radical concentration by resonance absorption.

(f) Photolysis of O<sub>3</sub>-H<sub>2</sub>O mixtures at 253.7 nm. The H<sub>2</sub> yield was measured by GC.

### Preferred Values

10  $k = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 200-350 K.

$k_1 = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_2 < 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_3 < 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### 15 Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$ .

$\Delta \log k_1 = \pm 0.1$  at 298 K.

20

### Comments on Preferred Values

The preferred value for  $k$  is a mean of the values of Streit et al.,<sup>1</sup> Amimoto et al.,<sup>2</sup> Lee and Slanger,<sup>3</sup> Gericke and Comes<sup>4</sup> and Wine and Ravishankara,<sup>5</sup> all of which

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are in good agreement. Our recommendations for  $k_2/k$  and  $k_3/k$  are based on the data of Zellner et al.<sup>6</sup> and Glinski and Birks<sup>8</sup> ( $k_2/k$ ), and Zellner et al.<sup>6</sup> and Wine and Ravishankara<sup>7</sup> ( $k_3/k$ ).

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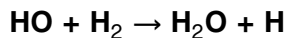
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$$\Delta H^\circ = -62.0 \text{ kJ}\cdot\text{mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$7.0 \times 10^{-15}$	300	Greiner, 1969 <sup>1</sup>	FP-RA
$(7.1 \pm 1.1) \times 10^{-15}$	298	Stuhl and Niki, 1972 <sup>2</sup>	FP-RF
$7.6 \times 10^{-15}$	298	Westenberg and deHaas, 1973 <sup>3</sup>	DF-EPR
$1.8 \times 10^{-11} \exp(-2330/T)$	210-460	Smith and Zellner, 1974 <sup>4</sup>	FP-RA
$7.1 \times 10^{-15}$			
$(5.79 \pm 0.26) \times 10^{-15}$	300	Overend et al., 1975 <sup>5</sup>	FP-RA
$5.9 \times 10^{-12} \exp[-(2008 \pm 151)/T]$	298-425	Atkinson et al., 1975 <sup>6</sup>	FP-RF
$(6.97 \pm 0.70) \times 10^{-15}$	298		
$4.12 \times 10^{-19} T^{2.44} \exp(-1281/T)$	298-992	Tully and Ravishankara, 1980 <sup>7</sup>	FP-RF
$(6.08 \pm 0.37) \times 10^{-15}$	298		
$6.1 \times 10^{-15}$	298	Zellner and Steinert, 1981 <sup>8</sup>	DF-RF
$(4.9 \pm 0.5) \times 10^{-12} \exp[-(1990 \pm 340)/T]$	250-400	Ravishankara et al., 1981 <sup>9</sup>	FP-RF
$(5.64 \pm 0.60) \times 10^{-15}$	295		
$7.2 \times 10^{-20} T^{2.69} \exp(-1150/T)$	230-420	Talukdar et al., 1996 <sup>10</sup>	FP/PLP-LIF(a)
$(6.65 \pm 0.36) \times 10^{-15}$	298		

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## Comments

(a) Both flash lamp and pulsed laser photolysis were used. The OH radical reactions with HD and D<sub>2</sub> were also studied.

## Preferred Values

5  $k = 6.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.  
 $k = 7.7 \times 10^{-12} \exp(-2100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200–450 K.

## Reliability

10  $\Delta \log k = \pm 0.1$  at 298 K.  
 $\Delta(E/R) = \pm 200 \text{ K}$ .

## Comments on Preferred Values

15 There are several studies in good agreement concerning both the temperature dependence and absolute values of the rate coefficient. The preferred value of  $k$  at 298 K is the mean of the results of Greiner,<sup>1</sup> Stuhl and Niki,<sup>2</sup> Westenberg and deHaas,<sup>3</sup> Smith and Zellner,<sup>4</sup> Overend et al.,<sup>5</sup> Atkinson et al.,<sup>6</sup> Tully and Ravishankara,<sup>7</sup> Zellner and Steinert<sup>8</sup> and Ravishankara et al.<sup>9</sup> The preferred value of  $E/R$  is the mean of the values of Smith and Zellner,<sup>4</sup> Atkinson et al.,<sup>6</sup> and Ravishankara et al.<sup>9</sup> The pre-exponential factor in the rate expression is calculated to fit the preferred value of  $k$  at 298 K and that of  $E/R$ . The results of Talukdar et al.<sup>10</sup> are in excellent agreement with this recommendation. There have been many quantum mechanical calculations of the rate coefficient for this reaction, and these are in reasonable agreement with experiment.<sup>11,12</sup> Brownsword et al.<sup>13</sup> have recently measured the branching ratio for

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H<sub>2</sub>O/HOD product formation of (1.2±0.2) in the OH + HD reaction in a PLP/VUV-LIF study under single collision conditions.

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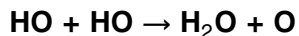
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$$\Delta H^\circ = -71.2 \text{ kJ}\cdot\text{mol}^{-1}$$

## 5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.3 \pm 0.3) \times 10^{-12}$	350	Westenberg and deHaas, 1973 <sup>1</sup>	DF-EPR
$(2.1 \pm 0.5) \times 10^{-12}$	298	McKenzie et al., 1973 <sup>2</sup>	DF-EPR
$(1.4 \pm 0.2) \times 10^{-12}$	300	Clyne and Down, 1974 <sup>3</sup>	DF-RF/RA
$(2.1 \pm 0.1) \times 10^{-12}$	300	Trainor and von Rosenberg, 1974 <sup>4</sup>	FP-RA
$(1.7 \pm 0.2) \times 10^{-12}$	298	Farquharson and Smith, 1980 <sup>5</sup>	DF-RF
$3.2 \times 10^{-12} \exp(-242/T)$	250-580	Wagner and Zellner, 1981 <sup>6</sup>	FP-RA
$(1.43 \pm 0.3) \times 10^{-12}$	298		
$(7.1 \pm 1.0) \times 10^{-13} \exp[(210 \pm 40)/T]$	233-360	Bedjanian et al., 1999 <sup>7</sup>	DF-MS
$1.4 \times 10^{-12}$	298		
$1.9 \times 10^{-12}$	298	IUPAC, 1997 <sup>8</sup>	(a)
$7.9 \times 10^{-14} (T/298)^{2.6} \exp(945/T)$	200-500		

## Comments

(a) Based on on 298 K values from refs. 1-6 and a temperature dependence from an ab-initio modelling study of Harding et al.<sup>13</sup>

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## Preferred Values

$k = 1.48 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 6.2 \times 10^{-14} (T/298)^{2.6} \exp(945/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-350 K.

5

### Reliability

$\Delta \log k = \pm 0.15$  at 298 K.

$\Delta(E/R) = \pm 250 \text{ K}$ .

10

### Comments on Preferred Values

There are a number of measurements of  $k$  at temperatures close to 298 K,<sup>1-6,9-12</sup> falling in the range  $(1.4-2.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The more recent studies<sup>3,5-7</sup> support the lower values for  $k(298)$  near  $1.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The negative temperature dependence reported by Bedjanian et al.<sup>7</sup> in the low temperature region, which is in conflict with the earlier works of Wagner and Zellner<sup>6</sup> supports the theoretically derived temperature dependence recommended by IUPAC.<sup>8</sup> The current recommendation is the IUPAC 1997 expression<sup>8</sup> with the temperature independent term adjusted to give a  $k(298\text{K})$  value of  $1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

20

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$$\Delta H^\circ = -210.7 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.5 \pm 0.3) \times 10^{-31} [\text{N}_2]$	300	Trainor and von Rosenberg, 1974 <sup>1</sup>	FP-RA
$6.9 \times 10^{-31} (T/300)^{-0.8} [\text{N}_2]$	253-353	Zellner et al., 1988 <sup>2</sup>	FP-RA
$3.7 \times 10^{-31} [\text{He}]$	298	Forster et al., 1995 <sup>3</sup>	PLP-LIF (a)

## Comments

10 (a) Measurements were carried out with saturated LIF at total gas densities in the range  $3.9 \times 10^{19}$  to  $3.4 \times 10^{21}$  molecule  $\text{cm}^{-3}$ , covering the major part of the falloff curve. The apparent discrepancy between the results of refs. 1 and 2 disappears when the contribution of the reaction  $\text{HO} + \text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$  is separated by means of the falloff plot. The theoretical analysis by Fulle et al.<sup>4</sup> indicates a change of the temperature coefficient of  $k_0$  from  $T^{-0.9}$  between 200 and 300 K to  $T^{-2.7}$  between 300 and 700 K (for the bath gas He).

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## Preferred Values

$k_0 = 6.9 \times 10^{-31} (T/300)^{-0.8} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-400 K.

### 5 *Reliability*

$\Delta \log k_0 = \pm 0.1$  at 298 K.

$\Delta n = \pm 0.5$ .

### 10 *Comments on Preferred Values*

The analysis of the complete falloff curve by Forster et al.<sup>3</sup> shows that the measurements from refs. 1-3 are all consistent. It is essential that falloff effects are taken into account, as noted in the comments on  $k_\infty$ .

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## High-pressure rate coefficients

### Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.5 \times 10^{-11}$	253-353	Zellner et al., 1988 <sup>2</sup>	FP-RA
$2.2 \times 10^{-11}$	298	Forster et al., 1995 <sup>3</sup>	PLP-LIF (a)
$(2.6 \pm 0.8) \times 10^{-11}$	200-400	Fulle et al., 1996 <sup>4</sup>	PLP-LIF (b)

### Comments

5 (a) See comment (a) for  $k_0$ .

(b) See comment (a) for  $k_0$ . Measurements were carried out over the temperature range 200-700 K, indicating a negative temperature coefficient of  $k_{\infty}$ , depending on uncertainties concerning the contribution from the reaction  $\text{HO} + \text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$  (see Ref. 5).

### 10 Preferred Values

$k_{\infty} = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 200-400 K.

### *Reliability*

15  $\Delta \log k_{\infty} = \pm 0.2$  over the temperature range 200-300 K.

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The measurements from refs. 3 and 4 now provide complete falloff curves of the reaction which are consistent with the preferred values of  $k_0$  and  $k_\infty$  and a value of  $F_C = 0.5 \pm 0.05$  over the temperature range 200-400 K. Earlier constructions of the falloff curve from refs. 6 and 7 are superseded by the results from refs. 3 and 4.

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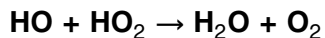
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$$\Delta H^\circ = -294.6 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.1^{+0.28}_{-0.39}) \times 10^{-10}$ (1 bar N <sub>2</sub> )	298	Braun et al, 1982 <sup>1</sup>	FP-UVA
$(1.1 \pm 0.28) \times 10^{-10}$	298	Dransfeld and Wagner, 1986 <sup>2</sup>	DF-LMR
$4.8 \times 10^{-11} \exp[(250 \pm 50)/T]$	254-383	Keyser, 1988 <sup>3</sup>	DF-RF
$(1.1 \pm 0.3) \times 10^{-10}$	299		
$(8.0) \times 10^{-11}$	298	Schwab et al., 1989 <sup>4</sup>	DF-LMR
$3.3 \times 10^{-11}$	1100	Hippler et al., 1995 <sup>5</sup>	(a)
$1.8 \times 10^{-11}$	1250		
$7.5 \times 10^{-11}$	1600		

### Comments

(a) Thermal decomposition of H<sub>2</sub>O<sub>2</sub> in a shock tube. HO radicals were monitored by resonance absorption.

### Preferred Values

$k = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 4.8 \times 10^{-11} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250-400 K.

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## Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

5  $\Delta(E/R) = \pm 200$  K.

## Comments on Preferred Values

10 There has been some controversy over the effects of pressure on the rate coefficient for this reaction. Early discharge-flow measurements at low pressures of 1.3-13 mbar (1-10 Torr) consistently gave values of  $k$  approximately a factor of 2 lower than those obtained by other techniques at pressures close to atmospheric. The discharge-flow study of Keyser<sup>1</sup> appears to have resolved the problem. These results<sup>1</sup> suggest that the presence of small quantities of H and O atoms present in previous discharge-flow studies led to erroneously low values of  $k$ , and that there is no evidence for any variation in  $k$  with pressure. These findings<sup>1</sup> are accepted and we take the expression of Keyser<sup>1</sup> for  $k$  as our recommendation. There are a number of other studies in excellent agreement with the value recommended for  $k$  at 298 K, including relative rate studies of DeMore<sup>6</sup> and Cox et al.<sup>7</sup> which demonstrate that  $k(298\text{ K})$  is unaffected by H<sub>2</sub>O pressure up to 21 mbar. The high temperature data suggest non-Arrhenius temperature dependence at temperatures above the range of our recommendation.

20 In another discharge-flow study, Keyser et al.,<sup>8</sup> by monitoring the  $\text{O}_2(\text{b}^1\Sigma) \rightarrow \text{X}(\text{a}^1\Sigma)$  transition at 762 nm, have shown that the yield of  $\text{O}_2(\text{b}^1\Sigma)$  from the reaction is small ( $< 1 \times 10^{-3}$ ). The anomalous temperature dependence observed in the recent high temperature study<sup>5</sup> suggests a mechanism involving intermediate complex formation.

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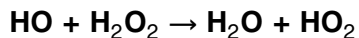
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$$\Delta H^\circ = -129.1 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.96 \times 10^{-12} \exp[-(164 \pm 52)/T]$ $(1.69 \pm 0.26) \times 10^{-12}$	250-459 298	Sridharan et al., 1980 <sup>1</sup>	DF-LIF
$2.51 \times 10^{-12} \exp[-(126 \pm 76)/T]$ $(1.64 \pm 0.32) \times 10^{-12}$	245-423 298	Keyser, 1980 <sup>2</sup>	DF-RF
$3.7 \times 10^{-12} \exp[-(260 \pm 50)/T]$ $(1.59 \pm 0.08) \times 10^{-12}$	273-410 297	Wine et al., 1981 <sup>3</sup>	PLP-RF
$(1.67 \pm 0.33) \times 10^{-12}$ $(1.81 \pm 0.24) \times 10^{-12}$	296 298	Temps and Wagner, 1982 <sup>4</sup> Marinelli and Johnston, 1982 <sup>5</sup>	DF-LMR PLP-RF
$2.93 \times 10^{-12} \exp[-(158 \pm 52)/T]$ $(1.79 \pm 0.14) \times 10^{-12}$	250-370 296	Kurylo et al., 1982 <sup>6</sup>	FP-RF
$2.76 \times 10^{-12} \exp[-(110 \pm 60)/T]$ $(1.86 \pm 0.18) \times 10^{-12}$	273-410 298	Vaghjiani et al., 1989 <sup>7</sup>	PLP-LIF

### Preferred Values

$k = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 2.9 \times 10^{-12} \exp(-160/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240-460 K.

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## Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta(E/R) = \pm 100$  K.

5

### Comments on Preferred Values

There are a number of studies in excellent agreement on the value of the rate coefficient  $k$ .<sup>1-7</sup> The recommended expression is a fit to the data in refs. 1-7. The high temperature study of Hippler et al.<sup>8</sup> shows that above 800 K there is a strong increase in  $k$  with temperature, the data being best represented by the biexponential expression  $k = \{3.3 \times 10^{-12} \exp(-215/T) + 2.8 \times 10^{-6} \exp(-14800/T)\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range  $240 \leq T \leq 1700$  K.

10

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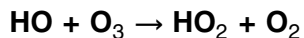
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$$\Delta H^\circ = -167.4 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.3 \times 10^{-12} \exp(-956/T)$	220-450	Anderson and Kaufman, 1973 <sup>1</sup>	DF-RF
$5.3 \times 10^{-14}$	298		
$(6.5 \pm 1.0) \times 10^{-14}$	298	Kurylo, 1973 <sup>2</sup>	FP-RF
$1.82 \times 10^{-12} \exp[-(930 \pm 50)/T]$	238-357	Ravishankara et al., 1979 <sup>3</sup>	PLP-RF
$(7.96 \pm 0.39) \times 10^{-14}$	298		
$(6.5 \pm 1.0) \times 10^{-14}$	300	Zahniser and Howard, 1980 <sup>4</sup>	DF-LMR (a)
$1.52 \times 10^{-12} \exp[-(890 \pm 60)/T]$	240-295	Smith et al., 1984 <sup>5</sup>	FP-RF (b)
$(7.46 \pm 0.16) \times 10^{-14}$	295		
$2.26 \times 10^{-12} \exp[-(976 \pm 50)/T]$	190-315	Nizkorodov et al., 2000 <sup>6</sup>	PLP-AS (c)
<i>Relative Rate Coefficients</i>			
$(7.0 \pm 0.8) \times 10^{-14}$	300	Zahniser and Howard, 1980 <sup>4</sup>	DF-LMR (d)

### Comments

(a) Discharge flow system used. HO radicals were generated from the H + NO<sub>2</sub> reaction and monitored by LMR.

(b) Flash photolysis of O<sub>3</sub>-H<sub>2</sub>O mixtures in 1 atm He. HO radicals were monitored by resonance fluorescence.

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(c) Pulsed laser photolysis of O<sub>3</sub>-H<sub>2</sub>O mixtures with OH detection by infrared laser spectroscopy. The sum of rate coefficients for the OH + O<sub>3</sub> and HO<sub>2</sub> + O<sub>3</sub> reactions ( $k + k(\text{HO}_2 + \text{O}_3)$ ) was measured directly and was described accurately by the Arrhenius expression over the entire temperature range. If the recommended expression for  $k(\text{HO}_2 + \text{O}_3)$  from this evaluation is used the resultant values of  $k$  are in excellent agreement with those from Ravishankara et al.<sup>3</sup> and Smith et al.<sup>5</sup>

(d) Discharge flow system used. HO radicals were generated from the H + NO<sub>2</sub> and H + O<sub>3</sub> reactions, and HO<sub>2</sub> radicals were generated from the reaction H + O<sub>2</sub> + M. HO<sub>2</sub> and HO radicals were monitored by LMR. A rate coefficient ratio of  $k/k(\text{HO}_2 + \text{O}_3) = 35 \pm 4$  (average of three systems studied) was obtained and placed on an absolute basis by use of  $k(\text{HO}_2 + \text{O}_3) = 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K (this evaluation).

### Preferred Values

$k = 7.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.70 \times 10^{-12} \exp(-940/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220–450 K.

### Reliability

$\Delta \log k = \pm 0.15$  at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$ .

### Comments on Preferred Values

There is good agreement among the various studies<sup>1–5</sup> for the rate coefficient  $k$ . The recommended value for  $E/R$  is the mean of the values of Ravishankara et al.,<sup>3</sup> Smith

et al.,<sup>5</sup> and Nizkorodov et al.,<sup>6</sup> except that the Anderson and Kaufman<sup>1</sup> study gave a somewhat slower rate, probably due to OH regeneration from the HO<sub>2</sub> + NO reaction which has been revised upwards since this early study. The recommended 298 K rate coefficient is the mean of the values from these studies<sup>1,3,5</sup> plus those of Kurylo<sup>2</sup> and Zahniser and Howard<sup>4</sup>. The pre-exponential factor is derived from the recommended values of *E/R* and the 298 K rate coefficient.

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$$\Delta H^\circ(1) = \Delta H^\circ(2) = -165.5 \text{ kJ}\cdot\text{mol}^{-1}$$

5 **Rate coefficient data ( $k = k_1 + k_2$ )**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.8 \times 10^{-14} \exp[(1250 \pm 200)/T]$ $(2.35 \pm 0.2) \times 10^{-12}$	273-339 298	Cox and Burrows, 1979 <sup>1</sup>	MM (a)
$2.4 \times 10^{-13} \exp[(560 \pm 200)/T]$ $(1.6 \pm 0.1) \times 10^{-12}$	298-359 298	Thrush and Tyndall, 1982 <sup>2</sup>	FP-TDLS (b)
$2.5 \times 10^{-12}$ (760 Torr N <sub>2</sub> ) $k_1 = (1.4 \pm 0.2) \times 10^{-12}$	296 296	Simonaitis and Heicklen, 1982 <sup>3</sup>	FP-UVA
$k_1 = 2.2 \times 10^{-13} \exp(620/T)$ $k_1 = (1.7 \pm 0.22) \times 10^{-12}$	230-420 298	Kircher and Sander, 1984 <sup>4</sup>	FP-UVA (c)
$k_2 = 1.9 \times 10^{-33} [\text{N}_2] \exp(980/T)$ $k_2 = (5.4 \pm 3.1) \times 10^{-32} [\text{N}_2]$	230-420 298	Kircher and Sander, 1984 <sup>4</sup>	FP-UVA (c)
$k_1 = 1.88 \times 10^{-12}$ $k_2 = 4.53 \times 10^{-32} [\text{O}_2]$	298 298	Kurylo et al., 1986 <sup>5</sup>	FP-UVA (d)
$k_2 = 5.95 \times 10^{-32} [\text{N}_2]$ $k_1 = 2.0 \times 10^{-13} \exp[(595 \pm 120)/T]$	298 253-390	Takacs and Howard, 1986 <sup>6</sup>	DF-LMR

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
$k_1 = (1.54 \pm 0.07) \times 10^{-12}$	294		
$(3.3 \pm 0.9) \times 10^{-12}$	298	Lightfoot et al., 1988 <sup>7</sup>	FP-UVA
$(1.5 \pm 0.5) \times 10^{-12}$	418		
$(8.8 \pm 1.2) \times 10^{-13}$	577		
$(8.2 \pm 2.0) \times 10^{-13}$	623		
$(8.1 \pm 1.5) \times 10^{-13}$	677		
$(7.6 \pm 1.4) \times 10^{-13}$	723		
$(9.1 \pm 2.5) \times 10^{-13}$	777		
$(2.44 \pm 0.20) \times 10^{-12}$ (1000 mbar O <sub>2</sub> )	298	Crowley et al., 1991 <sup>8</sup>	MMS
$(2.84 \pm 0.30) \times 10^{-12}$ (1000 mbar N <sub>2</sub> )	298		
$(3.5 \pm 1.0) \times 10^{-12}$ (1000 mbar SF <sub>6</sub> )	295	Sehested et al., 1997 <sup>9</sup>	PR-UVA

## Comments

- (a) HO<sub>2</sub> radicals were monitored by molecular modulation spectrometry. The data cited refer to a total pressure of 760 Torr and absence of H<sub>2</sub>O.
- 5 (b) HO<sub>2</sub> radicals were monitored by diode laser spectroscopy. Pressure = 9-27 mbar (720 Torr) of O<sub>2</sub>.
- (c) Pressure range was 0.133-0.933 bar (100-700 Torr) of Ar and N<sub>2</sub>. Enhancement of  $k$  by added water was observed, in a linear fashion independent of the pressure of other gases, according to the equation  $k_{obs} = k \times (1 + 1.4 \times 10^{-21} \exp(2200/T) [\text{H}_2\text{O}])$ .
- 10 (d) Total pressure range was 0.033-1.01 bar (25-760 Torr).

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## Preferred Values

$k_1 = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_2 = 5.2 \times 10^{-32} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_2 = 4.5 \times 10^{-32} [\text{O}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

5  $k_1 = 2.2 \times 10^{-13} \exp(600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230-420 K.

$k_2 = 1.9 \times 10^{-33} [\text{N}_2] \exp(980/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230-420 K.

In the presence of  $\text{H}_2\text{O}$  the expressions for  $k_1$  and  $k_2$  should be multiplied by the  
10 factor:  $\{1 + 1.4 \times 10^{-21} [\text{H}_2\text{O}] \exp(2200/T)\}$ , where  $[\text{H}_2\text{O}]$  is in  $\text{molecule cm}^{-3}$  units.

### Reliability

$\Delta \log k_1 = \Delta \log k_2 = 0.15$  at 298 K.

15  $\Delta(E_1/R) = \pm 200 \text{ K}$ .

$\Delta(E_2/R) = \pm 300 \text{ K}$ .

### Comments on Preferred Values

20 The preferred values given here are identical with the values derived by Kircher and Sander<sup>4</sup> and also recommended in the review by Wallington et al.<sup>10</sup>

At temperatures close to 298 K, the reaction proceeds by two channels, one bimolecular and the other termolecular. The preferred values for  $k_1$  are based on the work of Cox and Burrows,<sup>1</sup> Thrush and Tyndall,<sup>2</sup> Kircher and Sander,<sup>4</sup> Kurylo et al.,<sup>5</sup> Takacs and Howard<sup>6</sup> and Lightfoot et al.<sup>7</sup> The work of Kurylo et al.<sup>5</sup> and of Lightfoot et al.<sup>7</sup>  
25 has confirmed quantitatively the effects of pressure previously observed by Simonaitis and Heicklen<sup>3</sup> and Kircher and Sander.<sup>4</sup> The recommendations for  $k_2$  are based on the work of Kircher and Sander<sup>4</sup> and Kurylo et al.,<sup>5</sup> with the temperature coefficient of

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$k_2$  being taken from Kircher and Sander<sup>4</sup> and Lightfoot et al.<sup>7</sup> At higher temperatures,  $T > 600$  K, Hippler et al.<sup>14</sup> and Lightfoot et al.<sup>7</sup> observe a sharp change in the temperature coefficient with upward curvature of the Arrhenius plot.

The marked effect of water on this reaction was established in the work of Lii et al.<sup>15</sup> and Kircher and Sander.<sup>4</sup> The recommended multiplying factor for  $k_1$  and  $k_2$  in the presence of water is based on these two studies.<sup>4,15</sup>

Mozurkewich and Benson<sup>16</sup> have considered the  $\text{HO}_2 + \text{HO}_2$  reaction theoretically and conclude that the negative temperature dependence, the pressure dependence, and the observed isotope effects can most reasonably be explained in terms of a cyclic hydrogen bonded,  $\text{HO}_2 \text{O}_2\text{H}$ , intermediate to alternative structures suggested by others.

Sahetchian et al.<sup>17</sup> reported the formation of  $\text{H}_2$  ( $\sim 10\%$  at 500 K) in the reaction system but this is contrary to earlier evidence of Baldwin et al.<sup>18</sup> and the more recent and careful study of Stephens et al.,<sup>19</sup> who find less than 0.01 fractional contribution from the channel leading to  $\text{H}_2 + 2\text{O}_2$ . Keyser et al.<sup>20</sup> have measured a yield of  $\text{O}_2(\text{b}^1\Sigma())$  of  $< 3 \times 10^{-2}$  per  $\text{HO}_2$  consumed.

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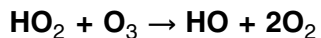
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$$\Delta H^\circ = -118 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.4 \times 10^{-14} \exp[(-580 \pm 100)/T]$	245-365	Zahniser and Howard, 1980 <sup>1</sup>	DF-LMR
$2.0 \times 10^{-15}$	298		
$1.8 \times 10^{-14} \exp[(-680 \pm 148)/T]$	253-400	Wang et al., 1988 <sup>2</sup>	DF (a)
$(1.3 \pm 0.3) \times 10^{-15}$	233-253		
$(1.9 \pm 0.3) \times 10^{-15}$	298		
$(103 \pm 51)[\exp[-(1323 \pm 160)/T] + 0.88] \times 10^{-15}$	197-297	Herndon et al., 2001 <sup>3</sup>	DF-TDLAS (b)
$(2.0 \pm 0.2) \times 10^{-15}$	295		

### Comments

(a) HO<sub>2</sub> radicals were monitored by photodissociation at 147 nm and HO radicals were detected by HO(A-X) fluorescence at 310 nm.

(b) Used turbulent flow reactor with pressure range 80-175 Torr. H<sup>18</sup>O<sub>2</sub> monitored in excess <sup>16</sup>O<sub>3</sub> to avoid reformation of reactant.

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## Preferred Values

$k = 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 2.03 \times 10^{-16} (T/300)^{4.57} \exp(693/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250-340 K.

### Reliability

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta(E/R) = \begin{matrix} +500K \\ -100K \end{matrix}$

### Comments on Preferred Values

A number of studies<sup>1-5</sup> are in close agreement on the value of  $k$  at 298 K, but there is some divergence concerning the temperature coefficient of  $k$ . The studies of Sinha et al.,<sup>5</sup> Wang et al.,<sup>2</sup> and Herndon et al.<sup>3</sup> agree that  $k$  exhibits non-Arrhenius behavior which is particularly noticeable at  $T < 250$  K. There are experimental difficulties in working at these temperatures. At higher temperature the results from these two studies<sup>2,5</sup> also diverge, giving values of  $k$  differing by nearly a factor of 2 at 400 K. We therefore limit the temperature range of our recommendation to  $T < 340$  K until this discrepancy is resolved.

The preferred value at 298 K is a mean of the results of Zahniser and Howard<sup>1</sup>, Wang et al.,<sup>2</sup>, Herndon et al.,<sup>3</sup> and Sinha et al.<sup>5</sup> The comparative dependent expression is obtained by putting an expression form  $AT^n \exp(E/RT)$  to the data of Herndon et al.<sup>3</sup> at  $T \leq 297$  K and the averaged data of Zahniser<sup>1</sup>, Wang<sup>2</sup> and Sinha<sup>5</sup> at  $298 < T < 340$  K.

Isotopic exchange studies<sup>7</sup> of the reaction between  $\text{H}^{18}\text{O}_2$  and  $\text{O}_3$  show that at room temperatures the reaction proceeds almost exclusively by H atom transfer rather than by transfer of an oxygen atom. Moreover there is little change in this finding with temperature over the range 226-355 K,<sup>7</sup> indicating that any curvature on the Arrhenius

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plot cannot be due to competition between these two reaction paths.

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## H<sub>2</sub>O + hν → products

### Primary photochemical transitions

Reactions		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
H <sub>2</sub> O + hν → H <sub>2</sub> + O( <sup>3</sup> P)	(1)	491.0	243
→ H + HO	(2)	492.8	242
→ H <sub>2</sub> + O( <sup>1</sup> D)	(3)	680.7	176

### Absorption cross-section data

Wavelength range/nm	Reference	Comments
176-185	Watanabe and Zelikoff, 1953 <sup>1</sup>	(a)
185-198	Thompson et al., 1963 <sup>2</sup>	(b)
175-182	Schurgers and Welge, 1968 <sup>3</sup>	(c)
183-193	Cantrell et al., 1997 <sup>4</sup>	(d)
184.9	Hofzumahaus et al., 1997 <sup>5</sup>	(e)
184.9	Creasey et al., 2000 <sup>6</sup>	(f)

### Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 \leq 0.003$	174	Chou et al., 1974 <sup>7</sup>	(g)

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## Comments

- (a) Static system. H<sub>2</sub>O was determined by pressure measurement over the range 0.08-8 Torr. Resolution was approximately 0.1 nm. Only graphical presentation of data.
- (b) Static system double beam spectrophotometer used with a 10 cm pathlength. H<sub>2</sub>O pressure was 27 mbar (20 Torr). No details of pressure measurement or resolution were given. Only graphical presentation of data.
- (c) Flowing system. H<sub>2</sub>O was determined using a membrane manometer. 0.5 m grating monochromator, with 0.25 nm bandwidth. Only graphical presentation of data.
- (d) Absolute cross sections measured at 184.9 nm using optically filtered Hg lamp and solar blind photomultiplier. Wide range of conditions with 4 separate methods for determination of H<sub>2</sub>O pressure. Temperature range 273-353 K.  $\sigma = (7.14 \pm 0.2) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$  at 298 K with a positive temperature dependence of 4% between 273 and 353 K. Spectrum recorded between 183-193 nm and cross sections in this range were calculated relative to  $\sigma$  (184.9nm).
- (e) Absolute cross sections measured at 184.9 nm.  $\sigma = 7.0 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$  at 298 K
- (f) Absolute cross sections measured at 184.9 nm using static and H<sub>2</sub>O-N<sub>2</sub> mixtures.  $\sigma = (7.14 \pm 0.2) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$  at 298 K and  $\sigma = 7.26 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$  at 305 K.
- (g) Photolysis involved HTO. It was shown that the decomposition path is almost entirely via the reactions  $\text{HTO} + h\nu \rightarrow \text{H} + \text{OT}$  and  $\text{HTO} + h\nu \rightarrow \text{T} + \text{HO}$ , with  $\leq 0.003$  of the molecules decomposing via the reaction  $\text{HTO} + h\nu \rightarrow \text{HT} + \text{O}$ .

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## Preferred Values

$\lambda/\text{nm}$	$10^{20}\sigma/\text{cm}^2$	$\phi_2$
175.5	263.0	1.0
177.5	185.0	1.0
180.0	100.0	1.0
182.0	29.8	1.0
183.0	16.9	1.0
184.0	12.1	1.0
185.0	6.78	1.0
186.0	4.39	1.0
187.0	2.71	1.0
188.0	1.77	1.0
189.0	1.08	1.0
190.0	0.672	1.0
191.0	0.464	1.0
192.0	0.277	1.0
193.0	0.175	1.0

### Comments on Preferred Values

5 Water vapour has a continuous spectrum between 175 and 190 nm, and the cross-section decreases rapidly towards longer wavelengths. The cross-section data at 184.9 nm from three recent studies<sup>4–6</sup> are in excellent agreement. They are all ~30% higher than data previously recommended by IUPAC<sup>8</sup>, which were taken from the review of Hudson,<sup>9</sup> and were obtained by drawing a smooth curve through the data of Watanabe and Zelikoff,<sup>1</sup> Thompson et al.,<sup>2</sup> and Schurgers and Welge.<sup>3</sup>

10 Recent data of Yoshino et al.<sup>10</sup> covers wavelengths down to 120 nm but above 183 nm are scattered and give higher values of  $\sigma$ , but an earlier value at 184.9 from

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DeMore<sup>11</sup> is consistent with the recent data. The recommended values at 298 K in the range 180-193 nm, are those of Cantrell et al.,<sup>4</sup> which were obtained using several independent measures of the H<sub>2</sub>O concentration. Values at shorter wavelength based on Hudson.<sup>9</sup> The recommended cross section at 184.9 nm is  $\sigma = 7.14 \times 10^{-20}$  cm<sup>2</sup>molecule<sup>-1</sup> at 298 K. The temperature dependence over the range 273 – 353 K is given by the expression:  $\log_{10}\{\sigma(T)/\sigma(298)\} = 2.14 \times 10^{-4}\{T - 298(K)\}$ , based also on the results of Cantrell et al.<sup>4</sup>

On the basis of the nature of the spectrum and the results of Chou et al.<sup>7</sup> on the photolysis of HTO, it is assumed that over the wavelength region 175-190 nm reaction (2) is the only primary process and that  $\phi_2 = 1.0$ .<sup>7</sup>

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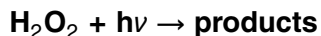
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### Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{H}_2\text{O}_2 + h\nu \rightarrow \text{HO} + \text{HO}$	(1)	215	557
$\rightarrow \text{H}_2\text{O} + \text{O}(^1\text{D})$	(2)	333	359
$\rightarrow \text{H} + \text{HO}_2$	(3)	369	324
$\rightarrow \text{HO} + \text{HO}(^2\Sigma)$	(4)	606	197

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### 5 Quantum Yield Data

$$(\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4)$$

Measurement	Wavelength Range/nm	Reference	Comments
$\phi_3 = 0.12$	193	Gerlach-Meyer et al., 1987 <sup>1</sup>	(a)
$\phi_1 = 1.04 \pm 0.18$	248	Vaghjiani and Ravishankara, 1990 <sup>2</sup>	(b)
$\phi_2 < 0.002$	248		
$\phi_3 < 0.0002$	248		
$\phi_1 = 1.01 \pm 0.17$	222	Vaghjiani et al., 1992 <sup>3</sup>	(c)
$\phi_2 < 0.002$	222		
$\phi_3 = 0.024 \pm 0.012$	222		
$\phi_3 = 0.16 \pm 0.04$	193		
$\phi_1 = 0.79 \pm 0.12$	248	Schiffman et al., 1993 <sup>4</sup>	(d)

## Comments

- (a) Pulsed laser photolysis of  $\text{H}_2\text{O}_2$  with H-atom detection by laser-induced fluorescence.
- 5 (b) Pulsed photolysis of flowing mixtures of  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$ - $\text{N}_2$  (or He) and of  $\text{O}_3$ - $\text{H}_2\text{O}$ - $\text{N}_2$  (or He) at 298 K.  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  were determined by UV absorption at 213.9 nm or 228.8 nm. Quantum yield of HO radical formation from  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$  mixture was measured relative to that from  $\text{O}_3$ - $\text{H}_2\text{O}$  mixture. These relative yields were placed on an absolute basis using the known quantum yield of HO radical production from the photolysis of  $\text{O}_3$ - $\text{H}_2\text{O}$  mixtures at 248 nm, taken as  $\phi(\text{HO}) = 1.73 \pm 0.09$ .<sup>2,5</sup> O and H atom yields were determined by resonance fluorescence.
- 10 (c) Pulsed laser photolysis of  $\text{H}_2\text{O}_2$ - $\text{N}_2$  or  $\text{SF}_6$  mixtures at 222 nm and 248 nm. [HO] monitored by LIF. The quantum yield of HO radical production at 248 nm was assumed to be 2.0 and the value at 222 nm was determined from this and the relative HO yields at the two wavelengths. H atom concentrations were monitored by resonance fluorescence. The quantum yield was determined by reference to  $\text{CH}_3\text{SH}$  photolysis at 193 nm.  $\text{O}(^3\text{P})$  atom formation was investigated using resonance fluorescence but only a very small signal was detected, possibly due to secondary chemistry.
- 15 (d) Pulsed laser photolysis of  $\text{H}_2\text{O}_2$  mixtures. Energy, and hence number of photons, of laser pulse absorbed determined by calorimetry. HO radical concentrations were monitored by infrared absorption using a color center dye-laser (2.35-3.40  $\mu\text{m}$ ) and interferometer for wavelength measurement. Absolute HO radical concentrations were obtained using integrated absorption cross-sections measured in the same laboratory.
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## Preferred Values

### Absorption Cross-sections at 298 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\phi_1$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\phi_1$
190	67.2		275	2.6	1.0
195	56.3		280	2.0	1.0
200	47.5		285	1.5	1.0
205	40.8		290	1.2	1.0
210	35.7		295	0.90	1.0
215	30.7		300	0.68	1.0
220	25.8	1.0	305	0.51	1.0
225	21.7	1.0	310	0.39	1.0
230	18.2	1.0	315	0.29	1.0
235	15.0	1.0	320	0.22	1.0
240	12.4	1.0	325	0.16	1.0
245	10.2	1.0	330	0.13	1.0
250	8.3	1.0	335	0.10	1.0
255	6.7	1.0	340	0.07	1.0
260	5.3	1.0	345	0.05	1.0
265	4.2	1.0	350	0.04	1.0
270	3.3	1.0			

### Quantum Yields

$\phi_1 = 1.0$  for  $\lambda > 230 \text{ nm}$ ;  $\phi_1 = 0.85$ ,  $\phi_3 = 0.15$  at 193 nm.

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There have been no new measurements of the absorption cross-sections and our recommendations are unchanged from those in our previous evaluation, , 1997.<sup>7</sup> The preferred values are the mean of those determined by Lin et al.,<sup>8</sup> Molina and Molina,<sup>9</sup> Nicovich and Wine<sup>10</sup> and Vaghjani and Ravishankara.<sup>11</sup> These agree with the earlier values of Holt et al.<sup>12</sup> The absorption cross-sections have also been measured at other temperatures by Troe<sup>13</sup> (220–290 nm at 600 K and 1100 K) and by Nicovich and Wine<sup>10</sup> (260–250 nm, 200–400 K). Both Nicovich and Wine<sup>10</sup> and Troe<sup>13</sup> have expressed their results in an analytical form.

It has long been assumed that channel (1) is the only significant primary photochemical channel at  $\lambda > 200$  nm. There are measurements by Vaghjani and Ravishankara<sup>2</sup> and Vaghjani et al.<sup>3</sup> at 248 nm and 222 nm which support this. However, measurements at 193 nm by Vaghjani et al.<sup>3</sup> show a decline in the HO radical quantum yield (1.51 relative to an assumed value of 2 at 248 nm) with a growth in the H atom quantum yield, a feature previously observed by Gerlach-Meyer et al.<sup>1</sup> The results of Schiffman et al.<sup>4</sup> also agree well with this relative change in HO radical production in going from 248 nm to 193 nm. However, Schiffman et al.<sup>4</sup> obtain much lower absolute values for the quantum yield of HO radical production than obtained by Vaghjani and Ravishankara.<sup>2</sup>

The evidence therefore indicates that there is a decline in the relative importance of channel (1) in going from 248 nm to 193 nm but the point of onset of this decline and its form are uncertain. Furthermore, the reason for the difference in the absolute values of the quantum yield between the studies of Schiffman et al.<sup>4</sup> and Vaghjani and Ravishankara<sup>2</sup> is unclear; further work is urgently required to clarify this. Recent measurements<sup>14</sup> of the translational energy of the H-atom photofragments from 193 nm photolysis of H<sub>2</sub>O<sub>2</sub> originate from the same upper state ( $\tilde{A}^1A$ ) which is responsible for OH production at longer wavelengths.

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We recommend the use of a quantum yield of 2 for HO radical production ( $\phi_1 = 1.0$ ) at  $\lambda > 230$  nm.

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## Appendix 3: NO<sub>x</sub> reactions



$$\Delta H^\circ = -306.2 \text{ kJ}\cdot\text{mol}^{-1}$$

### Low-pressure rate coefficients

#### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.55 \times 10^{-32} \exp[(584 \pm 35)/T] [\text{N}_2]$	217-250	Whytock et al., 1976 <sup>1</sup>	FP-RF
$(1.18 \pm 0.15) \times 10^{-31} (T/300)^{-1.82} [\text{N}_2]$			
$8.8 \times 10^{-32} (T/300)^{-1.44} [\text{N}_2]$	200-370	Schieferstein et al., 1983 <sup>2</sup>	FP-CL

### Preferred Values

10  $k_0 = 1.0 \times 10^{-31} (T/300)^{-1.6} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-300 K.

#### *Reliability*

15  $\Delta \log k_0 = \pm 0.1$  at 298 K.

$\Delta n = \pm 0.3$ .

#### *Comments on Preferred Values*

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The preferred values are based on the data from refs. 1 and 2, combined with measurements from refs. 3-5 in other bath gases and the relative efficiencies determined in ref. 2. The full falloff curve has been determined in the relative rate measurements from ref. 6, leading to  $k_{\infty} = 3 \times 10^{-11} (T/300)^{0.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $F_C = 0.85$  over the temperature range 200-300 K. Absolute rate measurements in ref. 7 of the full falloff curve over the temperature range 200-400 K at pressures between 2 and 200 bar of  $\text{N}_2$  led to  $k_{\infty} = 5 \times 10^{-11} (T/300)^{-0.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in good agreement with theoretical predictions from ref. 8. Deviations from third order behavior are negligible under atmospheric conditions.

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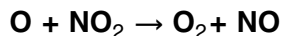
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$$\Delta H^\circ = -192.1 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$9.3 \times 10^{-12}$	296	Slanger et al., 1973 <sup>1</sup>	DF-CL (a)
$1.05 \times 10^{-11}$	240		
$(1.0 \pm 0.1) \times 10^{-11}$	298	Ongstad and Birks, 1984 <sup>2</sup>	DF-CL (a)
$6.58 \times 10^{-12} \exp[(142 \pm 23)/T]$	224-354	Ongstad and Birks, 1986 <sup>3</sup>	DF-CL (a)
$(1.03 \pm 0.09) \times 10^{-11}$	298		
$5.21 \times 10^{-12} \exp[(202 \pm 27)/T]$	233-357	Geers-Müller and Stuhl, 1987 <sup>4</sup>	PLP-CL (b)
$(1.02 \pm 0.02) \times 10^{-11}$	301		
$(9.3 \pm 1.0) \times 10^{-12}$	298	Paulson et al., 1995 <sup>5</sup>	PLP-RF (c)
$5.26 \times 10^{-12} \exp[(209 \pm 35)/T]$	220-412	Gierczak et al., 1999 <sup>6</sup>	PLP-RF (d)
$(1.06 \pm 0.08) \times 10^{-11}$	298		

### Comments

(a) O(<sup>3</sup>P) atoms were monitored by O + NO chemiluminescence.

(b) O(<sup>3</sup>P) atoms were generated by photolysis of NO. O(<sup>3</sup>P) were monitored by O + NO chemiluminescence. Values for  $k(\text{O} + \text{N}_2\text{O}_4)$  and  $k(\text{O} + \text{N}_2\text{O}_5)$  were also estimated from the results.

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(c) O(<sup>3</sup>P) atoms were generated by pulsed laser photolysis of NO<sub>2</sub> at 308 nm. NO<sub>2</sub> concentrations were determined by comparison of the UV absorption in pure NO<sub>2</sub> with that in the He/NO<sub>2</sub> mixtures which were flowed through the photolysis cell.

(d) O(<sup>3</sup>P) atoms were generated by pulsed laser photolysis of NO<sub>2</sub> at 308 nm. Three methods were used to determine the NO<sub>2</sub> concentration: (i) UV absorption, (ii) flow measurements based on the drop in pressure from a calibrated volume, (iii) chemical titration using an excess of O<sub>3</sub> to convert a measured flow of NO to NO<sub>2</sub>. The UV cross sections used were measured at 413 nm as a function of temperature and combined with those of Harder et al.,<sup>7</sup> with which they are in close agreement.

**Preferred Values** $k = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$  $k = 5.5 \times 10^{-12} \exp(188/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220\text{--}420 \text{ K.}$ *Reliability* $\Delta \log k = \pm 0.06 \text{ at } 298 \text{ K.}$  $\Delta(E/R) = \pm 80 \text{ K.}$ *Comments on Preferred Values*

The preferred value of  $k$  at 298 K is the average of the values obtained by Slanger et al.,<sup>1</sup> Ongsted and Birks,<sup>2,3</sup> Geers-Müller and Stuhl,<sup>4</sup> Paulson et al.,<sup>5</sup> and Gierczak et al.,<sup>6</sup> and the temperature dependence is from an unweighted least squares fit to the data from the same studies.<sup>1–6</sup>

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The earlier studies of Davis et al.<sup>8</sup> and Bemand et al.<sup>9</sup> are in satisfactory agreement with the other studies but show greater scatter than the more recent studies, and are not used in arriving at our preferred values.

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$$\Delta H^\circ = -208.6 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3 \times 10^{-31} (T/300)^{-1.75} [\text{N}_2]$	220-296	Burkholder and Ravishankara, 2000 <sup>1</sup>	PLP (a)
$(1.3 \pm 0.3) \times 10^{-31} (T/300)^{-1.5} [\text{N}_2]$	300-400	Hahn et al., 2000 <sup>2</sup>	PLP (b)
<i>Relative Rate Coefficients</i>			
$(9.2 \pm 1) \times 10^{-32} [\text{N}_2]$	297	Harker and Johnston, 1973 <sup>3</sup>	RR (c)
$(8.0 \pm 1) \times 10^{-32} [\text{N}_2]$	295	Hippler et al., 1975 <sup>4</sup>	RR (d)

## Comments

(a) Oxygen atoms generated by laser photolysis of  $\text{NO}_2$  at 352 nm,  $\text{NO}_3$  monitored by long-path diode laser absorption at 662 nm. Measurements were made in  $\text{N}_2$  over the pressure range 20-800 Torr; falloff curves were represented with  $F_c = 0.6$  and  $k_\infty = 3.75 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  independent of the temperature.

(b) Oxygen atoms generated by laser photolysis of  $\text{N}_2\text{O}$  at 193 nm,  $\text{NO}_3$  monitored by light absorption at 578 nm. Falloff curves measured at 300 and 400 K in  $\text{N}_2$  over the pressure range 1-900 bar. Falloff curves represented with  $F_c = 0.71 \exp$

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$(-T/1700)$ , which corresponds to  $F_c = 0.6$  at 300 K, and  $k_\infty = (2.3 \pm 0.2) \times 10^{-11} (T/300)^{0.24} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

(c)  $\text{O}(^3\text{P})$  atoms were generated by the photolysis of  $\text{NO}_2$  in the presence of 1 bar of  $\text{N}_2$ .  $\text{NO}_2$  and  $\text{N}_2\text{O}_5$  concentrations were monitored by IR absorption. The measured value of  $k/k(\text{O} + \text{NO}_2)$  was evaluated with  $k(\text{O} + \text{NO}_2) = 9.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The rate coefficient has been reevaluated by increasing the measured rate coefficient by 10% to account for a 10% falloff below  $k_0$ , as measured by in ref. 5.

(d)  $\text{O}(^3\text{P})$  atoms were generated by the photolysis of  $\text{NO}_2$  at various  $\text{N}_2$  pressures.  $\text{NO}_2$  was monitored by UV absorption. The measured value of  $k/k(\text{O} + \text{NO}_2)$  was evaluated with  $k(\text{O} + \text{NO}_2) = 9.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , taking  $\text{N}_2\text{O}_5$  reactions and falloff effects into account.

### Preferred Values

$k_0 = 1.3 \times 10^{-31} (T/300)^{-1.5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200–400 K.

### Reliability

$\Delta \log k_0 = \pm 0.30$  at 298 K.

$\Delta n = \pm 1$ .

### Comments on Preferred Values

The preferred values are from the falloff extrapolations of the absolute rate measurements of ref. 2 and the relative rate measurements of refs. 3–7. The discrepancy

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between the absolute rate measurements below 800 Torr from ref. 1 and above 1 bar from ref. 2 may be due to difficulties in separating the reactions  $O + NO_2 \rightarrow O_2 + NO$  and  $O + NO_2 + M \rightarrow NO_3 + M$  with subsequent  $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ . Because the data from ref. 2 are in much better consistency with the relative rate measurements from refs. 3-7, they are preferred here. It should be emphasized that falloff effects are important at atmospheric pressures; these effects are represented with  $F_c = 0.6$  and  $k_\infty = 2.3 \times 10^{-11} (T/300)^{0.24} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from the measurements and theoretical analysis of ref. 2.

### High-pressure rate coefficients

#### Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.3 \pm 0.2) \times 10^{-11} (T/300)^{0.24}$	300-400	Hahn et al., 2000 <sup>1</sup>	PLP (a)
<i>Relative Rate Coefficients</i>			
$(2.2 \pm 0.4) \times 10^{-11}$	300	Gaedtke and Troe, 1975 <sup>5</sup>	(b)

#### Comments

(a) See comment (b) for  $k_0$ .

(b) Analysis of the pressure dependence of the quantum yield of  $NO_2$  photolysis between 1 and 1000 bar of  $N_2$ . Measurements of  $k_\infty/k(O + NO_2 \rightarrow O_2 + NO)$  evaluated with  $k(O + NO_2) = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

## Preferred Values

$k_{\infty} = 2.3 \times 10^{-11} (T/300)^{0.24} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-400 K.

### 5 *Reliability*

$\Delta \log k_{\infty} = \pm 0.2$  over the temperature range 200-400 K.

*Comments on Preferred Values*

10 The absolute and relative rate measurements of the falloff curve over a very wide pressure range from refs. 2 and 5, on which the preferred values are based, allow for a reliable extrapolation to the high pressure limit of the reaction. Falloff curves are constructed with  $F_c = 0.6$  and  $k_0 = 1.3 \times 10^{-31} (T/300)^{-1.5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

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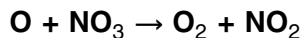
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$$\Delta H^\circ = -289.7 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.70 \pm 0.6) \times 10^{-11}$	297	Canosa-Mas et al., 1989 <sup>1</sup>	DF-RF/A (a)

### Comments

(a)  $[\text{O}(^3\text{P})]$  was monitored by RF and  $[\text{NO}_3]$  by absorption at 662 nm using  $\sigma = 1.9 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ . Excess of  $[\text{NO}_3]$  over  $[\text{O}]$  was not sufficient to give purely first order kinetics. Analysis of the data took account of this and of the possibility of other interfering reactions.

### Preferred Values

$k = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Reliability

$\Delta \log k = \pm 0.3$  at 298 K.

*Comments on Preferred Values*

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The preferred value is that reported by Canosa-Mas et al.,<sup>1</sup> which is the only direct measurement of the rate coefficient. The earlier relative value of Graham and Johnston,<sup>2</sup> of  $(1.0 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 297 K, is consistent with the preferred value, taking into account the experimental uncertainties. The temperature dependence is probably near zero, by analogy with the reaction of O(<sup>3</sup>P) atoms with NO<sub>2</sub>.

## References

<sup>1</sup> C. E. Canosa-Mas, P. J. Carpenter, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, 85, 697, 1989.

<sup>2</sup> R. A. Graham and H. S. Johnston, J. Phys. Chem., 82, 254, 1978.

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$$\Delta H^\circ = -356.9 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.8 \pm 0.8) \times 10^{-36} (T/300)^{-0.88}$	220-300	Estupiñán et al., 2001 <sup>1</sup>	(a)
<i>Relative Rate Coefficients</i>			
$2.8 \times 10^{-36} [\text{N}_2]$	300	Gaedtke et al., 1973 <sup>2</sup>	(b)
$6.5 \times 10^{-37} [\text{N}_2]$	296	Kajimoto and Cvetanovic, 1976 <sup>3</sup>	(c)
$(8.8 \pm 3.3) \times 10^{-37} [\text{N}_2]$	298	Maric and Burrows, 1992 <sup>4</sup>	(d)

## Comments

- (a) Laser flash photolysis of  $\text{O}_3$  generating  $\text{O}(^1\text{D})$  and diode laser absorption spectroscopy in a multipass cell detecting  $\text{N}_2\text{O}$ .
- 10 (b) Steady-state photolysis of  $\text{O}_3$ - $\text{O}_2$  mixtures at 260 nm in the presence of 1-200 bar of  $\text{N}_2$ . The rate of  $\text{N}_2\text{O}$  formation was measured relative to  $\text{O}_3$  consumption and analyzed in terms of the ratio  $k/k[\text{O}(^1\text{D}) + \text{O}_3 \rightarrow 2 \text{O}_2]$ .
- (c) See comment (b), measurements between 25 and 115 bar.
- (d) Steady-state photolysis of synthetic air at 185 and 254 nm.

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## Preferred Values

$$k_0 = 2.8 \times 10^{-36} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

### Reliability

$$\Delta \log k_0 = \pm 0.5 \text{ at } 298 \text{ K.}$$

### Comments on Preferred Values

The slow rate of the reaction, in competition with the fast electronic quenching reaction  $\text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{O}(^3\text{P}) + \text{N}_2$ , makes the measurement of the  $\text{N}_2\text{O}$  yield a difficult task. The differences between the four studies<sup>1-4</sup> reflect this experimental problem. Because of the agreement of the results from refs. 1 and 2, these are preferred, however, allowing for a large uncertainty. A theoretical analysis should be made in relation to the thermal decomposition of  $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}(^3\text{P})$  in the low- and high-pressure ranges.

## References

<sup>1</sup> E. G. Estupiñán, J. M. Nicovich, J. Li, D. M. Cunnold and P. H. Wine, *J. Phys. Chem. A*, 106, 5880, 2002.

<sup>2</sup> H. Gaedtke, K. Glänzer, H. Hippler, K. Luther, and J. Troe, 14th Int. Symp. on Combustion (The Combustion Institute, Pittsburgh, 1973), p. 295, 1993.

<sup>3</sup> O. Kajimoto and R. J. Cvetanovic, *J. Chem. Phys.* 64, 1005, 1976.

<sup>4</sup> D. Maric and J. P. Burrows, *J. Photochem. Photobiol. A*, 66, 291, 1992.

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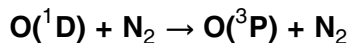
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$$\Delta H^\circ = -189.7 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.0 \times 10^{-11} \exp[(107 \pm 8)/T]$	104-354	Streit et al., 1976 <sup>1</sup>	PLP (a)
$(2.8 \pm 0.6) \times 10^{-11}$	300		
$(2.4 \pm 0.1) \times 10^{-11}$	295	Amimoto et al., 1979 <sup>2</sup>	PLP-RA (b)
$(2.77 \pm 0.40) \times 10^{-11}$	298	Brock and Watson, 1980 <sup>3</sup>	PLP-RF (b)
$(2.52 \pm 0.25) \times 10^{-11}$	297	Wine and Ravishankara, 1981 <sup>4</sup>	PLP-RF (b)
<i>Relative Rate Coefficients</i>			
$(2.6 \pm 0.3) \times 10^{-11}$	296	Shi and Barker, 1990 <sup>5</sup>	(c)

### Comments

(a) O(<sup>1</sup>D) atoms were monitored by time-resolved detection of O(<sup>1</sup>D) → O(<sup>3</sup>P) emission.

(b) O(<sup>3</sup>P) atom product monitored.

(c) The kinetics of deactivation of O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) were studied by time-resolved emission from O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) produced by the reaction of O(<sup>1</sup>D) atoms with O<sub>2</sub> following pulsed laser photolysis of O<sub>3</sub>. The effect of N<sub>2</sub> (and other quenchers) on the initial fluorescence intensity gave the rate coefficient for O(<sup>1</sup>D) deactivation relative to that

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for  $O_2$ .  $k$  has been calculated using a value of  $k[O(^1D) + O_2] = 4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation).

### Preferred Values

$k = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.8 \times 10^{-11} \exp(107/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 100-350 K.

### Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$ .

### Comments on Preferred Values

The preferred value at 298 K is the average of the results of Streit et al.,<sup>1</sup> Amimoto et al.,<sup>2</sup> Brock and Watson,<sup>3</sup> Wine and Ravishankara,<sup>4</sup> and Shi and Barker.<sup>5</sup> The temperature dependence obtained by Streit et al.<sup>1</sup> is accepted and the pre-exponential factor is adjusted to fit the value of  $k$  at 298 K.

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<sup>1</sup> G. E. Streit, C. J. Howard, A. L. Schmeltekopf, J. A. Davidson, and H. I. Schiff, J. Chem. Phys., 65, 4761, 1976.

<sup>2</sup> S. T. Amimoto, A. P. Force, R. G. Gulotty Jr., and J. R. Wiesenfeld, J. Chem. Phys., 71, 3640, 1979.

<sup>3</sup> J. C. Brock and R. T. Watson, results presented at the NATO Advanced Study Institute on Atmospheric Ozone, Portugal, 1979; see G. K. Moortgat's review in Report No.

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<sup>5</sup> J. Shi and J. R. Barker, Int. J. Chem. Kinet., 22, 1283, 1990.

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$$\Delta H^\circ(1) = -521.0 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(2) = -340.4 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.1 \pm 0.2) \times 10^{-10}$	204-359	Davidson et al., 1977 <sup>1</sup>	PLP (a)
$(1.20 \pm 0.1) \times 10^{-10}$	295	Amimoto et al., 1979 <sup>2</sup>	PLP-RA (b)
$(1.17 \pm 0.12) \times 10^{-10}$	298	Wine and Ravishankara, 1981 <sup>3</sup>	PLP-RF (b)
<i>Branching Ratios</i>			
$k_2/k = 0.62 \pm 0.02$	298	Marx et al., 1979 <sup>4</sup>	P-GC/CL
$k_2/k = 0.62 \pm 0.09$	177-296	Lam et al., 1981 <sup>5</sup>	P-CL
$k_2/k = 0.61 \pm 0.08$	296	Cantrell et al., 1994 <sup>6</sup>	(c)

### 10 Comments

(a) O(<sup>1</sup>D) atoms were monitored by time-resolved detection of O(<sup>1</sup>D) → O(<sup>3</sup>P) emission.

(b) O(<sup>3</sup>P) atom product monitored.

(c) Static photolysis of N<sub>2</sub>O-O<sub>3</sub> mixtures at  $\lambda > 240$  nm with product analysis by FTIR spectroscopy. The amount of NO formed in reaction (2) was determined

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from the yield of  $\text{HNO}_3$  formed by total oxidation and hydration of  $\text{NO}_x$  products, corrected for losses to the wall. The value of  $k_2/k$  obtained from the experimental data was  $0.57 \pm 0.08$ ; the value given in the table was obtained by averaging the experimental value with selected literature data.

## 5 Preferred Values

$k_1 = 4.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 200–350 K.

$k_2 = 7.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 200–350 K.

10

### Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.1$  at 298 K.

$\Delta(E_1/R) = (E_2/R) = \pm 100 \text{ K}$ .

15

### Comments on Preferred Values

The data and recommendation for the branching ratio at room temperature of  $k_2/k = 0.61 \pm 0.08$  given by Cantrell et al.<sup>6</sup> are in accord with the earlier results of Marx et al.<sup>4</sup> and Lam et al.<sup>5</sup> The overall rate coefficient values at room temperature are the average of the results of Davidson et al.,<sup>1</sup> Amimoto et al.<sup>2</sup> and Wine and Ravishankara,<sup>3</sup> all of which are in close agreement (see also data by Volltrauer et al.<sup>8</sup>) The temperature independence reported by Davidson et al.<sup>1,7</sup> is accepted.

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- <sup>4</sup> W. Marx, F. Bahe, and U. Schurath, *Ber. Bunsenges. Phys. Chem.*, **83**, 225, 1979.
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- <sup>7</sup> J. A. Davidson, C. J. Howard, H. I. Schiff and F. C. Fehsenfeld, *J. Chem. Phys.*, **70**, 1697, 1979.
- <sup>8</sup> H. N. Volltrauer, W. Felder, R. J. Pirkle, and A. Fontijn, *J. Photochem.*, **11**, 173, 1979.

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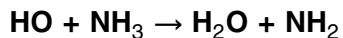
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$$\Delta H^\circ = -44.4 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.5 \pm 0.4) \times 10^{-13}$	298	Stuhl, 1973 <sup>1</sup>	FP-RF
$2.3 \times 10^{-12} \exp(-805/T)$	228-472	Zellner and Smith, 1974 <sup>2</sup> ; Smith	FP-RA
$1.58 \times 10^{-13}$	298	and Zellner, 1975 <sup>3</sup>	
$2.93 \times 10^{-12} \exp[-(861 \pm 151)/T]$	298-427	Perry et al., 1979 <sup>4</sup>	FP-RF
$(1.64 \pm 0.16) \times 10^{-13}$	298		
$5.41 \times 10^{-12} \exp[-(1067 \pm 72)/T]$	294-1075	Silver and Kolb, 1980 <sup>5</sup>	DF-RF
$(1.44 \pm 0.29) \times 10^{-13}$	294		
$4.55 \times 10^{-12} \exp[-(973 \pm 78)/T]$	297-364	Stephens, 1984 <sup>6</sup>	DF-RF
$(1.73 \pm 0.11) \times 10^{-13}$	297		
$3.29 \times 10^{-12} \exp[-(922 \pm 100)/T]$	273-433	Diau et al., 1990 <sup>7</sup>	FP/PLP-LIF (a)
$(1.47 \pm 0.07) \times 10^{-13}$	297		

### Comments

- (a) Pulsed laser photolysis and conventional flash photolysis of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$  were used as the sources of HO radicals. The total pressure was varied over the range 0.091-0.672 bar (68-504 Torr).

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## Preferred Values

$k = 1.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 3.5 \times 10^{-12} \exp(-925/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230-450 K.

### 5 *Reliability*

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$ .

### 10 *Comments on Preferred Values*

The preferred values are obtained from a least-squares fit to the data of Stuhl,<sup>1</sup> Smith and Zellner,<sup>2,3</sup> Perry et al.,<sup>4</sup> Stephens,<sup>6</sup> Diau et al.,<sup>7</sup> and the data of Silver and Kolb<sup>5</sup> below 450 K. The relative rate measurement of  $k/k(\text{HO} + \text{HONO})$  by Cox et al.<sup>8</sup> at 296 ± 2 K is in good agreement with the preferred value when the value of  $k(\text{HO} + \text{HONO})$  from this review is used. Results from other low temperature studies<sup>9-11</sup> are well outside the error limits obtained from the direct studies cited in the table above<sup>1-7</sup> and are not used in this evaluation.

There are numerous high temperature studies which, together with the studies cited here, indicate a distinct curvature on the Arrhenius plot.<sup>12</sup> However, the simple Arrhenius expression given here as the preferred expression for  $k$  is sufficiently precise over the temperature range cited.

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<sup>1</sup> F. Stuhl, J. Chem. Phys., 59, 635, 1973.

<sup>2</sup> R. Zellner and I. W. M. Smith, Chem. Phys. Lett., 26, 72, 1974.

<sup>3</sup> I. W. M. Smith and R. Zellner, Int. J. Chem. Kinet. Symp.1, 341, 1975.

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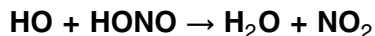
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$$\Delta H^\circ = -166.3 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.80 \times 10^{-11} \exp[-(390 \pm 80)/T]$ $(4.9 \pm 0.5) \times 10^{-12}$	278-342 298	Jenkin and Cox, 1987 <sup>1</sup>	MM-RA
$2.8 \times 10^{-12} \exp[(260 \pm 140)/T]$ $(7.05 \pm 1.41) \times 10^{-12}$	298-373 298	Burkholder et al., 1992 <sup>2</sup>	PLP-LIF (a)
<i>Relative Rate Coefficients</i>			
$(6.0 \pm 0.4) \times 10^{-12}$	296	Cox et al., 1976 <sup>3</sup>	(b)

### Comments

(a) HO radicals were monitored by LIF with HONO in excess. [HONO] and [NO<sub>2</sub>] were also monitored using *in situ* diode-array spectroscopy.

(b) Photolysis of HONO-NO and HONO-H<sub>2</sub> mixtures at a total pressure of 1 bar of N<sub>2</sub> or N<sub>2</sub>-O<sub>2</sub> diluent. A value of  $k/k(\text{HO} + \text{H}_2) = 945 \pm 48$  was obtained. The value of  $k$  given in the table is calculated using  $k(\text{HO} + \text{H}_2) = 6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K.<sup>4</sup>

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## Preferred Values

$k = 6.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 2.5 \times 10^{-12} \exp(260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290-380 K.

### 5 *Reliability*

$\Delta \log k = \pm 0.15$  at 298 K.

$\Delta(E/R) = \pm 260 \text{ K}$ .

### 10 *Comments on Preferred Values*

There are significant differences between the two direct studies of Jenkin and Cox<sup>1</sup> and Burkholder et al.<sup>2</sup> particularly with respect to the temperature dependence of  $k$ . The work of Burkholder et al.<sup>2</sup> has substantially better precision than that of Jenkin and Cox.<sup>1</sup> Furthermore, the small negative temperature dependence of  $k$  found by Burkholder et al.<sup>2</sup> is consistent with that observed for the analogous reaction of HO radicals with HONO<sub>2</sub>.

The preferred value of  $k$  at 298 K is an average of the room temperature rate coefficients of Jenkin and Cox,<sup>1</sup> Burkholder et al.<sup>2</sup> and Cox et al.<sup>3</sup> The temperature dependence of  $k$  is that given by Burkholder et al.<sup>2</sup> with the pre-exponential factor being adjusted to fit the preferred value of  $k$  at 298 K.

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<sup>1</sup> M. E. Jenkin and R. A. Cox, Chem. Phys. Lett., 137, 548, 1987.

<sup>2</sup> J. B. Burkholder, A. Mellouki, R. Talukdar, and A. R. Ravishankara, Int. J. Chem. Kinet.,  
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<sup>3</sup> R. A. Cox, R. G. Derwent, and P. M. Holt, J. Chem. Soc. Faraday Trans. 1, 72, 2031,

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<sup>4</sup> IUPAC, 2003, <http://www.iupac-kinetic.ch.cam.ac.uk/>

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$$\Delta H^\circ = -70.2 \text{ kJ mol}^{-1}$$

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### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.9 \pm 1.3) \times 10^{-14}$	272-464	Margitan et al., 1975 <sup>1</sup>	DF-RF (a)
$(8 \pm 2) \times 10^{-14}$	240-298	Smith and Zellner, 1975 <sup>2</sup>	FP-RA (b)
$1.52 \times 10^{-14} \exp[(649 \pm 69)/T]$	224-366	Wine et al., 1981 <sup>3</sup>	FP-RF
$(1.25 \pm 0.28) \times 10^{-13}$	298		
$(1.25 \pm 0.13) \times 10^{-13}$	298	Ravishankara et al., 1982 <sup>4</sup>	PLP-RA (c)
$5.7 \times 10^{-15} \exp[(896 \pm 145)/T]$	228-298	Margitan and Watson, 1982 <sup>5</sup>	FP-RF (d)
$(1.19 \pm 0.12) \times 10^{-13}$	298		
$1.05 \times 10^{-14} \exp[(759 \pm 100)/T]$	225-296	Kurylo et al., 1982 <sup>6</sup>	FP-RF (e)
$(1.38 \pm 0.20) \times 10^{-13}$	296		
$7.3 \times 10^{-15} \exp[(867 \pm 85)/T]$	251-403	Jourdain et al., 1982 <sup>7</sup>	DF-EPR (f)
$(1.25 \pm 0.07) \times 10^{-13}$	296		
$1.52 \times 10^{-14} \exp[(644 \pm 79)/T]$	218-363	Marinelli and Johnston, 1982 <sup>8</sup>	FP-RF (g)
$(1.31 \pm 0.24) \times 10^{-13}$	298		

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$8.3 \times 10^{-15} \exp[(850 \pm 40)/T]$	240-370	Smith et al., 1984 <sup>9</sup>	FP-RF (h)
$(1.36 \pm 0.04) \times 10^{-13}$	295		
$5.43 \times 10^{-15} \exp(843/T)$	253-295	Devolder et al., 1984 <sup>10</sup>	DF-RF (i)
$(9.3 \pm 1.0) \times 10^{-14}$	295		
$2.0 \times 10^{-14} \exp[(430 \pm 60)/T]$	237-330	Connell and Howard, 1985 <sup>11</sup>	DF-LMR
$(8.4 \pm 0.18) \times 10^{-14}$	301		
$(1.26 \pm 0.11) \times 10^{-13}$	297	Jolly et al., 1985 <sup>12</sup>	PLP-RA (j)
$(1.28 \pm 0.10) \times 10^{-13}$	297	Stachnik et al., 1986 <sup>13</sup>	PLP-RA (k)
See comment	200-373	Brown et al., 1999 <sup>14</sup>	PLP-LIF (l)

## Comments

- (a) The value given is the mean of the rate coefficients measured at 295, 420 and 464 K. A slightly higher value obtained at 272 K was considered<sup>1</sup> to be less reliable.
- (b) The measured rate coefficient was observed to increase with increasing temperature above 298 K, to  $1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 406 K.
- (c) The value of  $k$  tabulated is at 67 mbar (50 Torr) Ar;  $k$  was also measured at 80 mbar (60 Torr) SF<sub>6</sub> and at 251 K. The reaction stoichiometry was measured by monitoring NO<sub>3</sub> radical production using optical absorption at 662 nm and using the initial [HO] value. The figures given for the stoichiometry have since been revised as a result of a remeasurement of the absorption coefficient of NO<sub>3</sub>.<sup>15</sup> The new values are 0.85 at 298 K and 0.88 at 251 K for  $[\text{NO}_3]_{\text{produced}}/[\text{HO}]_{\text{consumed}}$ .

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- (d)  $k$  was found to depend on both temperature and pressure.  $k$  was reported to increase by 10% over the pressure range 27-133 mbar (20-100 Torr) He at 298 K and by 40% over the same pressure range at 238 K. The Arrhenius expression tabulated is a least-squares fit to the data at 53 mbar (40 Torr) He over the temperature range 228-298 K. Significant non-Arrhenius behavior was observed above 298 K at each value of the total pressure.  $k$  was also determined at 27 mbar (20 Torr) He and 133 mbar (100 Torr) He. For the linear portion of the Arrhenius plots (at or below 298 K) the following values of  $E/R$  are derived: -735 K (27 mbar He) and -1000 K (133 mbar He). The authors made linear extrapolations to zero pressure and reported an  $E/R$  value of -700K for data at or below 298 K.
- (e)  $k$  was studied over the temperature range 225-443 K and over the pressure range 40-67 mbar (30-50 Torr) of Ar and SF<sub>6</sub>. The rate coefficient  $k$  exhibited significant non-Arrhenius behavior above 296 K, with no dependence on total pressure.
- (f) Pressure  $\sim$ 1.3 mbar (1 Torr). The rate coefficient  $k$  was reported to exhibit linear Arrhenius behavior over the entire temperature range, but a greater temperature dependence ( $E/R = -1119$  K) is derived using only data at or below 298 K. The NO<sub>3</sub> radicals produced were measured by adding excess NO and monitoring its removal by EPR. The stoichiometry so obtained was  $[\text{NO}_3]_{\text{produced}}/[\text{HO}]_{\text{consumed}} = 1.03 \pm 0.05$ .
- (g) Pressure of 13-67 mbar (10-50 Torr) Ar.  $k$  was reported to exhibit linear Arrhenius behavior over the entire temperature range, but a greater temperature dependence ( $E/R = -697$  K) is derived using only data at and below 298 K.
- (h) The pressure was varied from 0.067-1.01 bar (50-760 Torr) He, with no observed effect on the value of  $k$ . Linear Arrhenius behavior was observed.
- (i) The rate coefficient was measured up to 373 K. The rate coefficient was observed to level off above room temperature. The Arrhenius expression tabulated applies to results below room temperature.

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(j) The value given is for pressures of 13–21 mbar (1–16 Torr) HNO<sub>3</sub>. Experiments were also carried out in the presence of 0.667 bar (500 Torr) N<sub>2</sub> and 0.800 bar (600 Torr) SF<sub>6</sub>. After corrections for the contribution of the reaction HO + NO<sub>2</sub> + M were made, no significant effect of total pressure on *k* was observed.

(k) Measurements were made at 248 and 297 K and at total pressures of 0.013, 0.080 and 0.973 bar (10, 60 and 730 Torr) of He, N<sub>2</sub> and SF<sub>6</sub> (the value cited being at 0.013 bar N<sub>2</sub>). NO<sub>2</sub> impurity levels were determined to be less than 0.1%. The data were fitted to the fall-off function given by Lamb et al.<sup>16</sup> The extrapolated zero-pressure rate constant corresponds to *E/R* = -710 K.

(l) Rate coefficients were measured as a function of pressure (27–677 mbar) for the diluent gases N<sub>2</sub>, O<sub>2</sub>, He and SF<sub>6</sub> over the temperature range 200–373 K. The measured rate coefficients increased with increasing pressure, with the pressure dependence being more marked at lower temperatures (and not being evident at temperatures ≥325 K), and a distinct dependence on the identity of the diluent gas was observed at temperatures ≤250 K. At temperatures ≤350 K, the measured rate coefficient at a given total pressure (of a specific diluent gas) increased with decreasing temperature, with the (negative) temperature dependence increasing with increasing total pressure. The data obtained, together with those of Margitan and Watson,<sup>5</sup> Devolder et al.<sup>10</sup> and Stachnik et al.,<sup>13</sup> for the diluent gases He, N<sub>2</sub> and SF<sub>6</sub> were fit to the expression proposed by Lamb et al.<sup>16</sup> (see Comments on Preferred Values).

### Preferred Values

$k = 1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and 1 bar of air.

See Comments on Preferred Values for the expression to be used under other conditions of temperature and pressure.

## Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

5

Similar error limits apply to values of  $k$  at other temperatures and pressures over the range 200-350 K.

## Comments on Preferred Values

10

The rate coefficient data have been carefully assessed by the NASA Panel,<sup>17</sup> and their recommendations and analysis are adopted in this evaluation. Based in large part on the recent extensive study of Brown et al.<sup>14</sup> on the HO + HNO<sub>3</sub> reaction, there is now general agreement on the following major features of the data for  $k$  at temperatures  $\leq 350$  K: (a) a negative temperature dependence (which appears to level off near 500 K); (b) a small but measurable pressure dependence at room temperature which increases at low temperatures

15

Lamb et al.,<sup>16</sup> have proposed a mechanism involving formation of a bound, relatively long-lived, intermediate complex (channel 2) as well as the direct reaction (channel 1). This mechanism gives a rate coefficient which combines a low pressure limiting rate constant,  $k_1$ , and a Lindemann-Hinshelwood expression for the pressure dependence. This mechanism has been used by Brown et al.<sup>14</sup> and by the NASA Panel<sup>17</sup> to fit the data of Brown et al.<sup>14</sup> Margitan and Watson,<sup>5</sup> Devolder et al.<sup>10</sup> and Stachnik et al.,<sup>13</sup> and their expression<sup>14,17</sup> is adopted here. The overall rate constant can be expressed as:

20

25

$$k = k_1(T) + k_2(M, T)$$

where  $k_2(M, T) = k_3[M]/(1 + k_3[M]/k_4)$ . The expressions for the elementary rate constants are:<sup>14,17</sup>

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$$k_1 = 2.4 \times 10^{-14} \exp(460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_3 = 6.5 \times 10^{-34} \exp(1335/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$k_4 = 2.7 \times 10^{-17} \exp(2199/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

- 5 The expressions are valid over the temperature range 200-350 K for air diluent.

This expression has been used to calculate the preferred value at 298 K and a pressure of 1 bar of air. There is no evidence for products other than  $\text{NO}_3$  and  $\text{H}_2\text{O}$ . Studies of the reaction stoichiometry have given values of 0.85<sup>4,15</sup> and 1.03.<sup>7</sup> Rate coefficients for the reaction  $\text{DO} + \text{DNO}_3$  as a function of temperature and pressure have been reported by Bossard et al.,<sup>18</sup> Singleton et al.<sup>19</sup> and Brown et al.,<sup>20</sup> and Brown et al.<sup>20</sup> have also investigated the kinetics of the reactions  $\text{DO} + \text{HNO}_3$ ,  $\text{HO} + \text{DNO}_3$  and  $\text{H}^{18}\text{O} + \text{HN}^{16}\text{O}_3$ .

15 Brown et al.<sup>20</sup> measured the  $\text{NO}_3$  radical formation yield from the  $\text{HO} + \text{HNO}_3$  reaction over the temperature and pressure ranges 240-330 K and 31-1027 mbar  $\text{N}_2$ , respectively, and from the  $\text{DO} + \text{DNO}_3$  reaction at 296 K and 99-480 mbar  $\text{N}_2$ . The  $\text{NO}_3$  radical formation yield from both reactions was determined to be unity, within the experimental uncertainties.<sup>20</sup>

20 Carl et al.<sup>21</sup> have shown, by monitoring the  $\text{NO}_3$  radical formation rate, that the rate coefficient at  $295 \pm 3$  K and 267 mbar  $\text{N}_2$  is independent of water vapor (0-13.3 mbar). These data<sup>21</sup> show that there will be no effect of water vapor on the rate coefficient  $k$  under atmospheric conditions.

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<sup>17</sup> NASA Evaluation No. 13, 2000 (see references in Introduction).

<sup>18</sup> A. R. Bossard, G. Paraskevopoulos, and D. L. Singleton, *Chem. Phys. Lett.*, 134, 583, 1987.

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$$\Delta H^\circ(1) = -193 \text{ kJ mol}^{-1}$$

$$5 \quad \Delta H^\circ(2) = -47 \text{ kJ mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.0 \pm 1.6) \times 10^{-12}$	246-324	Trevor et al., 1982 <sup>1</sup>	PLP-RF (a)
$5.9 \times 10^{-13} \exp[(650 \pm 30)/T]$	241-336	Smith et al., 1984 <sup>2</sup>	FP-RF (b)
$(5.2 \pm 1.1) \times 10^{-12}$	295		
<i>Relative Rate Coefficients</i>			
$(5.1 \pm 1.3) \times 10^{-12}$	268-295	Barnes et al., 1986 <sup>3</sup>	RR (c)

### 10 Comments

(a) The rate coefficient was independent of total pressure over the range 4-20 mbar He.

(b) The total pressure was 1.01 bar (760 Torr) of He.

(c) Relative rate study in a 420 L vessel. FTIR was used to monitor the concentration of  $\text{HO}_2\text{NO}_2$ , and the concentrations of the reference hydrocarbons ( $\text{C}_3\text{H}_6$ ,  $n\text{-C}_4\text{H}_{10}$ ) were monitored by GC. The effect of pressure was studied over the range  
 15 1.3-400 mbar (1-300 Torr) of He or  $\text{N}_2$ . The measured rate coefficient ratios have

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been placed on an absolute basis using the rate coefficient of  $k(\text{HO} + n\text{-C}_4\text{H}_{10}) = 1.69 \times 10^{-17} T^2 \exp(145/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and the fall-off expression for  $k(\text{HO} + \text{C}_3\text{H}_6)$  recommended by Atkinson.<sup>4</sup> The rate coefficients are observed to be pressure and temperature independent over the ranges studied. In particular, the rate coefficient, measured relative to that for HO + *n*-butane (which is pressure-independent), showed no effect of total pressure of He diluent over the range 6.7-400 mbar at 278 K. Results from this study supersede earlier results obtained using similar but less sensitive techniques.<sup>5</sup>

### Preferred Values

$k = 4.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.9 \times 10^{-12} \exp(270/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240-340 K.

### Reliability

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta(E/R) = \pm 500 \text{ K}$ .

### Comments on Preferred Values

The preferred values are based upon a least-squares fit to the data of Trevor et al.,<sup>1</sup> Smith et al.,<sup>2</sup> and Barnes et al.<sup>3</sup> Trevor et al.<sup>1</sup> studied the reaction from 246-324 K at low pressures [4-20 mbar (3-15 Torr He)] and recommended a temperature-independent rate coefficient but also reported an Arrhenius expression with  $E/R = (193 \pm 194) \text{ K}$ . In contrast, Smith et al.<sup>1</sup> reported a negative temperature dependence of  $k$  with  $E/R = -(650 \pm 30) \text{ K}$  over the range 241-336 K at 1.01 bar (760 Torr) of He. It is possible that this difference is due to the reaction mechanism being complex, leading to different temperature dependences at low and high pressure. At 220 K, the values of  $k$  derived

from these studies differ by a factor of 3 but the recommended error limits on  $E/R$  encompass the results from both studies.

The study by Barnes et al.<sup>3</sup> is the only one over an extended pressure range [6.7-400 mbar (5-300 Torr) He at 278 K]. Their data show the rate coefficient to be pressure independent over this range, and the same value of  $k$  was obtained at 295 K and 6.7 mbar He as at 268 K and 133 mbar He. They also observed no change with N<sub>2</sub> or synthetic air as the diluent gas. A TST calculation by Lamb et al.<sup>6</sup> suggests that the pressure dependence of this rate coefficient will be much less than that for the corresponding reaction of HO radicals with HNO<sub>3</sub>. Although no data are as yet available concerning the reaction products, channel (1) is expected to dominate.

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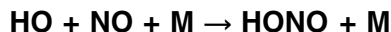
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$$\Delta H^\circ = -207.0 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.1 \pm 0.1) \times 10^{-30} [\text{N}_2]$	293	Burrows et al., 1983 <sup>1</sup>	DF-RF
$(7.0 \pm 2.0) \times 10^{-31} (T/300)^{-(2.6 \pm 0.3)} [\text{N}_2]$	90-220	Atkinson and Smith, 1994 <sup>2</sup>	DF-LIF (a)
$8.9 \times 10^{-31} (T/298)^{-2.1} [\text{N}_2]$	80-301	Sharkey et al., 1994 <sup>3</sup>	PLP-LIF (b)

## Comments

(a) HO radicals were generated by a cold cathode discharge and detected by LIF. The experiments were carried out in a supersonic expansion at total pressures corresponding to  $10^{16}$  to  $10^{18}$  molecule  $\text{cm}^{-3}$ .

(b) Experiments were carried out in a cryogenically cooled cell and in a supersonic expansion. At 52 K, rate coefficients have been determined at total gas densities from  $5.1 \times 10^{16}$  -  $8.2 \times 10^{17}$  molecule  $\text{cm}^{-3}$ .

## Preferred Values

15  $k_0 = 7.4 \times 10^{-31} (T/300)^{-2.4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-400 K.

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## Reliability

$\Delta \log k_0 = \pm 0.10$  at 298 K.

5  $\Delta n = \pm 0.5$ .

## Comments on Preferred Values

10 The preferred values are derived following the analysis given in ref. 14 of data from refs. 1-13 and from measurements of the falloff curve with M=He from ref. 14 and other bath gases from ref. 15. For measurements of  $k_0$  in the bath gas SF<sub>6</sub>, see ref. 16.

## High-pressure rate coefficients

### Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.0 \times 10^{-11}$	298	Zabarnick, 1993 <sup>15</sup>	PLP-LIF (a)
$3.3 \times 10^{-11}$	298	Forster et al., 1995 <sup>14</sup>	PLP-LIF (b)
$3.3 \times 10^{-11} (T/300)^{-0.3}$	250-400	Fulle et al., 1998 <sup>17</sup>	PLP-LIF (c)

## Comments

(a) Falloff extrapolations with M=Ar and SF<sub>6</sub> at pressures below 1 bar.

(b) Measurements in He up to 200 bar using saturated LIF for detection.

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(c) see (b); measurements in the bath gas He over the range 5-150 bar.

## Preferred Values

$k_{\infty} = 3.3 \times 10^{-11} (T/300)^{-0.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-400 K.

### Reliability

$\Delta \log k_{\infty} = \pm 0.2$  over the temperature range 200-400 K.

### Comments on Preferred Values

The preferred values are taken from the determination and analysis of the complete falloff curve from refs. 14 and 17. The falloff curve corresponds to  $F_c(300 \text{ K}) = 0.81$ . The measurements at pressures below 1 bar of the low pressure parts of the falloff curves from refs. 15 and 18 are consistent with this representation of the falloff curve.

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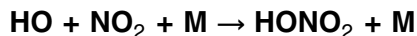
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$$\Delta H^\circ = -207.6 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.3 \times 10^{-30} (T/295)^{-2.5} [\text{N}_2]$	240-450	Anderson et al., 1974 <sup>1</sup>	DF-RF (a)
$2.9 \times 10^{-30} [\text{N}_2]$	296	Howard and Evenson, 1974 <sup>2</sup>	DF-LMR (b)
$2.6 \times 10^{-30} (T/296)^{-2.6} [\text{N}_2]$	220-550	Anastasi and Smith, 1976 <sup>3</sup>	FP-RA (c)
$(2.6 \pm 0.4) \times 10^{-30} (T/300)^{-2.8} [\text{N}_2]$	247-352	Wine et al., 1979 <sup>4</sup>	RP-RF (d)
$(2.7 \pm 0.2) \times 10^{-30} [\text{N}_2]$	295	Burrows et al., 1983 <sup>5</sup>	DF-RF (e)
$(3.39 \pm 0.26) \times 10^{-30} [\text{N}_2]$	300	Donahue et al., 1997 <sup>6</sup>	DF-LIF (f)
$2.47 \times 10^{-30} (T/300)^{-2.97} [\text{N}_2]$	220-250	Brown et al., 1999 <sup>7</sup>	PLP-LIF (g)
$2.85 \times 10^{-30} (T/300)^{-2.67} [\text{N}_2]$	220-300	Dransfield et al., 1999 <sup>8</sup>	DF-LIF (h)
$(2.5 \pm 0.3) \times 10^{-30} [\text{N}_2]$	298	D'Ottone et al., 2001 <sup>9</sup>	PLP-LIF(i)

## Comments

- (a) Measurements over the range 1.3-13 mbar (1-10 Torr). Evaluation assuming limiting third order behavior.
- 10 (b) Measurements over the range 0.5-6.7 mbar (0.4-5 Torr). Evaluation assuming limiting third order behavior.

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- (c) Measurements using bath gas concentrations of  $(3.2\text{--}160) \times 10^{17}$  molecule  $\text{cm}^{-3}$ . Falloff extrapolation using Kassel integrals towards  $k_0$  in agreement with data from refs. 1 and 2. Extrapolation towards  $k_\infty$  oversimplified, but data in the intermediate falloff range in agreement with later work.
- (d) Measurements using bath gas concentrations of  $(5.4\text{--}230) \times 10^{17}$  molecule  $\text{cm}^{-3}$ . Extrapolation of the falloff data with  $F_c = 0.7$  leads to the given  $k_0$ .
- (e) Measurements using bath gas concentrations of 1.3–6.7 mbar (1–5 Torr). Evaluation assuming limiting third order behavior.
- (f) Measurements over the range 2.6–780 mbar (2–600 Torr). Evaluation of the falloff curve with  $F_c = 0.3 \pm 0.03$  and  $k_\infty = (4.77 \pm 1.04) \times 10^{-11}$   $\text{cm}^3$  molecules $^{-1}$  s $^{-1}$ . Fit based on data from this work and refs. 1–5.
- (g) Measurements over the range 26–325 mbar (20–250 Torr). Evaluation of the falloff curve with  $F_c = 0.6$  and  $k_\infty = 1.45 \times 10^{-11} (T/300)^{-2.77}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ .
- (h) Measurements over the range 6.6–197 mbar (50–150 Torr). Evaluation of the falloff curve with  $F_c = \exp(-T/363)$  and  $k_\infty = 3.13 \times 10^{-11}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ . Fit based on data from this work and refs. 1–7.
- (i) Measurements over the range 40–920 mbar (30–700 Torr) at 273 and 298 K. Data evaluated with  $F_c = 0.6$  and  $k_\infty = (2.4 \pm 1.7) \times 10^{-11}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ . The use of  $F_c = 0.4$  would lead to  $k_0 = 3.7 \times 10^{-30} (T/300)^{-3.0} [\text{N}_2]$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$  and  $k_\infty = 4.6 \times 10^{-11}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ .

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## Preferred Values

$k_0 = 3.3 \times 10^{-30} (T/300)^{-3.0} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200–300 K.

### 5 *Reliability*

$\Delta \log k_0 = \pm 0.1$  at 298 K.

$\Delta n = \pm 0.5$ .

### 10 *Comments on Preferred Values*

The differences between the various values of  $k_0$  in part are due to different experimental results, in part they arise from different falloff expressions using either  $F_c = 0.6$  or smaller values of  $F_c$ . While the differences of the experiments are small near to the low pressure limit, they become increasingly pronounced towards the center of the falloff curve and the extrapolated  $k_\infty$ . There are essentially two groups of studies, those with higher rate constants (e.g. refs. 3, 4, 7, and 9) and those with lower values (e.g. refs. 6 and 8). As long as the reasons for the differences are not identified, we prefer an average of the results from refs. 6-9. The falloff extrapolation is done with the theoretical results for  $F_c = 0.4$  and the temperature coefficient of  $k_0$  from ref. 10.

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## High-pressure rate coefficients

### Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\geq 3.5 \times 10^{-11}$	297	Wine et al., 1979 <sup>4</sup>	FP-RF (a)
$\geq 3.0 \times 10^{-11}$	295	Robertshaw and Smith, 1982 <sup>11</sup>	PLP-LIF (b)
$7.5 \times 10^{-11}$	298	Forster et al., 1995 <sup>12</sup>	PLP-LIF (c)
$(4.77 \pm 1.04) \times 10^{-11}$	300	Donahue et al., 1997 <sup>6</sup>	DF-LIF (d)
$(7.5 \pm 2.2) \times 10^{-11}$	250-400	Fulle et al., 1998 <sup>13</sup>	PLP-LIF (e)
$1.45 \times 10^{-11} (T/300)$	220-250	Brown et al., 1999 <sup>7</sup>	PLP-LIF (f)
$3.13 \times 10^{-11}$	220-300	Dransfield et al., 1999 <sup>8</sup>	DF-LIF (g)
$(2.4 \pm 1.7) \times 10^{-11}$	298	D'Ottone et al., 2001 <sup>9</sup>	(h)
$(5.0 \pm 2) \times 10^{-11}$	250-400	Hippler et al., 2001 <sup>14</sup>	PLP-LIF (i)
$(4.8 \pm 0.8) \times 10^{-11}$	298	Smith and Williams, 1985 <sup>15</sup>	(j)

### Comments

- 5 (a) See comment (d) for  $k_0$ . Extrapolation of the falloff curve with  $F_c = 0.7$  leads to the given lower limit of  $k_{\infty}$ .
- (b) Measurements in the bath gases Ar up to 4 bar and  $\text{CF}_4$  up to 8.6 bar.
- (c) Measurements in a static high pressure cell in the bath gas He over the range  $7.6 \times 10^{18}$ - $3.6 \times 10^{21}$  molecule  $\text{cm}^{-3}$  (1-150 bar).
- 10 (d) See comment (f) for  $k_0$ .

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(e) See comment (c). Measurements in He at 250 K between 1.04 and 140 bar, at 300 K between 113 and 1330 bar, and at 400 K between 1.6 and 1370 bar. High pressure flow cell used below 8 bar, static cell used above 200 bar. Falloff extrapolations with  $k_0 = 1.6 \times 10^{-30} (T/300)^{-2.9} [\text{He}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $F_c = 0.45$  (268 K), 0.41 (300 K), and 0.33 (400 K).

(f) See comment (g) for  $k_0$ .

(g) See comment (h) for  $k_0$ .

(h) See comment (i) for  $k_0$ .

(i) See comment (c) and (e); repeated measurements in high pressure flow cells revealed that those measurements from refs. 12 and 13, which were done in a static high pressure cell (pressures above 200 bar), gave  $k_\infty$  values which are about 30 % too high. Nonexponential profiles of HO decay above 400 K at pressures around 100 bar suggest that HOONO isomers are formed besides HNO<sub>3</sub> which become thermally unstable on a  $\mu\text{s}$ -time scale under these conditions.

(j) Pulsed laser photolysis – LIF study of the vibrational relaxation HO ( $\nu = 1$ ) + NO<sub>2</sub> → HO ( $\nu = 0$ ) + NO<sub>2</sub>.

### Preferred Values

$k(1\text{bar}) = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_\infty = 4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-400 K.

### Reliability

$\Delta \log k(1\text{bar}) = \pm 0.3$  at 298 K.

$\Delta \log k_\infty = \pm 0.3$  at 298 K.

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$$\Delta n = \pm 0.5.$$

### Comments on Preferred Values

5 See comments on preferred values of  $k_0$ . The preferred value of  $k_\infty$  is the average of the falloff extrapolations from refs. 6, 8, and 9, using the theoretical value of  $F_c = 0.4$  from ref. 10, the revised high-pressure value from ref. 14 and the vibrational relaxation rate constant from ref. 15. The preferred value of  $k(1\text{bar})$  corresponds to the present preferred values of  $k_0$  and  $k_\infty$  and  $F_c = 0.4$ . It agrees with the results from ref. 9. The measurements from ref. 6 give a  $k(1\text{ bar})$  which is about a factor of 2 smaller. We discard this value because it is difficult to be reconciled with the results from ref. 14 and 15, unless complications with isomer formation show up, see the following.

10 There is only limited information on the extent of formation of HOONO isomers, e.g. discussed in the modeling in refs. 16-18, and on their fate. While spectroscopic in situ detection still has not been possible<sup>19</sup>, nonexponential HO-decays above 400 K at pressures near 100 bar in ref. 14 provided clear evidence for its formation. It remains unclear whether HOONO efficiently converts to HONO<sub>2</sub> at lower pressures by intramolecular processes, or whether HOONO is a final reaction product. Some information on a high barrier for the isomerization on HOONO  $\rightarrow$  HONO<sub>2</sub> is provided by ab initio calculations in ref. 20; however, isomerization in loosely bound structures cannot yet be ruled out. Isotopic scrambling experiments from ref. 21 provide some insight, suggesting that HONO<sub>2</sub> formation contributes only by about 1/5 to  $k_\infty$ . However, the theoretical analysis from ref. 10 seems to rule out a noticeable contribution of HOONO formation under atmospheric conditions.

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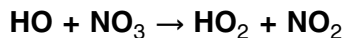
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$$\Delta H^\circ = -63.1 \text{ kJ mol}^{-1}$$

## 5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.6 \pm 0.6) \times 10^{-11}$	298	Mellouki et al., 1988 <sup>1</sup>	DF-EPR (a)
$(2.0 \pm 0.6) \times 10^{-11}$	298	Boodaghians et al., 1988 <sup>2</sup>	DF-RF (b)
$(1.22 \pm 0.35) \times 10^{-11}$	298	Becker et al., 1992 <sup>3</sup>	DF-RF/MS (c)
$(2.1 \pm 1.0) \times 10^{-11}$	297	Mellouki et al., 1993 <sup>4</sup>	DF-LMR (d)

## Comments

(a) Both [HO] and [HO<sub>2</sub>] (after conversion of HO<sub>2</sub> to HO) were monitored in the presence of excess NO<sub>3</sub> radicals. [NO<sub>3</sub>] was measured by titration with NO or 2,3-dimethyl-2-butene. A complex kinetic analysis accounting for secondary chemistry was required to extract values of *k*.

(b) The measured rate coefficient, *k*, was corrected for the effects of secondary reactions which accelerate the removal of HO radicals.

(c) [HO] was monitored by RF, and [NO<sub>3</sub>] and [HO<sub>2</sub>] were monitored by MS. Identical values of *k* were obtained from HO produced *in situ* by the H + NO<sub>2</sub> reaction or by injection of HO radicals produced from the H + NO<sub>2</sub> or F + H<sub>2</sub>O reactions. A

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complex analysis accounting for the secondary chemistry was required to extract values of  $k$ .

(d)  $[\text{HO}]$ ,  $[\text{HO}_2]$ , and  $[\text{NO}_2]$  were monitored by LMR in an excess of  $\text{NO}_3$  radicals.

### Preferred Values

5  $k_1 = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Reliability

$\Delta \log k = \pm 0.3$ .

10

### Comments on Preferred Values

15

The value of  $k$  obtained by Becker et al.,<sup>3</sup> is substantially lower than the values reported in the other three studies<sup>1,2,4</sup> which are in good agreement, although the error limits quoted are large. In all of the studies it proved necessary to make extensive corrections for the secondary reactions. The preferred value of  $k$  is a simple average of all of the reported values.

No measurements have been made of the temperature dependence of  $k$  but a small negative value is expected by analogy with similar reactions.

20

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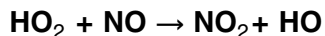
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$$\Delta H^\circ = -34.5 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.1 \pm 1.5) \times 10^{-12}$	296	Howard and Evenson, 1977 <sup>1</sup>	DF-LMR (a)
$3.3 \times 10^{-12} \exp[(254 \pm 50)/T]$	230-400	Howard, 1979 <sup>2</sup>	DF-LMR
$8.01 \times 10^{-12}$	299		
$5.7 \times 10^{-12} \exp[(130 \pm 270)/T]$	270-425	Leu, 1979 <sup>3</sup>	DF-RF (b)
$(9.8 \pm 1.6) \times 10^{-12}$	298		
$(1.1 \pm 0.3) \times 10^{-11}$	297	Glaschick-Schimpf et al., 1979 <sup>4</sup>	DF (c)
$(7.6 \pm 1.7) \times 10^{-12}$	293	Hack et al., 1980 <sup>5</sup>	DF-LMR/EPR (d)
$3.57 \times 10^{-12} \exp[(226 \pm 41)/T]$	423-1271	Howard, 1980 <sup>6</sup>	DF-LMR (e)
$7.6 \times 10^{-12}$	298*		
$(8.5 \pm 1.3) \times 10^{-12}$	297	Jemi-Alade and Thrush, 1990 <sup>7</sup>	DF-LMR (f)
$3.0 \times 10^{-12} \exp[(290 \pm 30)/T]$	206-295	Seeley et al., 1996 <sup>8</sup>	DF-MS (g)
$(8.0 \pm 0.5) \times 10^{-12}$	294		
$(9.6 \pm 1.5) \times 10^{-12}$	298	Bohn and Zetzsch, 1997 <sup>9</sup>	PLP-A (h)
<i>Relative Rate Coefficients</i>			
$(7.3 \pm 0.7) \times 10^{-12}$	298	Thrush and Wilkinson, 1981 <sup>10</sup>	DF-LMR (i)

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## Comments

- (a) [HO<sub>2</sub>] was monitored by LMR. An upper limit of  $4.5 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  was established for the rate coefficient of the potentially pressure dependent third-order channel.
- (b) [HO] was monitored.
- (c) [HO<sub>2</sub>] was monitored in excess NO by the light emitted at  $1.43 \mu\text{m}$  after energy transfer from O<sub>2</sub>(<sup>1</sup>Δ) produced by a microwave discharge in NO.
- (d) [HO<sub>2</sub>] was monitored by both LMR and EPR. The rate coefficient was observed to be pressure independent over the range 2.1-16.7 mbar (1.6-12.5 Torr).
- (e) The same technique was used as in similar earlier studies<sup>1,2</sup> from the same laboratory. The author combined the data from the present study with that at lower temperatures from the earlier studies<sup>1,2</sup> to derive the expression  $k = 3.51 \times 10^{-12} \exp[(240 \pm 30)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the temperature range 232-1271 K. The rate coefficient for the reverse reaction was also measured over the range 425-1115 K and from the two studies a value of  $\Delta H^\circ(\text{HO}_2) = (10 \pm 2.5) \text{ kJ mol}^{-1}$  at 298 K was derived. The value of  $k$  at 298 K tabulated is obtained by extrapolation of the high temperature expression.
- (f) [HO<sub>2</sub>] was monitored by LMR and HO radicals were scavenged by C<sub>2</sub>F<sub>3</sub>Cl.  $k$  was observed to be independent of pressure over the range 1.1-17 mbar (0.8-13 Torr).
- (g) Turbulent fast flow technique was used. [HO<sub>2</sub>], [HO], and [NO<sub>2</sub>] were monitored by high pressure chemical ionisation mass-spectrometry.  $k$  was found to independent of pressure over the range 93-253 mbar N<sub>2</sub> (70-190 Torr) at 294 K.
- (h) Pulsed laser photolysis at 248 nm of H<sub>2</sub>O<sub>2</sub>/NO/O<sub>2</sub> mixtures at total pressures of 0.1, 0.5, and 1 bar. [OH] was monitored by time resolved CW UV laser absorption in the 308 nm region. The value of  $k$  was found to be independent of pressure.

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The rate of OH formation and HO<sub>2</sub> removal were found to be identical within experimental error indicating an OH yield close to unity.

- (i) [HO] and [HO<sub>2</sub>] were monitored by LMR. The steady-state values of [HO] and [HO<sub>2</sub>] were measured in a system where their relative concentrations are related by [HO]/[HO<sub>2</sub>] =  $k/k(\text{HO}+\text{H}_2\text{O}_2)$ .  $k$  was calculated using a rate coefficient of  $k(\text{HO}+\text{H}_2\text{O}_2) = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation).

### Preferred Values

$k = 8.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 3.6 \times 10^{-12} \exp(270/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200-400 K.

### Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$ .

### Comments on Preferred Values

Since our previous evaluation, IUPAC, 1997,<sup>11</sup> the rate coefficient has been measured at 298 K by Gershenson et al.<sup>12</sup> and by Bohn and Zetzsch.<sup>9</sup> The latter study gave a value of  $k$  in good agreement with our preferred value. Gershenson et al.<sup>12</sup> using a novel EPR technique to follow the course of the reaction obtained a value of  $k = (7 \pm 2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  also in agreement with our preferred value within the fairly wide error limits of the experiment.

The preferred value of  $k$  at 298 K is the mean of the values of Howard and Evenson<sup>1</sup>, Howard,<sup>2</sup> Leu,<sup>3</sup> Hack et al.,<sup>5</sup> Jemi-Alade and Thrush,<sup>7</sup> Seeley et al.,<sup>8</sup> and Bohn and Zetzsch.<sup>9</sup> The temperature dependence is the mean of the values of Howard<sup>2</sup> and See-

ley et al.,<sup>8</sup> which are preferred to the less precise value of Leu.<sup>3</sup> The pre-exponential factor is adjusted to fit the preferred value of  $k$  at 298 K.

The *ab initio* calculation of Chakraborty et al.<sup>13</sup> based on formation and rapid decomposition of an HOONO intermediate, give values of the rate parameters in reasonably good agreement with our preferred values.

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<sup>1</sup> C. J. Howard and K. M. Evenson, *Geophys. Res. Lett.* 4, 437, 1977.

<sup>2</sup> C. J. Howard, *J. Chem. Phys.*, 71, 2352, 1979.

<sup>3</sup> M.-T. Leu, *J. Chem. Phys.*, 70, 1662, 1979.

<sup>4</sup> I. Glaschick-Schimpf, A. Leiss, P. B. Monkhouse, U. Schurath, K. H. Becker, and E. H. Fink, *Chem. Phys. Lett.*, 67, 318, 1979.

<sup>5</sup> W. Hack, A. W. Preuss, F. Temps, H. Gg. Wagner, and K. Hoyer mann, *Int. J. Chem. Kinet.*, 12, 851, 1980.

<sup>6</sup> C. J. Howard, *J. Am. Chem. Soc.*, 102, 851, 1980.

<sup>7</sup> A. A. Jemi-Alade and B. A. Thrush, *J. Chem. Soc. Faraday Trans.*, 86, 3355, 1990.

<sup>8</sup> J. V. Seeley, R. F. Meads, M. J. Elrod, and M. J. Molina, *J. Phys. Chem.*, 100, 4026, 1996.

<sup>9</sup> B. Bohn and C. Zetzsch, *J. Phys. Chem. A*, 101, 1488, 1997.

<sup>10</sup> B. A. Thrush and J. P. T. Wilkinson, *Chem. Phys. Lett.*, 81, 1, 1981.

<sup>11</sup> IUPAC, Supplement VI, *J. Phys. Chem. Ref. data*, 26, 1329, 1997

<sup>12</sup> Yu. M. Gershenson, S. D. Il'in, G. G. Politenkova, and R. G. Remorov, *Chem. Phys. Rep.*, 18, 91, 1999.

<sup>13</sup> D. Chakraborty, J. Park, and M. C. Lin, *Chem. Phys.*, 231, 39, 1998.

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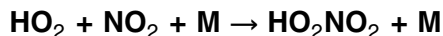
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$$\Delta H^\circ = -100.5 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.09 \pm 0.52) \times 10^{-31} [\text{N}_2]$	300	Howard, 1977 <sup>1</sup>	DF-LMR (a)
$(2.5 \pm 0.5) \times 10^{-31} [\text{N}_2]$	283	Cox and Patrick, 1979 <sup>2</sup>	(b)
$(2.3 \pm 0.6) \times 10^{-31} (T/300)^{-4.6} [\text{N}_2]$	229-362	Sander and Peterson, 1984 <sup>3</sup>	(c)
$1.5 \times 10^{-31} [\text{N}_2]$	298	Kurylo and Ouellette, 1986 <sup>4</sup>	(d)
$1.8 \times 10^{-31} (T/300)^{-3.2 \pm 0.4} [\text{N}_2]$	228-358	Kurylo and Ouellette, 1987 <sup>5</sup>	(d)

## Comments

(a) Discharge flow system study with laser magnetic resonance detection of HO<sub>2</sub>. The pressure range was 0.7-4 mbar (0.5-3 Torr). The linear plot of  $k_0$  as a function of [M] with a non-zero intercept was interpreted as contribution from the reaction HO<sub>2</sub> + NO<sub>2</sub> → HONO + O<sub>2</sub>. As this reaction channel is not present (see comments on preferred values), the nonzero intercept has to be attributed to a curved falloff plot.

(b) Molecular modulation UV spectrometry. HO<sub>2</sub> radicals were generated by Cl<sub>2</sub> photolysis in the presence of H<sub>2</sub> and O<sub>2</sub>. O<sub>2</sub>-N<sub>2</sub> mixtures used in the pressure range 53-800 mbar (40-600 Torr).

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(c) Flash photolysis-UV absorption study in the pressure range 67-930 mbar (50-700 Torr). A strong enhancement of reaction in the presence of water vapor was observed, suggested to be due to formation of HO<sub>2</sub>-H<sub>2</sub>O complexes.

5 (d) Flash photolysis of Cl<sub>2</sub>-CH<sub>3</sub>OH-NO<sub>2</sub> mixtures in the presence of O<sub>2</sub> or N<sub>2</sub>, with HO<sub>2</sub> detection at 225 nm. The falloff curve measured over the pressure range 33-800 mbar (25-600 Torr). The rate coefficient was evaluated using  $F_c = 0.6$  and  $k_\infty = 4.7 \times 10^{-12} (T/300)^{-1.4 \pm 1.0} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

**Preferred Values**

10  $k_0 = 1.8 \times 10^{-31} (T/300)^{-3.2} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220-360 K.

*Reliability*

$\Delta \log k_0 = \pm 0.10$  at 298 K.

15  $\Delta n = \pm 1$ .

*Comments on Preferred Values*

20 The studies of Howard,<sup>1</sup> Cox and Patrick,<sup>2</sup> Sander and Peterson<sup>3</sup> and Kurylo and Ouellette<sup>4,5</sup> are in reasonable agreement. The preferred values are based on the study of Kurylo and Ouellette,<sup>5</sup> with the rate coefficient  $k_0$  being evaluated with the value for  $k_\infty$  given below and  $F_c = 0.6$ . Modification of  $F_c$  will lead to minor changes in  $k_0$  and  $k_\infty$ . Unsuccessful search for HONO as a reaction product in ref. 6 indicates that the reaction HO<sub>2</sub> + NO<sub>2</sub> → HONO + O<sub>2</sub> (at a pressure of 120 Torr) does not occur.

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## High-pressure rate coefficients

### Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$>1.7 \times 10^{-12}$	283	Graham et al., 1977 <sup>8</sup>	(a)
$>(1.5 \pm 0.5) \times 10^{-12}$	283	Cox and Patrick, 1979 <sup>2</sup>	(b)
$(4.2 \pm 1.0) \times 10^{-12} (T/300)^{0.2 \pm 1.0}$	229-362	Sander and Peterson, 1984 <sup>3</sup>	(c)
$5.5 \times 10^{-12}$	298	Kurylo and Ouellette, 1986 <sup>4</sup>	(d)
$4.7 \times 10^{-12} (T/300)^{-1.4 \pm 1.0}$	228-358	Kurylo and Ouellette, 1987 <sup>5</sup>	(d)

### Comments

- (a) From thermal decomposition of  $\text{HO}_2\text{NO}_2$  in a static reactor with FTIR spectroscopic analysis of  $\text{HO}_2\text{NO}_2$ . Measurements at 1 bar of  $\text{N}_2$  converted to recombination rate coefficients with the equilibrium constants given in ref. 9.
- (b) See comment (b) for  $k_0$ . Determination of  $k_{\infty}$  by extrapolation of a curved Lindemann-Hinshelwood plot gave an internally consistent falloff plot. The measured value was  $k = 9.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 800 mbar (600 Torr) of a 1:1 mixture of  $\text{N}_2$  and  $\text{O}_2$ .

### Preferred Values

$k_{\infty} = 4.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 220-360 K.

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## Reliability

$\Delta \log k_{\infty} = \pm 0.2$  at 298 K.

$\Delta n = \pm 1$ .

5

### Comments on Preferred Values

10

The preferred values are based on the measurements from refs. 3-4 and the falloff analysis of Kurylo and Ouellette.<sup>5</sup> The  $k_0$  and  $k_{\infty}$  values are based on  $F_C = 0.6$ . Modification of the standard value of  $F_C$  will lead to minor changes in  $k_0$  and  $k_{\infty}$ . As long as a temperature independent  $F_C = 0.6$  is used and experimental uncertainties in the temperature coefficients of  $k_{\infty}$  remain large, we prefer a temperature independent value of  $k_{\infty}$ .

## References

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<sup>1</sup> C. J. Howard, J. Chem. Phys., 67, 5258, 1977.

<sup>2</sup> R. A. Cox and K. Patrick, Int. J. Chem. Kinet., 11, 635, 1979.

<sup>3</sup> S. P. Sander and M. E. Peterson, J. Phys. Chem., 88, 1566, 1984.

<sup>4</sup> M. J. Kurylo and P. A. Ouellette, J. Phys. Chem., 90, 441, 1986.

<sup>5</sup> M. J. Kurylo and P. A. Ouellette, J. Phys. Chem., 91, 3365, 1987.

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<sup>6</sup> T. J. Dransfield, N. M. Donahue, and J. G. Anderson, J. Phys. Chem. A, 105, 1507, 2001.

<sup>7</sup> R. A. Graham, A. M. Winer, and J. N. Pitts, Jr., J. Chem. Phys., 68, 4505, 1978.

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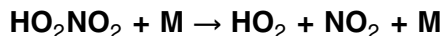
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$$\Delta H^\circ = 100.5 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.5 \times 10^{-20} [\text{N}_2]$	298	Cox and Patrick, 1979 <sup>1</sup>	(a)
$5.2 \times 10^{-6} \exp[-(10014 \pm 250)/T] [\text{N}_2]$	261-295	Graham et al., 1978 <sup>2</sup>	(b)
$1.3 \times 10^{-20} [\text{N}_2]$	298		
$4.1 \times 10^{-5} \exp[-(10645 \pm 260)/T] [\text{N}_2]$	261-307	Zabel, 1995 <sup>3</sup>	(c)
$1.2 \times 10^{-20} [\text{N}_2]$	298		

## Comments

(a) Derived from measurements of the reverse reaction. Conversion of the data to the dissociation reaction of  $\text{HO}_2\text{NO}_2$  using the equilibrium constant  $K_c = 1.68 \times 10^{28} \exp(-11977/T) \text{ cm}^3 \text{ molecule}^{-1}$  from ref. 4 and comparison with earlier dissociation data.

(b) FTIR study in a 5800 L chamber. Measurements were made at 1.3-9.3 mbar (1-7 Torr) of  $\text{N}_2$ . At higher pressures ( $\geq 9.3$  mbar), deviations from low pressure behavior were observed.

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(c) FTIR study in a 420 L chamber. The pressure range was 14-1027 mbar (10-772 Torr). The falloff curve was evaluated with  $F_c = 0.5$ .

### Preferred Values

$k_0 = 1.3 \times 10^{-20} [\text{N}_2] \text{ s}^{-1}$  at 298 K.

5  $k_0 = 4.1 \times 10^{-5} \exp(-10650/T) [\text{N}_2] \text{ s}^{-1}$  over the temperature range 260-300 K.

### Reliability

$\Delta \log k_0 = \pm 0.3$  at 298 K.

10  $\Delta(E/R) = \pm 500$  K.

### Comments on Preferred Values

15 The preferred values are from the study of Zabel,<sup>3</sup> and are in close agreement with those from Graham et al.<sup>2</sup> The data from ref. 3 provide the most consistent picture of all  $\text{RO}_2\text{NO}_2$  dissociation reactions. Falloff curves are constructed with  $F_c = 0.5$ .

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## High-pressure rate coefficients

### Rate coefficient data

$k_{\infty}/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
>0.018	278	Graham et al., 1978 <sup>2</sup>	(a)
$5.7 \times 10^{15} \exp(-11170/T)$	261-307	Zabel, 1995 <sup>3</sup>	(b)
0.30	298		

### Comments

- 5 (a) See comment (b) for  $k_0$ . This is a lower limit since a linear Lindemann-Hinshelwood evaluation of the falloff curve was made for the pressure range 0.013-1.01 bar (10-760 Torr) of  $\text{N}_2$ .
- (b) See comment (c) for  $k_0$ .

### Preferred Values

- 10  $k_{\infty} = 0.25 \text{ s}^{-1}$  at 298 K.  
 $k_{\infty} = 4.8 \times 10^{15} \exp(-11170/T) \text{ s}^{-1}$  over the temperature range 260-300 K.

### Reliability

- 15  $\Delta \log k_{\infty} = \pm 0.5$  at 298 K.  
 $\Delta(E/R) = \pm 500$ .

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## Comments on Preferred Values

See Comments on Preferred Values for  $k_0$ . The data from ref. 3 were reevaluated with  $F_c = 0.6$  such as used for the falloff curves of the reverse reaction  $\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2 + \text{M}$  and because  $F_c$  is identical for the forward and backward reaction. Since the measurements from ref. 3 were made close to the low pressure limit, only the extrapolation to  $k_\infty$  is noticeably influenced by the change of the used  $F_c$ .

## References

<sup>1</sup> R. A. Cox and K. Patrick, *Int. J. Chem. Kinet.*, **11**, 635, 1979.

<sup>2</sup> R. A. Graham, A. M. Winer, and J. N. Pitts, Jr., *Chem. Phys. Lett.*, **51**, 215 (1977); *J. Chem. Phys.*, **68**, 4505, 1978.

<sup>3</sup> F. Zabel, *Z. Phys. Chem.*, **188**, 119, 1995.

<sup>4</sup> W. M. Uselman, S. Z. Levine, W. H. Chan, J. G. Calvert, and J. H. Shaw, *Chem. Phys. Lett.*, **58**, 437, 1978.

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$$\Delta H^\circ(1) = -223.4 \text{ kJ mol}^{-1}$$

$$5 \quad \Delta H^\circ(2) = -17.9 \text{ kJ mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = (9.2 \pm 4.8) \times 10^{-13}$	298	Mellouki et al., 1988 <sup>1</sup>	DF-EPR (a)
$k_2 = (3.6 \pm 0.9) \times 10^{-12}$	298		
$2.3 \times 10^{-12} \exp[(170 \pm 270)/T]$	263-338	Hall et al., 1988 <sup>2</sup>	MM-UV/VIS (b)
$(4.1 \pm 0.8) \times 10^{-12}$	298		
$k_1 = (1.9 \pm 0.8) \times 10^{-12}$	298	Becker et al., 1992 <sup>3</sup>	DF-RF/MS (c)
$k_2 = (2.5 \pm 0.7) \times 10^{-12}$	298		
$(3.0 \pm 0.7) \times 10^{-12}$	297 ± 2	Mellouki et al., 1993 <sup>4</sup>	DF-LMR (d)

### 10 Comments

(a) [HO] and [NO<sub>3</sub>] were monitored in excess NO<sub>3</sub>. Kinetics of a complex mechanism were analysed to extract values of rate coefficients. Values of  $k(\text{HO} + \text{NO}_3)$  were also obtained (see the HO + NO<sub>3</sub> data sheet).

15 (b) [HO<sub>2</sub>] and [NO<sub>3</sub>] were monitored by visible and UV spectroscopy. The kinetics of a complex mechanism were simulated to extract values of rate coefficients. An

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upper limit of  $k_2/k < 0.6$  was obtained from measurements of [HO] by modulated resonance absorption.

(c) [HO] monitored by RF, and [NO<sub>3</sub>] and [HO<sub>2</sub>] monitored by MS. A quasi-steady state of [HO<sub>2</sub>] and [HO] is produced by reaction of HO with NO<sub>3</sub>, in excess, to reform HO<sub>2</sub> radicals.  $k_1$  was inferred from the extra loss of HO<sub>2</sub> following the establishment of the quasi-steady state.

(d) [HO], [HO<sub>2</sub>], and [NO<sub>2</sub>] were all monitored by LMR. Three different methods for generation of NO<sub>3</sub> were used.  $k$  could be obtained under pseudo-first-order conditions by using an excess of NO<sub>3</sub> and adding C<sub>2</sub>F<sub>3</sub>Cl to scavenge HO radicals. A value of the branching ratio was obtained by simulation of the time dependences of [HO] and [HO<sub>2</sub>] using a simple mechanism.

### Preferred Values

$k = 4.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Reliability

$\Delta \log k = \pm 0.2$ .

### Comments on Preferred Values

Although the study of Mellouki et al.<sup>4</sup> gives a value of  $k$  at 298 K some 30% lower than obtained in the earlier studies,<sup>1–3</sup> all of the values are within the reported error limits, which are substantial. The preferred value is a mean of the data from all four studies.<sup>1–4</sup> Measurements of the branching ratio  $k_2/k$  at 298 K range from  $< 0.6^2$  to  $1.0^4$ . The study of Mellouki et al.,<sup>4</sup> in which HO yields were measured, appears to be the most direct, and suggests that the reaction proceeds almost entirely through

the second channel, but at this stage no recommendation is made for the branching ratio because of the experimental uncertainties. Similarly, data on the temperature dependence is considered to be too uncertain to make a recommendation.

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## NH<sub>2</sub> + O<sub>2</sub> → Products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$< 6 \times 10^{-21}$	296	Tyndall et al., 1991 <sup>1</sup>	(a)

### Comments

- 5 (a) Photolysis of NH<sub>3</sub> in the presence of excess O<sub>2</sub>. The concentrations of NO, NO<sub>2</sub>, and N<sub>2</sub>O, the only likely products, were measured by FTIR spectroscopy. The upper limit to the rate coefficient was based on computer simulation of a substantial reaction mechanism.

### Preferred Values

- 10  $k < 6 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Comments on Preferred Values

- 15 This reaction has several energetically feasible channels, including those leading to NO + H<sub>2</sub>O and HNO + HO. The measurements of Tyndall et al.<sup>1</sup> set an upper limit to the channels leading directly, or indirectly, to NO, NO<sub>2</sub>, and N<sub>2</sub>O. This result confirms earlier conclusions that the reaction is very slow,<sup>2-6</sup> making it unimportant in the atmosphere.

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## NH<sub>2</sub> + O<sub>3</sub> → Products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.2 \times 10^{-12} \exp[-(1250 \pm 250)/T]$	298-380	Kurusawa and Lesclaux, 1980 <sup>1</sup>	FP/LIF
$(6.3 \pm 1.0) \times 10^{-14}$	298		
$(1.2 \pm 0.3) \times 10^{-13}$	298	Bulatov et al., 1980 <sup>2</sup>	FP (a,b)
$2.01 \times 10^{-12} \exp[-(710 \pm 50)/T]$	250-358	Hack et al., 1981 <sup>3</sup>	DF-LIF (b)
$(1.84 \pm 0.16) \times 10^{-13}$	295		
$1.57 \times 10^{-11} \exp[-(1151 \pm 123)/T]$	272-348	Patrick and Golden, 1984 <sup>4</sup>	PLP-RA
$(3.25 \pm 0.27) \times 10^{-13}$	298		
$(1.5 \pm 0.3) \times 10^{-13}$	298	Cheskis et al., 1985 <sup>5</sup>	PLP-LIF (c)

### Comments

- 5 (a) [NH<sub>2</sub>] monitored by intracavity laser spectroscopy.
- (b) Deviation from first order kinetics observed at high O<sub>3</sub> pressures, and interpreted as due to formation of NH<sub>2</sub>O, which regenerates NH<sub>2</sub> by reaction with O<sub>3</sub>.
- 10 (c) The rate coefficients of reaction of vibrationally excited NH<sub>2</sub> with O<sub>3</sub> were also measured and found to be a factor of 10 greater than that of NH<sub>2</sub> in its ground vibrational state.

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## Preferred Values

$k = 1.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 4.9 \times 10^{-12} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–380 K.

5

### *Reliability*

$\Delta \log k = \pm 0.5$  at 298 K.

$\Delta(E/R) = \pm 500$  K.

### 10 *Comments on Preferred Values*

The reported rate coefficients at 298 K vary by a factor of 5. There is no convincing argument for rejecting any of the studies and, therefore, the preferred rate coefficient at 298 K is taken as the average of the results of Kurasawa and Lesclaux,<sup>1</sup> Bulatov et al.,<sup>2</sup> Hack et al.,<sup>3</sup> Patrick and Golden,<sup>4</sup> and Cheskis et al.<sup>5</sup> The temperature dependence of  $k$  is obtained by averaging the values of Kurasawa and Lesclaux,<sup>1</sup> Hack et al.,<sup>3</sup> and Patrick and Golden.<sup>4</sup> Although the products of the reaction have not been characterized, the most likely process is transfer of an oxygen atom to form  $\text{NH}_2\text{O} + \text{O}_2$ . It has been suggested<sup>2,3</sup> that  $\text{NH}_2$  may be regenerated by reaction with  $\text{O}_3$ , but the study of Patrick and Golden<sup>4</sup> indicates that this reaction must be slow.

20

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$$\Delta H^\circ(1) = -520.8 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(3) = -23.8 \text{ kJ mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.7 \times 10^{-11}$	300	Gordon et al., 1971 <sup>1</sup>	(a)
$(8.3 \pm 1.7) \times 10^{-12}$	298	Gehring et al., 1973 <sup>2</sup>	DF-MS (b)
$2.1 \times 10^{-8} T^{-1.25}$	300-500	Lesclaux et al., 1975 <sup>3</sup>	FP (c)
$(1.8 \pm 0.3) \times 10^{-11}$	300		
$(2.1 \pm 0.2) \times 10^{-11}$	298	Hancock et al., 1975 <sup>4</sup>	FP-LIF
$(1.7 \pm 0.4) \times 10^{-11}$	298	Sarkisov et al., 1978 <sup>5</sup>	FP (d)
$4.5 \times 10^{-7} T^{-1.85}$	210-500	Hack et al., 1979 <sup>6</sup>	DF-LIF
$9.7 \times 10^{-12}$	298		
$2.77 \times 10^{-7} T^{-1.67}$	216-480	Stief et al., 1982 <sup>7</sup>	FP-LIF (e)
$(2.10 \pm 0.31) \times 10^{-11}$	298		
$4.4 \times 10^{-5} T^{-2.3} \exp(-684/T)$	294-1215	Silver and Kolb, 1982 <sup>8</sup>	DF-LIF (f)

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.59 \pm 2.4) \times 10^{-11}$	298		
$(1.7 \pm 0.5) \times 10^{-11}$	295	Andresen et al., 1982 <sup>9</sup>	PLP (g)
$(1.81 \pm 0.12) \times 10^{-11}$	297	Whyte and Phillips, 1983 <sup>10</sup>	PLP-LIF
$1.7 \times 10^{-11}$	298	Dreier and Wolfrum, 1985 <sup>11</sup>	PLP (h)
$(1.3 \pm 0.4) \times 10^{-11}$	298		
$1.3 \times 10^{-8} T^{-(1.17 \pm 0.25)}$	294-1027	Atakan et al., 1990 <sup>12</sup>	PLP-LIF (i)
$(1.67 \pm 0.25) \times 10^{-11}$	298		
$5.6 \times 10^{-6} T^{-2.2}$	295-620	Bulatov et al., 1989 <sup>13</sup>	FP (d)
$2.2 \times 10^{-11}$	298	Pagsberg et al., 1991 <sup>14</sup>	(j)
$5.43 T^{-4.02} \exp(-1034/T)$	293-612	Wolf et al., 1994 <sup>15</sup>	PLP-LIF
$(1.9 \pm 0.1) \times 10^{-11}$	295		
$2.2 \times 10^{-12} \exp[(525 \pm 80)/T]$	297-673	Diau et al., 1994 <sup>16</sup>	PLP (k)
$(1.45 \pm 0.08) \times 10^{-11}$	297		
$1.4 \times 10^{-11}$	298	Yu and Lin, 1994 <sup>17</sup>	PLP (d)
$(1.9 \pm 0.3) \times 10^{-11}$	299	Imamura and Washida, 1995 <sup>18</sup>	PLP (l)
$1.38 \times 10^{-10} T^{-0.57} \exp(300/T)$	305-1037	Park and Lin, 1997 <sup>19</sup>	PLP-MS (m)
$(8.59 \pm 0.40) \times 10^{-12}$	305		
$(k_2 + k_3) = 1.4 \times 10^{-14} T^{0.53} \exp(502/T)$	300-1000		
$k_1 = 1.37 \times 10^{-9} T^{-0.93} \exp(192/T)$	300-1000		
$1.65 \times 10^{-7} T^{-1.54} \exp(-93/T)$	203-813	Wolf et al., 1997 <sup>20</sup>	PLP-LIF (n)
$(1.87 \pm 0.02) \times 10^{-11}$	295		

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Branching Ratios</i>			
$(k_2 + k_3)/k = 0.10 \pm 0.02$	295	Bulatov et al., 1989 <sup>13</sup>	FP-AS (d)
$(k_2 + k_3)/k = 0.10 \pm 0.025$	300	Atakan et al., 1990 <sup>12</sup>	PLP-LIF (i)
$k_1/k = 0.85$	295	Stephens et al., 1993 <sup>21</sup>	PLP-AS (o)
$(k_2 + k_3)/k = 0.10$	295		
$k_1/k = 0.7 \pm 0.2$	298	Quandt and Hershberger, 1996 <sup>22</sup>	PLP (p)
$k_1/k = 0.90$	300	Park and Lin, 1996 <sup>23</sup> ; 1997 <sup>19</sup>	PLP-MS (q)
$(k_3 + k_4)/k = 0.10$	300		
$(k_2 + k_3)/k = 0.090 \pm 0.002$	298	Wolf et al., 1997 <sup>20</sup>	DF-MS (r)

## Comments

- (a) Pulse radiolysis of  $\text{NH}_3\text{-NO}$  mixtures at 670 mbar (500 Torr) total pressure.  $[\text{NH}_2]$  monitored by time-resolved absorption spectroscopy.
- 5 (b)  $\text{NO}_2$  was added to an excess of H atoms followed by addition of  $\text{NH}_3$ . Analysis by time-of-flight mass-spectrometry. Vibrationally excited  $\text{H}_2\text{O}$  was observed as a product. The addition product  $\text{NH}_2\text{NO}$  was also observed to the extent of 5% of the  $\text{N}_2$  formed.
- 10 (c)  $[\text{NH}_2]$  was monitored by absorption spectroscopy. No pressure dependence of  $k$  was observed over the range 2.7-930 mbar (2-700 Torr) of  $\text{N}_2$ .
- (d)  $[\text{NH}_2]$  was monitored by intracavity laser absorption.
- (e)  $[\text{NH}_2]$  was monitored by LIF. Production of HO was looked for by resonance fluorescence and found under static conditions but not under flowing conditions. An upper limit of  $(k_2 + k_3)/k \leq 0.22$  was obtained.

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(f)  $[\text{NH}_2]$  was monitored by LIF. HO production was detected by RF or by LIF. A rate coefficient ratio  $(k_2 + k_3)/k = 0.4 \pm 0.1$  was obtained but the data were later reanalysed by the authors to give a value of 0.12. H-atom production was looked for using RF; an upper limit of 0.05 was found for the branching ratio of channels leading to H atoms.

(g) The rate coefficient was obtained by monitoring the production of vibrationally excited  $\text{H}_2\text{O}$  by observation of infrared and visible emissions. RA and LIF were used to monitor  $[\text{HO}]$ .  $k_2/k \geq 0.65$  was obtained with the H-atom yield being  $\leq 0.05$ .

(h)  $[\text{NH}_2]$  and  $[\text{N}_2]$  were monitored by coherent anti-Stokes Raman spectroscopy (CARS). Another independent value of the rate constant was obtained by monitoring the IR fluorescence of vibrationally excited  $\text{H}_2\text{O}$ .

(i)  $[\text{HO}]$  was monitored by LIF. The HO yield was determined by using HO production from  $\text{H}_2\text{O}_2$  photolysis to calibrate for  $[\text{HO}]$ .

(j) Pulse radiolysis, of  $\text{Ar-SF}_6\text{-NH}_3\text{-NO}$  mixtures at a total pressure of  $\sim 50$  mbar.  $[\text{NH}_2]$  and  $[\text{HO}]$  were monitored by time-resolved UV absorption spectroscopy. The observed yield of HO was small suggesting a value of  $(k_2 + k_3)/k \approx 0.07$ .

(k)  $[\text{NH}_2]$  was monitored by cavity ring down absorption spectroscopy at 537.6 nm.

(l)  $[\text{NH}_2]$  was monitored by photoionization mass spectrometry.

(m) Pulsed laser photolysis of  $\text{NH}_3\text{-NO}$  mixtures.  $[\text{H}_2\text{O}]$  and  $[\text{NO}]$  were monitored by time-resolved mass-spectrometry and values of  $k$  were derived from detailed modelling of the  $[\text{H}_2\text{O}]$  and  $[\text{NO}]$  profiles. In a subsequent publication<sup>24</sup> the data are reanalysed and expressions derived giving  $k_1$  and  $(k_2 + k_3)$  up to temperatures above 2000 K but these expressions agree very closely with those cited here for  $T \leq 1000$  K.

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(n) The expression  $k = 2.66 \times 10^{-8} T^{-1.27} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  also provides a good fit to the data.

(o) Pulsed laser photolysis of  $\text{NH}_3\text{-NO}$  mixtures.  $[\text{H}_2\text{O}]$ ,  $[\text{HO}]$ ,  $[\text{NH}_3]$ , and  $[\text{NH}_2]$  were monitored by infrared absorption spectroscopy.

(p) Pulsed laser photolysis of  $\text{NH}_3\text{-NO}$  mixtures.  $[\text{H}_2\text{O}]$  and  $[\text{NH}_2]$  were monitored by infrared absorption spectroscopy. This was a preliminary study to an investigation of the branching in the  $\text{NH}_2 + \text{NO}_2$  reaction.

(q) Pulsed laser photolysis of  $\text{NH}_3\text{-NO-CO}$  mixtures. Time-resolved mass-spectrometric measurements of  $[\text{H}_2\text{O}]$ ,  $[\text{NO}]$  and of  $[\text{CO}_2]$  produced by scavenging of HO by the CO.

(r)  $\text{NH}_2$  radicals were generated by the  $\text{F} + \text{NH}_3$  reaction in a flow He carrier gas to which an NO-CO-He mixture was added downstream of the  $\text{NH}_2$  generation point.  $[\text{N}_2]$  and  $[\text{CO}_2]$  were determined by mass-spectrometry. The  $\text{ND}_2 + \text{NO}$  reaction was also studied.

### Preferred Values

$k = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.6 \times 10^{-11} (T/298)^{-1.4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 210-500 K.

$k_1/k = 0.9$  at 298 K.

$(k_2 + k_3)/k = 0.1$  at 298 K.

### Reliability

$\Delta \log k = \pm 0.15$  at 298 K.

$\Delta n = \pm 0.5$ .

$$\Delta k_1/k = \pm 0.05 \text{ at } 298 \text{ K.}$$

$$\Delta(k_2 + k_3)/k = \pm 0.03 \text{ at } 298 \text{ K.}$$

### Comments on Preferred Value

The values of the rate coefficients obtained in the pulsed photolysis studies are significantly higher than those obtained using the discharge flow technique. The reason for this discrepancy is not known. The preferred value at 298 K is therefore taken as the mean of the values reported in Refs. 1-20. The temperature dependence is based on the data below 500 K in the temperature dependence studies of Lesclaux et al.,<sup>3</sup> Hack et al.,<sup>6</sup> Stief et al.,<sup>7</sup> Silver and Kolb,<sup>8</sup> Atakan et al.,<sup>12</sup> Bulatov et al.,<sup>13</sup> Wolf et al.,<sup>15,20</sup> Diau et al.,<sup>16</sup> and Park and Lin.<sup>19</sup>

The preferred values of the branching ratios are based on the direct measurements of Atakan et al.,<sup>12</sup> Stephens et al.,<sup>21</sup> Park and Lin<sup>19,23</sup> and Wolf et al.<sup>20</sup> The less direct study of Bulatov et al.<sup>13</sup> and the preliminary study of Quandt and Hershberger<sup>22</sup> are in satisfactory agreement with the preferred values.

There are now reasonably consistent measurements of the branching ratios up to ~ 1700 K. The value of  $(k_2 + k_3)/k$  remains virtually independent of temperature over the range covered by our recommendations but begins to rise steadily at temperatures in excess of 600 K reaching a value of ~ 0.53 at 1700 K.<sup>24</sup>

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$$\Delta H^\circ(1) = -381.7 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -358.2 \text{ kJ mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.8 \times 10^{-8} T^{-1.30}$	298-505	Kurasawa and Lesclaux, 1979 <sup>1</sup>	FP-LIF (a)
$(2.3 \pm 0.2) \times 10^{-11}$	298		
$(2.11 \pm 0.18) \times 10^{-11}$	297	Whyte and Phillips, 1983 <sup>2</sup>	PLP-LIF (a)
$(2.26 \pm 0.08) \times 10^{-11}$	298	Xiang et al., 1985 <sup>3</sup>	PLP-LIF (b)
$(2.1 \pm 0.4) \times 10^{-11} (T/298)^{-1.7}$	295-620	Bulatov et al., 1989 <sup>4</sup>	FP (c)
$1.35 \times 10^{-7} T^{-1.44} \exp(-135/T)$	300-910	Park and Lin, 1997 <sup>5</sup>	PLP-MS (d)
$(1.39 \pm 0.07) \times 10^{-11}$	300		
<i>Branching Ratios</i>			
$k_1/k = 0.14 \pm 0.02$	298	Quandt and Hershberger, 1996 <sup>6</sup>	PLP-TDLS (e)
$k_1/k = 0.59 \pm 0.03$	298	Meunier et al., 1996 <sup>7</sup>	PR-TDLS (f)
$k_3/k = 0.40 \pm 0.05$			
$k_1/k = 0.19 \pm 0.02$	300-990	Park and Lin, 1997 <sup>5,8</sup>	PLP-MS (g)
$k_1/k = 0.24 \pm 0.04$	298	Lindholm and Hershberger, 1997 <sup>9</sup>	PLP-TDLS (h)
$k_3/k = 0.76 \pm 0.1$			

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## Comments

- (a)  $[\text{NH}_2]$  monitored by time resolved LIF at 598 nm.
- (b) Pulsed infrared multiphoton dissociation  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$ , or  $\text{N}_2\text{H}_4$  used for  $\text{NH}_2$  production. State selected  $\text{NH}_2$  concentration monitored by time resolved LIF at 533 nm. The rate constant for  $\text{NH}_2(v''=1)$  was also measured and found to be less than that for ground state  $\text{NH}_2$ .
- (c)  $[\text{NH}_2]$  was monitored by intracavity absorption.  $k$  was found to be independent of pressure over the range 13-870 mbar (10-650 Torr).
- (d)  $\text{NH}_2$  produced by pulsed laser photolysis at 193 nm of  $\text{NH}_3$ .  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ , and  $\text{O}_2$  were detected by quadrupole mass spectrometry. Values of  $k$  were obtained from the concentration profiles of the  $[\text{NO}_2]$  decay and from the formation of  $\text{H}_2\text{O}$  and  $\text{N}_2\text{O}$ . Substantial modelling was used to correct for effects of secondary chemistry.
- (e) Pulsed laser photolysis at 193 nm of  $\text{NH}_3\text{-NO}_2\text{-SF}_6$  mixtures.  $[\text{N}_2\text{O}]$ ,  $[\text{NO}]$ , and  $[\text{H}_2\text{O}]$  were monitored by time resolved infrared diode laser absorption spectroscopy. Large yields of  $\text{NO}$  are produced by unidentified secondary chemistry precluding determination of  $k_3/k$ .
- (f) Pulse radiolysis, of  $\text{Ar-SF}_6\text{-NH}_3\text{-NO}_2$  mixtures at a total pressure of 40 mbar.  $[\text{NH}_2]$ ,  $[\text{N}_2\text{O}]$ , and  $[\text{NO}]$  were monitored by time resolved infrared diode laser spectroscopy.
- (g) Technique as in (d). Branching ratios based on the  $\text{N}_2\text{O}$  yields. The value of  $k_1/k$  derived depends on the expression for  $k$  used in the detailed modelling of the system. In one of the studies<sup>8</sup> the expression for  $k$  of Glarborg et al.<sup>10</sup> was used and in the other study<sup>5</sup> values of  $k$  measured in the same study<sup>5</sup> were used. The same values of  $k_1/k$  was obtained in the two studies.

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(h) Technique basically as in (e) but  $\text{NH}_2$  generated by photolysis of ICN at 248 nm in the presence of  $\text{NH}_3$ , leading to the fast reaction  $\text{CN} + \text{NH}_3 \rightarrow \text{HCN} + \text{NH}_2$ . Use of this source eliminates excessive NO production by secondary chemistry and allows derivation of  $k_3/k$  from the measured NO yield  $[\text{NH}_2]$ ,  $[\text{N}_2\text{O}]$ , and  $[\text{NO}]$  were monitored.

### Preferred Values

$k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 2.0 \times 10^{-11} (T/298)^{-1.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250-500 K.

$k_1/k = 0.25$  over the temperature range 298-500 K.

$k_3/k = 0.75$  over the temperature range 298-500 K.

### Reliability

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta n = \pm 0.7$

$\Delta k_1/k = \Delta k_3/k = \pm 0.15$  over the temperature range 298-500 K.

### Comments on Preferred Values

At 298 K the results of Kurasawa and Lesclaux,<sup>1</sup> Whyte and Phillips,<sup>2</sup> Xiang et al.,<sup>3</sup> Bulatov et al.<sup>4</sup> and Park and Lin<sup>5</sup> are in reasonable agreement and our preferred value for  $k(298 \text{ K})$  is taken as an average of the values from these studies. Other studies are those of Hack et al.<sup>11</sup> and Pagsberg et al.<sup>12</sup> Hack et al.,<sup>11</sup> using a discharge flow technique over the range 250-500 K, obtained a significantly lower value at 298 K than those from the other studies, and this discrepancy increases at higher temperatures, approaching a factor of 4 at 500 K. The pulse radiolysis study of Pagsberg et al.<sup>12</sup> also gives a low value at 298 K.

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There are also significant differences in the values found for the temperature dependence of  $k$ . The results of Kurasawa and Lesclaux<sup>1</sup> and of Park and Lin<sup>5</sup> are in excellent agreement and are the basis for the temperature dependence of  $k$  in our preferred expression. Bulatov et al.<sup>4</sup> observe a slightly greater temperature dependence but their results fall within the error limits assigned. Only the larger temperature dependence observed by Hack et al.<sup>11</sup> ( $k \propto T^{-3.0}$ ) appears to be incompatible with the other studies.

Theoretical treatments<sup>13</sup> of the reaction mechanism suggest that channels (1) and (3) are the most probable and the experimental studies confirm this qualitatively but the quantitative agreement on the branching ratios is poor. The early study by Hack et al.<sup>11</sup> suggested that channel (1) should predominate to the extent of 95% of the total reaction and Glarborg et al.,<sup>10</sup> who studied the  $\text{NH}_3/\text{NO}_2$  reaction in a flow reactor over the range 850–1350 K, from their modelling of the changes in reactant and product concentrations concluded also that channel (1) predominates at low temperatures, but channel (3) is the more important at high temperatures. However the direct measurements favour channel (3) at all temperatures up to 900 K.<sup>5,8</sup> The studies of Lindholm and Hershberger<sup>9</sup> and of Park and Lin<sup>5,8</sup> appear to be the most direct and are in reasonable agreement. Provisionally, the recommended branching ratios are based on these studies<sup>5,8,9</sup> but with substantial error limits.

No evidence has been found for the occurrence of channel (2) or for the other exothermic channels leading to  $\text{N}_2 + 2\text{OH}$  and  $2\text{HNO}$ .<sup>9</sup>

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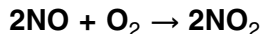
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$$\Delta H^\circ = -114.1 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.0 \pm 0.1) \times 10^{-38}$	298	Stedman and Niki, 1973 <sup>1</sup>	(a)
$1.8 \times 10^{-47} \exp(1600/T)$	226-758	Olbregts, 1985 <sup>2</sup>	(b)
$2.1 \times 10^{-38}$	298		

### Comments

(a) Static system. Photolysis of 1-100 ppm mixing ratios of  $\text{NO}_2$  in air using chemiluminescence detectors to monitor  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{O}_3$ .

(b) Static 1 L reactor. Total pressure was measured with a differential micromanometer, and  $[\text{NO}_2]$  measured in absorption at 436 nm. Pressures of  $\text{NO}$  and  $\text{O}_2$  ranged up to 35 mbar (26 Torr.). Non-Arrhenius behaviour was observed with  $k$  first decreasing with increasing temperature, reaching a minimum value at 600 K, and then increasing with increasing temperature.

### Preferred Values

$k = 2.0 \times 10^{-38} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 3.3 \times 10^{-39} \exp(530/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270-600 K.

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## Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta(E/R) = \pm 400$  K.

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### Comments on Preferred Values

The preferred values are those recommended in the evaluation of Baulch et al.,<sup>3</sup> which are based on the evaluation of a substantial quantity of consistent data reported up to 1972. The results of studies performed since that evaluation, which are given in the Table, are in excellent agreement with the preferred values.

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Olbrechts<sup>2</sup> observed non-Arrhenius behaviour over the entire temperature range studied and expressed  $k$  by a modified Arrhenius expression and, also, as the sum of two Arrhenius expressions. However, from 250 K to about 600 K the total rate coefficients of Olbrechts<sup>2</sup> are in good agreement with the values calculated from the expression recommended here, which is adequate for atmospheric modelling purposes. Olbrechts<sup>2</sup> interpreted his results in terms of a multi-step mechanism involving  $\text{NO}_3$  or the dimer  $(\text{NO})_2$

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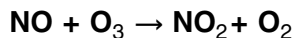
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$$\Delta H^\circ = -199.8 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.34 \times 10^{-12} \exp[-(1450 \pm 50)/T]$ $(1.73 \pm 0.09) \times 10^{-14}$	203-361 297	Birks et al., 1976 <sup>1</sup>	(a)
$4.3 \times 10^{-12} \exp[-(1598 \pm 50)/T]$ $(2.14 \pm 0.11) \times 10^{-14}$	283-443 304	Lippmann et al., 1980 <sup>2</sup>	(b)
$3.16 \times 10^{-12} \exp[-(1556 \pm 40)/T]$ $(1.80 \pm 0.04) \times 10^{-14}$	212-422 299	Ray and Watson, 1981 <sup>3</sup>	DF-MS
$2.6 \times 10^{-12} \exp[-(1435 \pm 64)/T]$ $(2.0 \pm 0.2) \times 10^{-14}$	195-369 298	Michael et al., 1981 <sup>4</sup>	(c)
$8.9 \times 10^{-19} T^{2.2} \exp(-765/T)$ $(1.72 \pm 0.04) \times 10^{-14}$	204-353 298	Borders and Birks, 1982 <sup>5</sup>	(d)
$5.1 \times 10^{-12} \exp[-(1670 \pm 100)/T]$ $(1.90 \pm 0.19) \times 10^{-14}$	263-328 298	Moonen et al., 1998 <sup>6</sup>	(e)

### Comments

(a) Fast flow system with O<sub>3</sub> in excess and with [NO] monitored by mass spectrometry.

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- (b) First order decay of  $[O_3]$  in the presence of excess NO in a 220 m<sup>3</sup> stainless steel spherical vessel at pressures below 0.13 mbar (0.1 Torr). Chemiluminescence was monitored under stopped flow conditions
- (c) Three independent low pressure fast-flow studies were carried out. The extent of reaction was monitored by NO<sub>2</sub> chemiluminescence under conditions of excess NO or excess O<sub>3</sub>. In other experiments the decay of [NO] in excess O<sub>3</sub> was monitored by RF. The results from all of the studies were in good agreement. An Arrhenius plot of the data showed significant curvature with  $E/R$  varying from 1258 K over the temperature range 195-260 K, to 1656 K over the temperature range 260-369 K.
- (d) Dual flow tube technique with NO<sub>2</sub> chemiluminescence used to monitor the reaction progress. The authors claim that this technique gives accurate values of  $E/R$  over temperature intervals as small as 10 K. Nonlinear Arrhenius behaviour was observed with  $E/R$  increasing from a value of 1200 K at the lowest temperature studied to 1470 K at the highest temperature.
- (e) A novel flow technique was used in which the reaction chamber consisted of PTFE tubing immersed in a thermostat. Different reaction times were achieved by varying the tube length. The carrier gas was artificial air at atmospheric pressure into which small concentrations ( $\sim 10^{-12}$  molecule cm<sup>3</sup>) of NO and O<sub>3</sub> were introduced in comparable amounts so that the reaction occurred under second order conditions. Concentrations at the outlet of the reactor were measured by means of an NO/NO<sub>x</sub> chemiluminescence analyser. Some experiments were carried out at 200 K but are not included in the derivation of the Arrhenius expression because of their uncertain reliability.

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## Preferred Values

$k = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.4 \times 10^{-12} \exp(-1310/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 195–308 K.

### Reliability

$\Delta \log k = \pm 0.08$  at 298 K.

$\Delta(E/R) = \pm 200$  K.

### Comments on Preferred Values

The preferred Arrhenius expression is based on a least squares analysis of the data over the range 195–308 K reported by Birks et al.,<sup>1</sup> Lippmann et al.,<sup>2</sup> Ray and Watson,<sup>3</sup> Michael et al.,<sup>4</sup> Borders and Birks,<sup>5</sup> and Moonen et al.<sup>6</sup> The data at closely spaced intervals reported by Lippmann et al.<sup>2</sup> and by Borders and Birks<sup>5</sup> were grouped to give approximately equal weight to the six studies. The temperature range was limited because of the non-linear Arrhenius behaviour observed by Clyne et al.,<sup>7</sup> Clough and Thrush,<sup>8</sup> Birks et al.,<sup>1</sup> Michael et al.,<sup>4</sup> and by Borders and Birks.<sup>5</sup> Earlier room temperature results of Stedman and Niki<sup>9</sup> and Bemand et al.<sup>10</sup> are in good agreement with the preferred value at 298 K.

Clyne et al.,<sup>11</sup> Birks et al.,<sup>1</sup> Schurath et al.,<sup>11</sup> and Michael et al.<sup>4</sup> have reported individual Arrhenius expressions for each of two primary channels, one to produce  $\text{NO}_2$  in its electronic ground state and the other leading to electronically excited  $\text{NO}_2$ .

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$$\Delta H^\circ = -40.6 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.7 \pm 0.6) \times 10^{-33} [\text{Ar}]$	$207 \pm 2$	Smith and Yarwood, 1987 <sup>1</sup>	FP (a)
$(9.1 \pm 0.7) \times 10^{-33} [\text{N}_2]$	$208 \pm 2$		
$(2.8 \pm 2.8) \times 10^{-15} T^{-(7.7 \pm 0.8)} [\text{Ar}]$	227-260	Markwalder et al., 1993 <sup>3</sup>	(b)
$4.1 \times 10^{-33} [\text{Ar}]$	$208 \pm 2$		

## Comments

(a) Partial photodissociation of  $\text{N}_2\text{O}_3$  in equilibrium  $\text{NO}_2\text{-N}_2\text{O}_4\text{-NO-N}_2\text{O}_3\text{-M}$  mixtures with  $\text{M} = \text{He, Ar, Ne, N}_2$  and  $\text{CF}_4$  (see also ref. 2). The relaxation to equilibrium was monitored by observing the absorption of  $\text{N}_2\text{O}_3$  at the  $\nu_1$  band at  $1829.59 \text{ cm}^{-1}$ . The total pressure was 253-667 mbar (190-500 Torr). Falloff curves were extrapolated using  $F_c = 0.60$  for Ar and  $\text{N}_2$ .

(b) CO laser-induced temperature jump measurements with  $\text{NO}_2\text{-N}_2\text{O}_4\text{-N}_2\text{O}_3\text{-NO-SiF}_4\text{-Ar}$  equilibrium mixtures. The subsequent relaxation toward equilibrium was monitored by UV absorption of  $\text{N}_2\text{O}_3$  at 253 nm.

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## Preferred Values

$k_0 = 3.1 \times 10^{-34} (T/300)^{-7.7} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-300 K.

### 5 Reliability

$\Delta \log k_0 = \pm 0.3$  at 298 K.

$\Delta n = \pm 1$ .

### 10 Comments on Preferred Values

The preferred values are based on the data from Markwalder et al.,<sup>3</sup> after conversion by the ratio  $k_0(\text{N}_2)/k_0(\text{Ar}) = 1.36$  of Smith and Yarwood.<sup>1</sup>  $F_c = 0.6$  is chosen.

## High-pressure rate coefficients

### 15 Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.4 \pm 1) \times 10^{-12}$	208	Smith and Yarwood, 1987 <sup>1</sup>	FP (a)
$(2.7 \pm 0.9) \times 10^{-15} T^{(1.4 \pm 0.2)}$	227-260	Markwalder et al., 1993 <sup>3</sup>	(b)
$4.7 \times 10^{-12}$	208		

## Comments

(a) See comment (a) for  $k_0$ .

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(b) See comment (b) for  $k_0$ .

### Preferred Values

$k_\infty = 7.9 \times 10^{-12} (T/300)^{1.4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-300 K.

#### 5 *Reliability*

$\Delta \log k_\infty = \pm 0.3$  at 298 K.

$\Delta n = \pm 0.5$ .

#### 10 *Comments on Preferred Values*

The preferred values are those from ref. 3, where the largest ranges of the falloff curve were investigated. At 208 K, the values of  $k_\infty$  from refs. 1 and 3 are in reasonable agreement.

#### 15 **References**

<sup>1</sup> I. W. M. Smith and G. Yarwood, Faraday Disc. Chem. Soc., 84, 205, 1987.

<sup>2</sup> I. W. M. Smith and G. Yarwood, Chem. Phys. Lett., 130, 24, 1986.

<sup>3</sup> B. Markwalder, P. Gozel, and H. van den Bergh, J. Phys. Chem., 97, 5260, 1993.

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$$\Delta H^\circ = 40.6 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.0 \times 10^{14} T^{-(8.7 \pm 0.9)} \exp(-4880/T)$ [Ar]	225-260	Markwalder et al., 1993 <sup>1</sup>	(a)

## Comments

10 (a) CO<sub>2</sub> laser-induced temperature jump measurements with NO<sub>2</sub>-N<sub>2</sub>O<sub>4</sub>-N<sub>2</sub>O<sub>3</sub>-NO-SiF<sub>4</sub>-Ar equilibrium mixtures. The subsequent relaxation toward equilibrium was monitored by UV absorption of N<sub>2</sub>O<sub>3</sub> at 253 nm. Dissociation rate coefficients were derived from the measured recombination rate coefficients and the equilibrium constant from Chao et al.,<sup>2</sup> of  $K_c = 1.8 \times 10^{29} T^{-1} \exp(-4880/T)$  molecule cm<sup>-3</sup>. Falloff curves with M=Ar were obtained over the pressure range 0.5-200 bar and extrapolated to  $k_0$  and  $k_\infty$  with  $F_c = 0.6$ .  $k_0(\text{N}_2)/k_0(\text{Ar}) = 1.36$  was taken from Smith and Yarwood<sup>3</sup> (see reaction NO + NO<sub>2</sub> + M → N<sub>2</sub>O<sub>3</sub> + M).

15

## Preferred Values

$$k_0 = 1.6 \times 10^{-14} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 1.9 \times 10^{-7} (T/300)^{-8.7} \exp(-4880/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 225-$$

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300 K.

### Reliability

- 5  $\Delta \log k_0 = \pm 0.4$  at 298 K.  
 $\Delta n = \pm 1$ .  
 $\Delta(E/R) = \pm 200$  K.

### Comments on Preferred Values

10

The preferred values are based on the data of ref. 1, which are consistent with a theoretical analysis of the results (leading to collision efficiencies  $\beta_c(\text{Ar}) = 0.3$ ). The preferred values correspond to an analysis of the falloff curve with  $F_c = 0.6$  and the value of  $k_\infty$  given below.

## 15 High-pressure rate coefficients

### Rate coefficient data

$k_\infty/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.8 \times 10^{14} T^{(0.4 \pm 0.1)} \exp(-4880/T)$	225-260	Markwalder et al., 1993 <sup>1</sup>	(a)

### Comments

- (a) See comment (a) for  $k_0$ .

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## Preferred Values

$$k_{\infty} = 3.6 \times 10^8 \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_{\infty} = 4.7 \times 10^{15} (T/300)^{0.4} \exp(-4880/T) \text{ s}^{-1} \text{ over the temperature range } 225\text{-}300 \text{ K.}$$

### 5 *Reliability*

$$\Delta \log k_{\infty} = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 1.$$

$$\Delta(\text{textitE}/R) = \pm 100 \text{ K.}$$

10

### *Comments on Preferred Values*

The preferred values are based on the values of ref. 1 converted to dissociation data with the equilibrium constant from ref. 2.

### 15 **References**

<sup>1</sup> B. Markwalder, P. Gozel, and H. van den Bergh, J. Phys. Chem., 97, 5260, 1993.

<sup>2</sup> J. Chao, R. C. Wilhoit, and B. J. Zwolinski, Thermochim. Acta, 10, 359, 1974.

<sup>3</sup> I. W. M. Smith and G. Yarwood, Faraday Disc. Chem. Soc., 84, 205, 1987.

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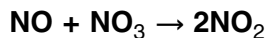
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$$\Delta H^\circ = -97.6 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.55 \times 10^{-11} \exp[(195 \pm 39)/T]$	209-299	Hammer et al., 1986 <sup>1</sup>	DF-LIF (a)
$(2.95 \pm 0.16) \times 10^{-11}$	299-414		
$1.59 \times 10^{-11} \exp(122/T)$	224-328	Sander and Kircher, 1986 <sup>2</sup>	FP-A (b)
$(2.41 \pm 0.48) \times 10^{-11}$	298		
$1.68 \times 10^{-11} \exp[(103 \pm 50)/T]$	223-400	Tyndall et al., 1991 <sup>3</sup>	DF-LIF (c)
$(2.34 \pm 0.24) \times 10^{-11}$	298		
$(2.6 \pm 0.2) \times 10^{-11}$	296	Brown et al., 2000 <sup>4</sup>	(d)

### Comments

(a) Arrhenius behaviour was observed for  $k$  over the temperature range 209-299 K, but  $k$  was independent of temperature over the range 299-414 K.

(b)  $[\text{NO}_3]$  was monitored by optical absorption. Total pressure was varied over the range 67- 930 mbar (50-700 Torr) of He and  $\text{N}_2$ .

(c)  $\text{NO}_3$  was produced either by the  $\text{F} + \text{HNO}_3$  reaction or the  $\text{NO}_2 + \text{O}_3$  reaction. In these experiments  $[\text{NO}_3]$  was monitored by LIF in an excess of NO. In other experiments the decay of  $[\text{NO}]$  in excess  $\text{NO}_3$  was monitored by chemilumines-

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cence. The value at 298 K is the mean of the values obtained in these different systems.

(d) Cavity ring-down spectroscopy was used to follow the kinetics of the NO + NO<sub>3</sub> reaction by monitoring the loss of light intensity from an optical cavity in which the NO + NO<sub>3</sub> reaction was occurring. NO<sub>3</sub> radicals were generated by pulsed laser photolysis of N<sub>2</sub>O<sub>5</sub> at 248 nm in the presence of an excess of NO contained in the laser cavity. Ring-down profiles were obtained using laser pulses at wavelengths of 622 nm or 623 nm, which are absorbed by the NO<sub>3</sub> radicals.

*Preferred Values*

$k = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.8 \times 10^{-11} \exp(110/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220–420 K.

*Reliability*

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$ .

*Comments on Preferred Values*

Since our previous evaluation, IUPAC 1997,<sup>5</sup> Brown et al.,<sup>4</sup> have measured  $k$  at 298 K using a new technique based on cavity ring down spectroscopy and obtain a value of  $k$  in excellent agreement with our preferred value. The preferred value of  $k$  at 298 K is the mean of the values reported by Hammer et al.,<sup>1</sup> Sander and Kircher,<sup>2</sup> Tyndall et al.,<sup>3</sup> and Brown et al.,<sup>4</sup> which are in excellent agreement, and the preferred value of  $E/R$  is the average of the values obtained by Sander and Kircher<sup>2</sup> and Tyndall et al.<sup>3</sup> The pre-exponential factor in the Arrhenius expression is adjusted to fit the values of  $k$  at 298 K.

## References

- <sup>1</sup> P. D. Hammer, E. J. Dlugokencky, and C. J. Howard, *J. Phys. Chem.*, 90, 2491, 1986.
- <sup>2</sup> S. P. Sander and C. C. Kircher, *Chem. Phys. Lett.*, 126, 149, 1986.
- <sup>3</sup> G. S. Tyndall, J. J. Orlando, C. A. Cantrell, R. E. Shetter, and J. G. Calvert, *J. Phys. Chem.*, 95, 4381, 1991.
- <sup>4</sup> S. S. Brown, A. R. Ravishankara, and H. Stark, *J. Phys. Chem. A*, 104, 7044, 2000.
- <sup>5</sup> IUPAC, Supplement VI, 1997, *J. Phys. Chem. Ref. Data*, 26, 1329, 1997.

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3, 6179–6699, 2003

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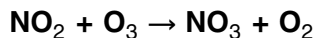
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$$\Delta H^\circ = -102.2 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.2 \pm 0.5) \times 10^{-17}$	298	Ghormley et al., 1973 <sup>1</sup>	FP (a)
$9.76 \times 10^{-14} \exp[-(2427 \pm 140)/T]$	260-343	Davis et al., 1974 <sup>2</sup>	(b)
$(3.42 \pm 0.27) \times 10^{-17}$	303		
$1.34 \times 10^{-13} \exp[-(2466 \pm 30)/T]$	231-298	Graham and Johnston, 1974 <sup>3</sup>	(c)
$(3.49 \pm 0.23) \times 10^{-17}$	298		
$1.57 \times 10^{-13} \exp[-(2509 \pm 76)/T]$	259-362	Huie and Herron, 1974 <sup>4</sup>	(d)
$(3.78 \pm 0.07) \times 10^{-17}$	297		
$(3.45 \pm 0.12) \times 10^{-17}$	296	Cox and Coker, 1983 <sup>5</sup>	(e)

### Comments

- (a) Flash photolysis system.  $[\text{O}_3]$  and  $[\text{NO}_2]$  were monitored by optical absorption.
- (b) Stopped flow system with detection of  $\text{O}_3$  by time-of-flight mass spectrometry. The exponential term given in the abstract is incorrect; the correct value is tabulated here (D. D. Davis, private communication).
- (c) Long path static cell.  $[\text{O}_3]$  and  $[\text{NO}_2]$  monitored in separate experiments by UV absorption spectrometry. Stoichiometric ratio ( $\Delta\text{NO}_2/\Delta\text{O}_3$ ) was measured to be  $1.89 \pm 0.08$ .

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(d) Stopped flow system.  $[O_3]$  monitored by molecular-beam sampling mass spectrometry.

(e) Static system. Experiments performed with both  $NO_2$  and  $O_3$  in excess. Time resolved absorption spectroscopy was used to monitor  $[N_2O_5]$  with a diode laser infrared source, and  $[NO_2]$  and  $[O_3]$  were monitored at 350 nm and 255 nm, respectively, using conventional UV techniques. Total pressure 13 mbar (10 Torr)  $N_2$ .  $N_2O_5$  was shown to be the only nitrogen containing product. Overall stoichiometry ( $\Delta NO_2/\Delta O_3$ ) was determined to have the value  $1.85 \pm 0.09$ . Minor role for unsymmetrical  $NO_3$  species were suggested to account for a stoichiometric factor less than 2.

### Preferred Values

$k = 3.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.4 \times 10^{-13} \exp(-2470/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230–360 K.

### Reliability

$\Delta \log k = \pm 0.06$  at 298 K.

$\Delta(E/R) = \pm 150 \text{ K}$ .

### Comments on Preferred Values

The preferred value at 298 K is taken as the mean of the five values tabulated,<sup>1–5</sup> corrected where necessary for the difference between the temperature of the measurement and 298 K. The temperature coefficient is taken as the mean of the values obtained by Davis et al.,<sup>2</sup> Graham and Johnston,<sup>3</sup> and Huie and Herron,<sup>4</sup> which are in

excellent agreement. Verhees and Adema<sup>6</sup> obtained a significantly higher temperature coefficient for  $k$  and a higher pre-exponential factor, but wall corrections were shown to be important in their work. There are also a number of other measurements of  $k$  at, or close to, 298 K which have not been used in deriving the preferred values because of their substantial deviation from the majority of the other studies.

## References

<sup>1</sup> J. A. Ghormley, R. L. Ellsworth, and C. J. Hochenadel, *J. Phys. Chem.*, 77, 1341, 1973; Erratum, 78, 2698, 1974.

<sup>2</sup> D. D. Davis, J. Prusaczyk, M. Dwyer, and P. Kim, *J. Phys. Chem.*, 78, 1775, 1974.

<sup>3</sup> R. A. Graham and H. S. Johnston, *J. Chem. Phys.*, 60, 4628, 1974.

<sup>4</sup> R. E. Huie and J. T. Herron, *Chem. Phys. Lett.*, 27, 411, 1974.

<sup>5</sup> R. A. Cox and G. B. Coker, *J. Atmos. Chem.*, 1, 53, 1983.

<sup>6</sup> P. W. C. Verhees and E. H. Adema, *J. Atmos. Chem.*, 2, 387, 1985.

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$$\Delta H^\circ = -57.3 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.4 \pm 0.2) \times 10^{-33} [\text{N}_2]$	298	Borrell et al., 1988 <sup>1</sup>	PLP (a)
$(1.0 \pm 0.1) \times 10^{-33} [\text{N}_2]$	224	Brunning et al., 1988 <sup>2</sup>	FP (b)
$(2.1 \pm 0.2) \times 10^{-12} T^{(-9.0 \pm 0.9)} [\text{He}]$	255-273	Markwalder et al., 1992 <sup>3</sup>	(c)

## Comments

- 10 (a) Relaxation of  $\text{NO}_2$ - $\text{N}_2\text{O}_4$ - $\text{N}_2$  equilibrium mixtures after low intensity pulsed laser photolysis of  $\text{N}_2\text{O}_4$  at 248 nm. The relaxation to equilibrium was obtained by measuring the change in  $\text{N}_2\text{O}_4$  absorption at 220 nm. Falloff curves (1-207 bar) were extrapolated with  $F_c = 0.40$  and  $N = 1.26$ .
- (b) Perturbation of equilibrium mixture of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  by photolysis of a fraction of the  $\text{N}_2\text{O}_4$ . The relaxation rate was monitored by IR absorption of  $\text{N}_2\text{O}_4$  at  $1565.5 \text{ cm}^{-1}$ .
- 15 (c) Temperature jumps induced by IR absorption of  $\text{SiF}_4$  in equilibrium mixtures of  $\text{NO}_2$ - $\text{N}_2\text{O}_4$ -He- $\text{SiF}_4$ . The relaxation to equilibrium was followed by measuring  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  concentrations by absorption spectroscopy at 420 and 250 nm,

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respectively. Falloff curves (0.3-200 bar) were extrapolated with  $F_c = 0.52$  and  $N = 1.10$  (see also earlier data from ref. 4).

### Preferred Values

$k_0 = 1.4 \times 10^{-33} (T/300)^{-3.8} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 300-500 K.

### Reliability

$\Delta \log k_0 = \pm 0.3$  at 298 K.

$\Delta n = \pm 1$ .

### Comments on Preferred Values

The preferred values are from the most extensive study of Borrell et al.,<sup>1</sup> where a complete falloff curve was measured. Earlier less extensive measurements are in reasonable agreement with this curve, which uses  $F_c = 0.40$ . The temperature dependence given is from the theoretical modeling of ref. 1, rather than from the limited experimental information of ref. 3.

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## High-pressure rate coefficients

### Rate coefficient data

$k_{\infty} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.3 \pm 1.0) \times 10^{-13}$	298	Borrell et al., 1988 <sup>1</sup>	PLP (a)
$(3.7 \pm 0.3) \times 10^{-18} T^{(2.3 \pm 0.2)}$	255-273	Markwalder et al., 1992 <sup>3</sup>	(b)

### Comments

- 5 (a) See comment (a) for  $k_0$ .  
(b) See comment (b) for  $k_0$ .

### Preferred Values

$k_{\infty} = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 250-300 K.

10 *Reliability*

$\Delta \log k_{\infty} = \pm 0.3$  over the temperature range 250-300 K.

15 *Comments on Preferred Values*

The preferred rate coefficient is the mean of the values of Borrell et al.<sup>1</sup> and Markwalder et al.<sup>3</sup> The temperature dependence of  $k_0$  and  $k_{\infty}$  derived from the measure-

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ments of ref. 3 appears to be inadequate because it results from the fitting of incomplete falloff curves.  $F_c = 0.4$  is chosen such as derived in ref. 1.

## References

- <sup>1</sup> P. Borrell, C. J. Cobos, and K. Luther, J. Phys. Chem., 92, 4377, 1988.
- <sup>2</sup> J. Brunning, M. J. Frost, and I. W. M. Smith, Int. J. Chem. Kinet., 20, 957, 1988.
- <sup>3</sup> B. Markwalder, P. Gozel, and H. van den Bergh, J. Chem. Phys., 97, 5472, 1992.
- <sup>4</sup> P. Gozel, B. Calpini, and H. van den Bergh, Isr. J. Chem., 24, 210, 1984.

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$$\Delta H^\circ = 57.3 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.29 \times 10^{-5} (T/300)^{-3.8} \exp(-6460/T) [\text{N}_2]$	300-500	Borrell et al., 1988 <sup>1</sup>	PLP (a)
$1.6 \times 10^{19} T^{-(10.0 \pm 1.0)} \exp[-(6790 \pm 700)/T] [\text{He}]$	255-273	Markwalder et al., 1992 <sup>3</sup>	(b)

## Comments

10 (a) Relaxation of  $\text{NO}_2$ - $\text{N}_2\text{O}_4$ - $\text{N}_2$  equilibrium mixtures after pulsed laser photolysis of  $\text{N}_2\text{O}_4$  at 248 nm. The relaxation to equilibrium was followed by observing  $\text{N}_2\text{O}_4$  in absorption at 220 nm. Falloff curves (1-207 bar) were extrapolated with  $F_c = 0.40$  and  $N = 1.26$ . The equilibrium constant from ref. 2 was employed.

15 (b) Temperature jumps induced by IR absorption of  $\text{SiF}_4$  in equilibrium mixtures of  $\text{NO}_2$ - $\text{N}_2\text{O}_4$ -He- $\text{SiF}_4$ . The relaxation to equilibrium was followed by absorption spectroscopy of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  at 420 and 250 nm, respectively. Falloff curves (0.3-200 bar) were extrapolated with  $F_c = 0.52$  and  $N = 1.10$ . Equilibrium constants from ref. 4 were employed.

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## Preferred Values

$k_0 = 6.1 \times 10^{-15} [\text{N}_2] \text{ s}^{-1}$  at 298 K.

$k_0 = 1.3 \times 10^{-5} (T/300)^{-3.8} \exp(-6400/T) [\text{N}_2] \text{ s}^{-1}$  over the temperature range 300-500 K.

### Reliability

$\Delta \log k_0 = \pm 0.3$  at 298 K.

$\Delta(E/R) = \pm 500$  K.

### Comments on Preferred Values

The preferred values are from the measurements of Borrell et al.<sup>1</sup> in combination with the equilibrium constants from ref. 2. These data are based on the most complete falloff curve at 300 K, using  $F_c = 0.40$ .

## High-pressure rate coefficients

### Rate coefficient data

$k_\infty/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$7.7 \times 10^{15} (T/300)^{-1.1} \exp(-6460/T)$	300-600	Borrell et al., 1988 <sup>1</sup>	PLP (a)
$2.8 \times 10^{13} T^{(1.3 \pm 0.2)} \exp[-(6790 \pm 700)/T]$	255-273	Markwalder et al., 1992 <sup>3</sup>	(b)

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## Comments

(a) See comment (a) for  $k_0$ .

(b) See comment (b) for  $k_0$ .

## Preferred Values

5  $k_\infty = 4.4 \times 10^6 \text{ s}^{-1}$  at 298 K.

$k_\infty = 1.15 \times 10^{16} \exp(-6460/T) \text{ s}^{-1}$  over the temperature range 250-300 K.

### *Reliability*

10  $\Delta \log k_\infty = \pm 0.4$  at 298 K.

$\Delta(E/R) = \pm 500 \text{ K}$ .

### *Comments on Preferred Values*

15 The preferred rate coefficient at room temperature is the average of the values of Borrell et al.<sup>1</sup> and Markwalder et al.<sup>3</sup> The recommended temperature coefficient corresponds to a temperature-independent value of  $k_\infty$  for the reverse recombination. Measurements from refs. 5 and 6 in the intermediate falloff range at 298 K are consistent with the preferred values of  $k_0$ ,  $k_\infty$  and  $F_c = 0.4$  at 300 K.

## References

20 <sup>1</sup> P. Borrell, C. J. Cobos, and K. Luther, J. Phys. Chem., 92, 4377, 1988.

<sup>2</sup> J. Chao, R. C. Wilhoit, and B. J. Zwolinski, Thermochem. Acta, 10, 359, 1974.

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$$\Delta H^\circ = -95.6 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$9.6 \times 10^{-33} \exp(1550/T) [\text{N}_2]$	262-295	Connell and Johnston, 1979 <sup>1</sup>	(a)
$1.7 \times 10^{-30} [\text{N}_2]$	298		
$1.35 \times 10^{-32} \exp(1270/T) [\text{N}_2]$	285-384	Viggiano et al., 1981 <sup>2</sup>	(b)
$9.6 \times 10^{-31} [\text{N}_2]$	298		
$(4.5 \pm 1.1) \times 10^{-30} (T/300)^{-(3.4 \pm 1.3)} [\text{N}_2]$	236-358	Kircher et al., 1984 <sup>3</sup>	FP-A (c)
$2.12 \times 10^{-30} [\text{N}_2]$	298	Smith et al., 1985 <sup>4</sup>	DF-A (d)
$2.8 \times 10^{-30} (T/300)^{-3.5} [\text{N}_2]$	236-358	Orlando et al., 1991 <sup>5</sup>	DF-LIF (e)

## Comments

(a) From study of  $\text{N}_2\text{O}_5$  decomposition. Static reaction vessel with multi-reflection White-cell optical arrangement for the time-resolved detection of  $\text{N}_2\text{O}_5$  by IR absorption at  $8.028 \mu\text{m}$ . Converted to recombination rate coefficients with the equilibrium constant  $K_c = 8.4 \times 10^{26} \exp(-11180/T) \text{ molecule cm}^{-3}$  from ref. 6.

(b) From study of  $\text{N}_2\text{O}_5$  decomposition. Flow system reactors of various size.  $\text{N}_2\text{O}_5$  was detected by ion-molecule reactions in a flowing afterglow system. Measure-

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ments were carried out at  $[N_2] = 2.5 \times 10^{17}$  to  $2.7 \times 10^{19}$  molecule  $\text{cm}^{-3}$ . Converted to recombination rate coefficients with the equilibrium constant  $K_c = 8.4 \times 10^{26} \exp(-11180/T)$  molecule  $\text{cm}^{-3}$  from ref. 6.

(c) Visible absorption of  $\text{NO}_3$  monitored under pseudo-first order conditions. Falloff curve measured over the pressure range 27-930 mbar (20-700 Torr) and extrapolated using reduced falloff curve representation with  $F_c = 0.34$  at 298 K.

(d) Visible absorption of  $\text{NO}_3$  monitored. Pressure range 1.3-10.7 mbar (1-8 Torr) in He, and 0.7-8 mbar (0.5-6 Torr) in  $\text{N}_2$ . Reduced falloff curves extrapolated with  $F_c = 0.47$  for  $\text{N}_2$  at 298 K.

(e) Detection of  $\text{NO}_3$ . Experiments were conducted over the pressure range 0.7-10.7 mbar (0.5-8 Torr) and the data evaluated using  $F_c = \{2.5 \exp(-1950/T) + 0.9 \exp(-T/430)\}$  ( $F_c(298 \text{ K}) = 0.45$ ).

### Preferred Values

$k_0 = 3.6 \times 10^{-30} (T/300)^{-4.1} [N_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-300 K.

### Reliability

$\Delta \log k_0 = \pm 0.10$  at 298 K.

$\Delta n = \pm 0.5$ .

### Comments on Preferred Values

The preferred values are based on the data of Orlando et al.,<sup>5</sup> and the falloff extrapolation from ref. 7 using the theoretically derived  $F_c = 0.35$  independent of the tem-

perature between 200 and 400 K. The temperature dependence is from the theoretical modelling of ref. 7. Different choices of  $F_c$  lead to different values of the extrapolated  $k_0$  and  $k_\infty$ , although the various representations all agree well with the experimental data.

## 5 High-pressure rate coefficients

### Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.1 \times 10^{-10} \exp(-1360/T)$	262-295	Connell and Johnston, 1979 <sup>1</sup>	(a)
$2.2 \times 10^{-12}$	298		
$1.5 \times 10^{-10} \exp(-1610/T)$	285-384	Viggiano et al., 1981 <sup>2</sup>	(b)
$6.8 \times 10^{-13}$	298		
$(2.2 \pm 0.5) \times 10^{-12}$	293	Croce de Cobos et al., 1984 <sup>8</sup>	(c)
$(1.65 \pm 0.15) \times 10^{-12} (T/300)^{-(0.4 \pm 0.5)}$	236-358	Kircher et al., 1984 <sup>3</sup>	FP-A (d)
$1.85 \times 10^{-12}$	298	Smith et al., 1985 <sup>4</sup>	DF-A (e)
$1.7 \times 10^{-12} (T/300)^{-0.2}$	236-358	Orlando et al., 1991 <sup>5</sup>	DF-LIF (f)
$(1.9 \pm 0.3) \times 10^{-12} (T/300)^{0.2}$	300-400	Hahn et al., 2000 <sup>7</sup>	PLP (g)

### Comments

(a) See comment (a) for  $k_0$ .

10 (b) See comment (b) for  $k_0$ . Data obtained from extrapolation of data in a relatively narrow pressure range near to the center of the falloff curve.

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(c) Laser flash photolysis of  $\text{N}_2\text{O}$  in the presence of  $\text{NO}_2$ .  $\text{NO}_3$  radicals were monitored by visible absorption under pseudo-first order conditions. The falloff curve was measured over the pressure range 1-200 bar in  $\text{N}_2$ , and extrapolated with  $F_c = 0.34$ .

5 (d) See comment (c) for  $k_0$ .

(e) See comment (d) for  $k_0$ .

(f) See comment (e) for  $k_0$ .

(g) See comment (c); measurements over the pressure range 30-900 bar evaluated with  $k_0$  from ref. 5 and  $F_c = 0.35$ .

## 10 Preferred Values

$k_\infty = 1.9 \times 10^{-12} (T/300)^{0.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-400 K.

### *Reliability*

15  $\Delta \log k_\infty = \pm 0.2$  at 298 K.

$\Delta n = \pm 0.6$ .

### *Comments on Preferred Values*

20 The preferred values are based on the high pressure measurements from ref. 7 which within experimental uncertainty agree well with the extrapolated values from refs. 3-5 and 8. The theoretically calculated value of  $F_c = 0.35$  does not influence the  $k_\infty$ -value but influences the extrapolated value of  $k_0$ .

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$$\Delta H^\circ = 95.6 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.04 \times 10^{-3} (T/300)^{-3.5} \exp(-11\,000/T) [\text{N}_2]$	253-384	Cantrell et al., 1993 <sup>1</sup>	(a)

## Comments

(a) Thermal decomposition of  $\text{N}_2\text{O}_5$  in the presence of  $\text{NO}$  in  $\text{N}_2$ . FTIR analysis of  $\text{N}_2\text{O}_5$  in a stainless steel cell equipped with multiple path optics. Falloff curves over the gas density  $4.3 \times 10^{14}$  to  $1.1 \times 10^{20}$  molecule  $\text{cm}^{-3}$  were analyzed using  $F_c = [2.5 \exp(-1950/T) + 0.9 \exp(-T/430)] [F_c(298 \text{ K}) = 0.45]$ . In the analysis, data from refs. 2 and 3 were also taken into account.

## Preferred Values

$$k_0 = 1.2 \times 10^{-19} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$15 \quad k_0 = 1.3 \times 10^{-3} (T/300)^{-3.5} \exp(-11\,000/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 200\text{--}400 \text{ K.}$$

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## Reliability

$\Delta \log k_0 = \pm 0.2$  at 298 K.

$\Delta n = \pm 0.5$ .

5

### Comments on Preferred Values

10

The preferred values are based on the study of Cantrell et al.,<sup>1</sup>, such as derived from the kinetic data; however, instead of  $F_c = 0.45$ , the modeled value of  $F_c = 0.35$  independent of the temperature was used for extrapolation to the low pressure limit. The recombination and dissociation rate coefficients are internally consistent. At room temperature, the equilibrium constant  $K_c = 2.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$  compares well with the values from refs. 4 and 5.

## High-pressure rate coefficients

15

### Rate coefficient data

$k_\infty/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$6.22 \times 10^{14} (T/300)^{-0.2} \exp(-11\,000/T)$	253-384	Cantrell et al., 1993 <sup>1</sup>	(a)

## Comments

(a) See comment (a) for  $k_0$ .

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## Preferred Values

$$k_{\infty} = 6.9 \times 10^{-2} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_{\infty} = 9.7 \times 10^{14} (T/300)^{0.1} \exp(-11080/T) \text{ s}^{-1} \text{ over the temperature range } 200\text{-}300 \text{ K.}$$

### 5 *Reliability*

$$\Delta \log k_{\infty} = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 0.2.$$

### 10 *Comments on Preferred Values*

The preferred values are based on the evaluation of Malko and Troe,<sup>6</sup> which agrees well with the recent determination of Cantrell et al.,<sup>1</sup> For the equilibrium constant, see comments on preferred values for  $k_0$ .

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$$\Delta H^\circ(1) = \Delta H^\circ(2) = -39. \text{ kJ mol}^{-1}$$

## 5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = 2.5 \times 10^{-22}$	290-293	Wahner et al., 1998 <sup>1</sup>	(a)
$k_2 = 1.8 \times 10^{-39}[\text{H}_2\text{O}]$			

## Comments

(a)  $[\text{NO}_2]$ ,  $[\text{N}_2\text{O}_5]$ , and  $[\text{HNO}_3]$  in a 250 m<sup>3</sup> FEP-Teflon chamber were monitored simultaneously by *in-situ* FTIR.  $[\text{O}_3]$  was monitored by UV absorption. The wall area was varied by placing extra Teflon sheets in the chamber. The  $[\text{N}_2\text{O}_5]$  decay kinetics were found to have a second order and a third order gas phase component and a contribution from reaction on the chamber walls. Rate coefficients were derived for the three decay channels by fitting the  $[\text{HNO}_3]$  and  $[\text{N}_2\text{O}_5]$  temporal profiles.

## 15 Preferred Values

$$k_1 = 2.5 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 290 \text{ K.}$$

$$k_2 = 1.8 \times 10^{-39} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \text{ at } 290 \text{ K.}$$

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$$\Delta \log k_1 = \Delta \log k_2 = \pm 0.3 \text{ at } 290 \text{ K.}$$

5 *Comments on Preferred Values*

The study of Wahner et al.<sup>1</sup> shows that channels (1) and (2) may both be significant under atmospheric conditions. The values of  $k_1$  and  $k_2$  obtained in their study are compatible with earlier studies<sup>2-7</sup> which only yielded upper limits. The values of  
10 Wahner et al.<sup>1</sup> are accepted as our preferred values but with substantial error limits until confirmatory studies are made.

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## HONO + $h\nu$ → products

### Primary photochemical transitions

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HONO + $h\nu$ → HO + NO	(1)	207	578
→ H + NO <sub>2</sub>	(2)	331	361
→ HNO + O( <sup>3</sup> P)	(3)	442	271

### Absorption cross-section data

Wavelength range/nm	Reference	Comments
185-270	Kenner et al., 1986 <sup>1</sup>	(a)
300-400	Bongartz et al., 1991 <sup>2</sup> ; 1994 <sup>3</sup>	(b)

### Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1 = 0.92 \pm 0.16$	365 ± 5	Cox and Derwent, 1976 <sup>4</sup>	(c)
$\phi(\text{HO}^*)$	193	Kenner et al., 1986 <sup>1</sup>	(d)
$\phi(\text{H})$	351	Wollenhaupt et al., 2000 <sup>5</sup>	(e)

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## Comments

- (a) A relative absorption spectrum was measured in the range 185-270 nm with absolute determinations at 193 nm and 215 nm. A value of  $\sigma = 1.6 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  was obtained at 193 nm. Two different methods used to prepare HONO gave similar results. The  $\sigma$  values agree with those of Cox and Derwent<sup>4</sup> in the wavelength region 220-270 nm, but the peak at 215 nm seen in the Cox and Derwent<sup>4</sup> study, which could have been due to NO absorption, was not observed.
- (b) Absolute absorption cross-sections were determined using conventional absorption spectroscopy, and with low, non-equilibrium concentrations of HONO determined by a combination of gas-phase and wet chemical analysis. Spectral resolution was 0.1 nm; cross sections averaged over 0.5 nm are given in a table. In their later work, improved conditions were used, specifically, higher HONO mole fractions, greater stability of HONO in the absorption chamber, and determination of the  $\text{NO}_2$  present by interference free optical absorption at 440 nm.
- (c) Rates of photon absorption and decomposition of  $\text{NO}_2$  and HONO were measured in the same photolysis cell. The value of  $\phi$  obtained supersedes an earlier estimate<sup>6</sup> using the same technique but based on less reliable absorption cross-section data.
- (d) Laser photolysis of HONO at 193 nm.  $\text{HO}^*$  was measured by emission spectroscopy. A small quantum yield of  $\sim 10^{-5}$  was determined.
- (e) Pulsed laser photolysis at 351 nm of flowing HONO -  $\text{N}_2$  (or Ar) mixtures was used to generate HO and the system was investigated using resonance absorption at 121.6 nm to discover the extent of any concomitant production of H. The system was calibrated for [H] by 248 nm photolysis of  $\text{CH}_3\text{SH}$ . An upper limit of 1% was obtained for  $\phi$  (H).

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## Preferred Values

### Absorption cross-sections of HONO at 298 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
190	127	260	8.0	330	9.3
195	172	265	5.2	335	6.5
200	197	270	3.4	340	16.8
205	220	275	2.5	345	9.6
210	214	280	-	350	11.5
215	179	285	-	355	23.6
220	146	290	-	360	8.0
225	120	295	-	365	16.1
230	86	300	0.0	370	20.5
235	60	305	0.7	375	4.9
240	42	310	1.6	380	9.2
245	30	315	2.5	385	14.5
250	18.5	320	4.4	390	2.4
255	12.4	325	5.0	395	0.6

### Quantum Yields at 298 K

<sup>5</sup>  $\phi_1 = 1.0$  throughout the wavelength range 190-400 nm.

#### *Comments on Preferred Values*

<sup>10</sup> Since our previous evaluation, IUPAC 1997,<sup>7</sup> Wang and Zhang<sup>8</sup> have measured the absorption cross-sections at 352.2 nm, 354.2 nm and 357.0 nm and there have been

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three other new determinations by Stutz et al.,<sup>9</sup> Pagsberg et al.,<sup>10</sup> and Brust et al.,<sup>11</sup> of the absorption cross-sections over a range of wavelengths in the 300–400 nm range. The results of Wang and Zhang,<sup>8</sup> Stutz et al.,<sup>9</sup> and Pagsberg et al.<sup>10</sup> are in good agreement but the values obtained by Brust et al.<sup>11</sup> are much lower. The reason for this discrepancy is not clear.

The studies of Wang and Zhang,<sup>8</sup> Stutz et al.,<sup>9</sup> and Pagsberg et al.<sup>10</sup> are also in agreement with the earlier studies of Stockwell and Calvert,<sup>12</sup> Vasudev,<sup>13</sup> and Bongartz et al.,<sup>2,3</sup> which were the basis of the preferred values for the absorption cross-section given in our previous evaluation, IUPAC, 1997,<sup>7</sup> which are therefore unchanged. The preferred values of the cross-sections tabulated for the 300–395 nm range are obtained from the data of Bongartz et al.<sup>2,3</sup> In their later work,<sup>3</sup> cross-sections were measured under better controlled conditions than in their earlier study<sup>2</sup> and it was shown that their earlier data were consistently too high by, on average, 14.5%. The preferred values have been obtained, therefore, by averaging the data from Ref. 2 over 5 nm intervals centred on the wavelength specified in the Table and reducing these values by 14.5% as directed in Ref. 3.

The HONO spectrum consists of a diffuse structured band between 300 and 390 nm and a broad structureless band from 270 nm to below 180 nm, peaking at ~210 nm. The only direct determination of the  $\phi(\text{HO})$  in this region is that of Cox and Derwent<sup>4</sup> who showed that channel (1) is the dominant process between 330 nm and 380 nm and obtained a quantum yield for HO production of  $0.92 \pm 0.16$  at 365 nm. There is some indirect evidence for H atom production at ~350 nm<sup>14</sup> but Wollenhaupt et al.<sup>5</sup> have shown  $\phi(\text{H})$  to be less than 0.01. We therefore take  $\phi(\text{HO})$  to be unity throughout this band.

In the second absorption band, cross-sections over the range 185–275 nm are based on the data of Kenner et al.,<sup>1</sup> which show that channel (1) is the main photodissociation channel in this region also, but minor H atom producing channels in the 193.3 nm photodissociation of a beam of jet-cooled HONO<sup>15</sup> have also been observed.

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## HONO<sub>2</sub> + hν → products

### Primary photochemical transitions

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HONO <sub>2</sub> + hν → HO + NO <sub>2</sub> (X <sup>2</sup> A <sub>1</sub> )	(1)	198	604
→ HONO + O( <sup>3</sup> P)	(2)	305	393
→ HO + NO <sub>2</sub> (1 <sup>2</sup> B <sub>2</sub> )	(3)	314	381
→ H + NO <sub>3</sub>	(4)	427	278
→ HONO + O( <sup>1</sup> D)	(5)	495	242
→ HONO(a <sup>3</sup> A'') + O( <sup>3</sup> P)	(6)	554	216

### Absorption cross-section data

Wavelength range/nm	Reference	Comments
195-350	Burkholder et al., 1993 <sup>1</sup>	(a)

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## Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(\text{OH}) = 1.0$	200-315	Johnston et al., 1974 <sup>2</sup>	(b)
$\phi(\text{OH}) = 0.89 \pm 0.08$	222	Jolly et al., 1986 <sup>3</sup>	(c)
$\phi[\text{HO}], \phi[\text{O}(^3\text{P})]$	248, 222, 193	Turnipseed et al., 1992 <sup>4</sup>	(d)
$\phi[\text{O}(^1\text{D})], \phi[\text{H}(^2\text{S})]$			
$\phi(1), \phi(2), \phi(3), \phi(5), \phi(6)$	193	Myers et al., 1997 <sup>5</sup>	(e)
$\phi(4)$	193	Li et al., 2001 <sup>6</sup>	(f)

## Comments

5 (a) The temperature dependences of  $\text{HNO}_3$  absorption cross-sections were measured between 240 K and 360 K using a diode array spectrometer with a resolution of < 0.4 nm. Absorption cross-sections were determined using both absolute pressure measurements at 298 K and a dual cell arrangement to measure absorptions at various temperatures relative to 298 K. A review of all previous experimental values was given together with an assessment of temperature-dependence effects on the stratospheric photolysis rate of  $\text{HNO}_3$ .

10 (b) Photolysis of  $\text{HNO}_3$  in the presence of excess CO and excess  $\text{O}_2$  to prevent complications due to secondary reactions. Results were interpreted by a complex reaction scheme.

15 (c) Pulsed laser photolysis with a KrCl excimer laser. HO radicals were detected by time-resolved resonance absorption at 308.3 nm. The error estimate quoted does not include the uncertainty of +17%, -8% resulting from an analysis of potential systematic errors.

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(d) Quantum yields for HO radicals,  $[O(^3P)+O(^1D)]$  atoms,  $O(^1D)$  atoms, and H atoms were measured in pulsed laser photolysis systems at 248 nm, 222 nm, and 193 nm, using LIF detection for  $HO(X^2\Pi)$  radicals and atomic resonance fluorescence for  $O(^3P)$  and  $H(^2S)$  atoms.  $\phi(HO)$  was measured relative to the yield of HO radicals from  $H_2O_2$  photolysis at 248 nm [ $\phi(HO) = 2.00 \pm 0.05$ ]<sup>7</sup> and at 193 nm [ $\phi(HO) = 1.51 \pm 0.18$ ].<sup>8</sup>  $\phi [O(^3P) + O(^1D)]$  was measured relative to the O atom yield from  $O_3$  photolysis at 248 nm ( $\phi = 1$ ) and 193 nm ( $\phi = 1.20 \pm 0.15$ ).<sup>9</sup>  $\phi[H(^2S)]$  was measured relative to the H atom yield from the photolysis of  $O_3-H_2$  mixtures where the H atoms are produced in the  $O(^1D) + H_2$  reaction. Measurements gave:  $\phi(HO) = 0.95 \pm 0.09$  at 248 nm,  $0.90 \pm 0.11$  at 222 nm, and  $0.33 \pm 0.06$  at 193 nm.  $\phi[O(^3P) + O(^1D)]$  was observed to be  $0.031 \pm 0.010$ ,  $0.20 \pm 0.03$ , and  $0.81 \pm 0.13$ , at 248 nm, 222 nm, and 193 nm respectively, with exclusively  $O(^3P)$  production at 248 nm.  $\phi[O(^1D)]$  was  $0.074 \pm 0.03$  at 222 nm and  $0.28 \pm 0.13$  at 193 nm. H atom yields were low; only at 193 nm were any H atoms detected, with  $\phi[H(^2S)] \leq 0.012$ .

(e) Photofragment translational spectroscopy investigation of  $HONO_2$  photolysis at 193 nm. The primary processes and their relative yields were deduced from photofragment time-of-flight signals at masses 16 ( $O^+$ ), 17 ( $HO^+$ ), 30 ( $NO^+$ ), and 46 ( $NO_2^+$ ). Two HO distributions arising from channels (1) and (3) were resolved and gave  $\phi_1 + \phi_3 = 0.33 \pm 0.04$ ,  $\phi_3/\phi_1 = 0.45$ . Two main O-atom producing channels were identified and attributed to channels (5) and (6), with quantum yields  $\phi_5 + \phi_6 = 0.67 \pm 0.04$ ,  $\phi_5/\phi_6 = 4.0$ .

(f) Photodissociation at 193 nm in a supersonic jet was studied using LIF and REMPI-TOF techniques. A bimodal rotational state distribution was observed for HO, consistent with the bimodal translational distribution found for HO by Myers et al.<sup>5</sup> An additional decay channel yielding  $O(^3P)$  was observed and attributed to channel (2), with a quantum yield of  $\sim 0.06$ .

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## Preferred Values

### Absorption cross-sections at 298 K<sup>a</sup>

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$10^3 \text{ B/K}^{-1}$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$10^3 \text{ B/K}^{-1}$
190	1360	0	270	1.62	1.45
195	1016	0	275	1.38	1.60
200	588	1.66	280	1.12	1.78
205	280	1.75	285	0.858	1.99
210	104	1.97	290	0.615	2.27
215	36.5	2.17	295	0.412	2.61
220	14.9	2.15	300	0.263	3.10
225	8.81	1.90	305	0.150	3.64
230	5.78	1.80	310	0.081	4.23
235	3.75	1.93	315	0.041	5.20
240	2.58	1.97	320	0.020	6.45
245	2.11	1.68	325	0.0095	7.35
250	1.97	1.34	330	0.0043	9.75
255	1.95	1.16	335	0.0022	10.1
260	1.91	1.14	340	0.0010	11.8
265	1.80	1.20	345	0.0006	11.2
			350	0.0004	9.30

<sup>a</sup> Temperature dependence given by the expression:  $\log_e \sigma = \log_e \sigma(298) + B(T - 298)$   
with T in K.

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	$\lambda/\text{nm}$		
	$\geq 248$	222	193
$\phi(\text{OH})$	$>0.97$	$0.90 \pm 0.10$	$0.33 \pm 0.06$
$\phi[\text{O}(^1\text{D}) + \text{O}(^3\text{P})]$	$0.03 \pm 0.03$	$0.20 \pm 0.03$	$0.81 \pm 0.13$
$\phi(^1\text{D})$	$<0.003$	$0.08 \pm 0.01$	$0.28 \pm 0.11$
$\phi(\text{H})$	$<0.01$	$<0.01$	$<0.01$

*Comments on Preferred Values*

The results of Burkholder et al.<sup>1</sup> for the cross-sections provide a high quality and comprehensive data set over the range of temperatures and wavelengths of significance for atmospheric photolysis of HNO<sub>3</sub>. Over the wavelength range 205-310 nm there is good agreement with the earlier studies of Rattigan et al.,<sup>10</sup> Biaueme,<sup>11</sup> Molina and Molina,<sup>12</sup> and Johnston and Graham.<sup>13</sup> At  $\lambda < 205$  nm, the data from different studies show small and unexplained discrepancies. At  $\lambda > 310$  nm the room temperature results of Burkholder et al.<sup>1</sup> are increasingly higher than all previously reported data except those of Rattigan et al.,<sup>10</sup> which are in good agreement. The preferred values are those given by Burkholder et al.<sup>1</sup>

The temperature dependences reported by Burkholder et al.<sup>1</sup> are weaker than those reported by Rattigan et al.<sup>10</sup> However, if the data at the lowest temperature (239 K) in the study of Rattigan et al.<sup>10</sup> are omitted, the agreement is good. Burkholder et al.<sup>1</sup> give values for the temperature coefficient,  $B$ , based on the two data sets<sup>1,10</sup> (excluding the 239 K data of Rattigan et al.<sup>10</sup>), and these are adopted here.

The quantum yield measurements confirm that, although channels (1) and (3) are the dominant channels at  $\lambda > \sim 260$  nm with  $\phi(\text{OH})$  close to unity, other channels become important at shorter wavelengths as suggested by the earlier work of Kenner et al.<sup>14</sup> The quantum yield measurements of Turnipseed et al.<sup>4</sup> and Schiffman et al.<sup>15</sup> are in

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excellent agreement at 248 nm when the two sets of measurements are normalized to the same value of the quantum yield for HO radical production from  $\text{H}_2\text{O}_2$ . The agreement is less good at 193 nm, where the direct measurements of Schiffman et al.<sup>15</sup> give an HO radical yield higher by about 50%. The value of  $\phi(\text{H}_2\text{O}_2)$  obtained by Schiffman et al.<sup>15</sup> is about 25% lower at both 248 nm and 193 nm than the values obtained by Vaghjani et al.<sup>8,9</sup> (2.0 at 248 nm and 1.5 at 193 nm). The preferred values for the quantum yields at  $\lambda \geq 248$  nm are based on the indirect studies of Johnston et al.<sup>2</sup> and the direct observation of Turnipseed et al.<sup>4</sup> The small yield of O atoms observed by Turnipseed et al.<sup>4</sup> is in agreement with the value of  $\phi(\text{O}) = 0.03$  at 266 nm obtained by Margitan and Watson.<sup>16</sup> At 222 nm the preferred values are based on the data of Turnipseed et al.<sup>4</sup> and Jolley et al.<sup>3</sup>

The photolysis of  $\text{HONO}_2$  at 193 nm has been clarified by recent the recent molecular beam studies of Myers et al.<sup>5</sup> and Li et al.,<sup>6</sup> which employed LIF and TOF techniques to detect the photolysis products and to measure their energy distributions. They obtained evidence for the occurrence of channels (1), (2), (3), (5), and (6), with O atom production becoming a major process at this wavelength, directly through channels (2), (5), and (6), and indirectly through dissociation of the internally excited  $\text{NO}_2$  produced via channel (1). The minor pathway ( $\phi_2 \approx 0.06$ ) detected by Li et al.<sup>6</sup> also produces internally excited HONO capable of subsequent dissociation. There are also pulsed laser photolysis studies at 193 nm on bulk gas samples from Turnipseed et al.<sup>4</sup> and Schiffman et al.<sup>16</sup> As previously mentioned, in the study of Schiffman et al.<sup>16</sup> there are inconsistencies in the measurements of HO yields from  $\text{H}_2\text{O}_2$  dissociation at  $\lambda \geq 260$  nm. The results of Turnipseed et al.<sup>4</sup> are therefore preferred and are the basis of our preferred values for the quantum yields at 193 nm. The value  $\phi(\text{OH})$  obtained by Turnipseed et al.<sup>4</sup> is the same as that from the molecular beam study of Myers et al.,<sup>5</sup> and the value of  $\phi[\text{O}(^3\text{P})+\text{O}(^1\text{D})]$  of Turnipseed et al.<sup>4</sup> can also be reconciled with the molecular beam results when production of O atoms from dissociation of internally excited  $\text{NO}_2$  from channel (1) is allowed for. However the value of  $\phi(^1\text{D}) = 0.28$  obtained by Turnipseed et al.<sup>4</sup> is much smaller than the value of  $\phi_5 = 0.52$  found by Myers et



al.,<sup>5</sup> and this discrepancy remains to be resolved. The upper limits to the H-atom yield obtained by Turnipseed et al.,<sup>4</sup> suggest that channel (4) is unimportant at  $\lambda \geq 193$  nm.

Photodissociation of HONO<sub>2</sub> via high-lying O-H overtone absorptions in the visible region of the spectrum is energetically possible for the 5 $\nu_{OH}$  and higher overtones.

Brown et al.,<sup>17</sup> have used cavity ring down spectroscopy to measure absorption cross-sections at 296 K and 251 K for the 4 $\nu_{OH}$  and 5 $\nu_{OH}$  transitions. The values obtained agree well with those from other studies<sup>18,19</sup> and imply that the contribution of these absorptions to HO production in the atmosphere is small, but larger than previous calculations<sup>18,20</sup> suggest.

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## HO<sub>2</sub>NO<sub>2</sub> + hν → products

### Primary photochemical transitions

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HO <sub>2</sub> NO <sub>2</sub> + hν → HO <sub>2</sub> + NO <sub>2</sub>	(1)	100	1191
→ HO + NO <sub>3</sub>	(2)	164	731

### Absorption cross-section data

Wavelength range/nm	Reference	Comments
190-330	Molina and Molina, 1981 <sup>1</sup>	(a)
210-330	Singer et al., 1989 <sup>2</sup>	(b)

### Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_2$	248	Mac Leod et al., 1988 <sup>3</sup>	(c)
$\phi_1$	248	Roehl et al., 2001 <sup>4</sup>	(d)

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- (a) Measured at 298 K and 1 bar total pressure.  $\text{HO}_2\text{NO}_2$  was prepared in a flowing  $\text{N}_2$  stream in the presence of  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{HO}_2$ . The composition of the mixture was established by FTIR spectroscopy, by the absorption spectrum in the visible, and by chemical titration after absorption in aqueous solutions. Two methods were used to prepare the  $\text{HO}_2\text{NO}_2$ . In the first, 70% nitric acid was mixed with 90%  $\text{H}_2\text{O}_2$ , while in the second method solid nitroniumtetrafluoroborate ( $\text{NO}_2\text{BF}_4$ ) was added to a solution of 90%  $\text{H}_2\text{O}_2$ .
- (b) Cross-sections were measured at 298 K, 273 K, and 253 K. Pernitric acid was produced *in situ* by photolysis of  $\text{Cl}_2$ - $\text{H}_2$ - $\text{NO}_2$ -air mixtures and averaged absorption measurements were made at small extents of reaction. The relative spectrum over the range 210-230 nm was measured at a resolution of 1 nm in flowing mixtures of pernitric acid vapour obtained from the reaction of  $\text{BF}_4\text{NO}_2$  and  $\text{H}_2\text{O}_2$ . The spectrum was corrected for the impurities  $\text{NO}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{HNO}_3$ , which were determined by IR spectroscopy.
- (c) Laser photolysis of pernitric acid at 248 nm. The HO radicals were detected by LIF and their yield determined relative to the HO yield from  $\text{H}_2\text{O}_2$  photolysis, with the assumption that the rotational distribution of the HO from the  $\text{HO}_2\text{NO}_2$  and the  $\text{H}_2\text{O}_2$  was the same under the conditions of the experiment. A value of  $\phi_2 = 0.34 \pm 0.16$  was obtained after correction for impurities in the pernitric acid sample. Fluorescence from  $\text{NO}_2^*$  was observed after photolysis and was assigned to production via channel (1). The upper limit for  $\text{NO}_2^*$  production was 30%. It was concluded that under atmospheric conditions  $\phi_1 \approx 0.65$  and  $\phi_2 \approx 0.35$ .
- (d) Laser photolysis of pernitric acid at 248 nm. The  $\text{NO}_2$  was detected by LIF at 511 nm. The quantum yield for  $\text{NO}_2$  production was obtained by comparison with  $\text{HNO}_3$  photolysis under the same conditions and taking the quantum yield for  $\text{NO}_2$

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production from  $\text{HNO}_3$  to be unity. Experiments made over a range of pressures and concentrations gave  $\phi(\text{NO}_2) = 0.56 \pm 0.17$ .

## Preferred Values

### Absorption cross-sections of $\text{HO}_2\text{NO}_2$ at 296 K

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
190	1010	265	22.9
195	816	270	18.0
200	563	275	13.3
205	367	280	9.3
210	239	285	6.2
215	161	290	3.9
220	118	295	2.4
225	93.2	300	1.4
230	78.8	305	0.85
235	68.0	310	0.53
240	57.9	315	0.39
245	49.7	320	0.24
250	41.1	325	0.15
255	34.9	330	0.09
260	28.4		

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## Quantum Yields at 298 K

$\phi_1 = 0.59$  at 248 nm.

$\phi_2 = 0.41$  at 248 nm.

### 5 *Comments on Preferred Values*

The preferred values of the absorption cross-sections are based on the data of Molina and Molina<sup>1</sup> and of Singer et al.<sup>2</sup> which are in excellent agreement at wavelengths in the range 210-300 nm. Between 300 nm and 320 nm the cross-sections of  
10 Singer et al.<sup>2</sup> are approximately a factor of 2 lower. A simple mean of the two data sets is taken over the whole wavelength range.

When the value of  $\phi(\text{HO})$  determined by Mac Leod et al.<sup>3</sup> at 248 nm is revised to take into account the present recommendation for the absorption cross-section for  $\text{H}_2\text{O}_2$  a slightly higher value of 0.39 is obtained. This is in very good agreement with the value  
15 of 0.44 implied by the recent measurement of  $\phi(\text{NO}_2)$  by Roehl et al.<sup>4</sup> at 248 nm. The preferred values of  $\phi_1$  and  $\phi_2$  are the average of the values from the studies of Roehl et al.<sup>4</sup> and Mac Leod et al.<sup>3</sup> The uncertainties in the quantum yields are large and it should be noted that the recommendations are restricted to a single wavelength.

Photodissociation of  $\text{HO}_2\text{NO}_2$  via high-lying O-H overtone absorptions in the visible  
20 region of the spectrum is energetically possible for the  $3\nu_{\text{OH}}$  and higher overtones. Zhang et al.<sup>5</sup> have measured absorption cross-sections at 273 K for the  $3\nu_{\text{OH}}$  and  $4\nu_{\text{OH}}$  transitions using conventional long-path-length absorption spectroscopy. Assuming that such absorptions are dissociative for  $\text{HO}_2\text{NO}_2$  the values obtained imply that these modes will play a small role in the photochemistry of the lower stratosphere.

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## NO<sub>2</sub> + hν → products

### Primary photochemical transitions

Reaction		$\Delta H^\circ/\text{kJ} \cdot \text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
NO <sub>2</sub> + hν → NO + O( <sup>3</sup> P)	(1)	301	398
→ NO + O( <sup>1</sup> D)	(2)	490	244

### Absorption cross-section data

Wavelength range/nm	Reference	Comments
300-500	Merienne et al., 1995 <sup>1</sup>	(a)
400-500	Coquart et al., 1995 <sup>2</sup>	(b)
380-830	Vandaele et al., 1996 <sup>3</sup>	(c)
200-300	Jenouvrier et al., 1996 <sup>4</sup>	(d)
350-585	Harder et al., 1997 <sup>5</sup>	(e)
360-470	Yoshino et al., 1997 <sup>6</sup>	(f)
200-400	Merienne et al., 1997 <sup>7</sup>	(g)
238-1000	Vandaele et al., 1998 <sup>8</sup>	(h)
231-794	Burrows et al., 1998 <sup>9</sup>	(i)

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## Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1$	295-445	Jones and Bayes, 1973 <sup>10</sup>	(j)
$\phi_1$	375-420	Harker et al., 1977 <sup>11</sup>	(k)
$\phi_1$	390-420	Davenport, 1978 <sup>12</sup>	(l)
$\phi_1$	334-404	Gardner et al., 1987 <sup>13</sup>	(m)
$\phi_1$	388-411	Roehl et al., 1994 <sup>14</sup>	(n)

## Comments

- (a) Cross-sections were measured at  $293 \pm 0.3$  K with  $\text{NO}_2$  concentrations of  $(3-9) \times 10^{14}$  molecule  $\text{cm}^{-3}$ . A conventional spectrometer was used with a multipass cell giving a total path length of 60.7 m. The spectral bandwidths were  $< 0.01$  nm at  $\lambda > 400$  nm and  $< 0.15$  at  $\lambda < 400$  nm. Cross-sections were measured at 0.01 nm intervals with a wavelength accuracy of 0.01 nm. Corrections were made for the presence of  $\text{N}_2\text{O}_4$  and for adsorption on the cell walls. Averaged cross-sections over 5 nm intervals were given for the range 305-425 nm.
- (b) Technique as in (a). Data were obtained at 0.01 nm intervals at 220 and 240 K. Averaged data are also given at 1 nm intervals at 293, 240 and 220 K over the range 400-500 nm. Features in the spectrum sharpen with decrease in temperature but there are no significant changes in the cross-sections at this resolution.
- (c) Cross-sections were measured at 293 K with dilute  $\text{NO}_2\text{-O}_2$  mixtures at a total pressure of 1 bar in a cell of 5.15 cm path length. A Bruker FT spectrometer was used and spectra were measured at resolutions of 0.02 nm and 0.3 nm. Effects of  $\text{NO}_2$  adsorption on cell walls and of  $\text{N}_2\text{O}_4$  formation were checked and corrections made.

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- (d) Technique as in (a). Data were obtained at 293 K, at  $\text{NO}_2$  concentrations of  $(0.4\text{--}1.5) \times 10^{14}$  molecules  $\text{cm}^{-3}$ . Measurements were made at 0.01 nm intervals at bandwidths in the range 0.016–0.065 nm.
- (e) Cross-sections of 84.1 ppmv mixtures of  $\text{NO}_2/\text{N}_2\text{O}_4$  in air at total pressures in the range 0.13–0.79 bar were measured at 217 K, 230 K, 239 K and 294 K using a FT spectrometer employing path lengths of 418.2 cm and 1220.6 cm and having a resolution of  $0.15 \text{ cm}^{-1}$ . Corrections for absorption by  $\text{N}_2\text{O}_4$  were made using literature values of the equilibrium constant and values obtained in this study. The data are compared with data from other studies and a detailed analysis of potential sources of instrumental error is given.
- (f) Cross-sections were measured at 293 K using a conventional vacuum grating spectrometer with a resolution of 0.003 nm and optical path length of 42.3 cm. Measurements were made at several  $\text{NO}_2$  pressures and the values extrapolated to zero pressure to obtain the cross-section at each wavelength. Results agree extremely closely with those of Merienne et al.<sup>1</sup>
- (g) This study is an extension of the low temperature measurements of Coquart et al.<sup>2</sup> into the 200–300 nm wavelength range. The technique was as in (b) but measurements were made only at 220 K, the optical path length was reduced to 20.8 m, and measurements were made at several pressures of  $\text{NO}_2/\text{N}_2\text{O}_4$  in the range 0.0026–0.098 mbar to allow corrections to be made for  $\text{N}_2\text{O}_4$  absorption.
- (h) This study combines the high resolution FT technique of Vandaele et al.<sup>3</sup> (Comment c) with the long path cell technique of Merienne et al.<sup>1,2,4,7</sup> (Comments a, b, d, g). Cross-sections were measured at 294 K over the pressure range 0.013–1.3 mbar and at 220 K over the pressure range 0.009–1.3 mbar. Measurements were made using a Bruker FT spectrometer equipped with a multi-pass cell having a path length of 60 m and at a resolution of  $2 \text{ cm}^{-1}$ . At 294 K contributions from  $\text{N}_2\text{O}_4$  absorption are less than 0.1% but at 220 K measurements were made over

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- a range of pressures to correct for the  $N_2O_4$  contribution. A significant pressure effect was observed in the visible at both temperatures but it may also be present in other spectral regions since only low pressures were used. Careful comparisons were made with a number of other studies.
- (i) Relative cross-sections of  $NO_2$ -air mixtures were measured at temperatures of 221 K, 241 K, 273 K, and 293 K using a four-channel Si-diode array spectrometer at a resolution of 0.2 nm below 405 nm and about 0.3 nm above 405 nm. The optical path length was varied between 985 cm and 1465 cm. Relative cross-sections were put on an absolute basis by measuring the spectrum at 293 K on a Bruker FT spectrometer over the range 400–550 nm. Corrections for  $N_2O_4$  were made by measurements made at several  $NO_2$  partial pressures. Comparisons are made with several other studies.
- (j) Relative quantum yields for NO production were measured using mass-spectrometric detection of the NO, and were normalized to literature values at 313 nm and 366 nm. Measurements were made at 5 or 10 nm intervals in the range 295–445 nm and at 492 nm, 546 nm, and 579 nm.
- (k) Quantum yield for  $NO_2$  photodissociation by pulsed dye laser measured at 1 nm intervals. The change in  $[NO_2]$  was obtained by absorption spectroscopy using absorption cross-sections measured in the same study. The absorbed quanta were calculated from measurements of the light intensity with joulemeters calibrated by ferrioxalate actinometry.
- (l) Quantum yield for NO production measured relative to NO production from NOCl photolysis at six wavelengths for  $T = 300$  K and 223 K.
- (m) The primary quantum yield,  $\phi_1$ , was derived from measurements of (1) quantum yield of  $NO_2$  loss (optical absorption), (2) quantum yield of NO formation (mass spectrometry), (3) quantum yield of  $O_2$  formation (mass spectrometry). Light intensity was measured by NOCl actinometry.  $\phi_1$  was found to be close to unity

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for wavelengths less than 395 nm. At 404 nm measurements were also made for 273 K to 370 K. The results were found to be in qualitative agreement with the simple theory that for  $\lambda > 395$  nm the energy deficiency for dissociation is made up from internal rotational and vibrational energy of the NO<sub>2</sub> molecules. On the basis of later experiments in the same laboratory by Calvert et al.,<sup>15</sup> in which the absorption cross-section at 404.7 nm was measured from 273 K to 370 K, the authors concluded that vibrationally excited molecules absorb more strongly than the unexcited molecules. They were thereby able to derive a reasonable fit to the variation of primary quantum yield with temperature for photodecomposition in the energy-deficient region at 404.7 nm.

(n) The quantum yield for NO production from dye laser photodissociation of NO<sub>2</sub> was measured at 248 K and 298 K relative to NO production from NOCl photolysis. Quantum yields were measured at high resolution (0.001 nm).

## Preferred Values

### Absorption cross-sections of NO<sub>2</sub> at 298 K and 220 K.

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$10^{20} \sigma/\text{cm}^2$
	298 K	220 K		298 K	220 K		298 K	220 K
205	33.81	34.29	305	16.04	15.85	405	57.68	56.17
210	44.51	42.46	310	18.82	18.70	410	61.53	60.82
215	48.87	45.80	315	21.64	21.96	415	58.92	57.53
220	46.72	44.03	320	25.42	24.94	420	59.50	58.43
225	39.04	36.96	325	28.79	27.53	425	56.70	55.22
230	27.65	26.11	330	31.88	29.82	430	54.04	52.95
235	16.53	14.57	335	35.87	33.62	435	55.54	55.09
240	8.30	7.54	340	40.20	37.81	440	48.42	47.33
245	3.75	3.29	345	41.75	39.11	445	48.84	47.77
250	1.46	1.14	350	46.10	43.71	450	48.13	48.61
255	1.09	0.84	355	49.82	47.55	455	41.24	39.68
260	1.54	1.04	360	50.77	49.24	460	42.97	42.76
265	2.18	1.96	365	55.01	54.18	465	40.87	40.54
270	2.92	3.00	370	56.07	55.93	470	33.56	31.97
275	4.06	4.16	375	58.88	58.96	475	38.49	37.95
280	5.27	5.33	380	59.24	58.33	480	33.44	32.52
285	6.82	6.73	385	59.42	58.97	485	25.18	23.33
290	8.64	8.79	390	62.00	62.20	490	30.74	30.17
295	10.64	10.64	395	59.20	58.01	495	29.30	28.63
300	12.99	12.82	400	63.85	63.20			

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## Quantum Yields at 298 K and 248 K

$\lambda/\text{nm}$	$\phi$		$\lambda/\text{nm}$	$\phi$	
	298 K	248 K		298 K	248 K
300-398	1.00	1.00	407	0.26	0.18
399	0.95	0.94	408	0.22	0.14
400	0.88	0.86	409	0.18	0.12
401	0.75	0.69	410	0.15	0.10
402	0.62	0.56	411	0.13	0.08
403	0.53	0.44	412	0.11	0.07
404	0.44	0.34	413	0.09	0.06
405	0.37	0.28	414	0.08	0.04
406	0.30	0.22	415	0.06	0.03

### Comments on Preferred Values

5 Since our previous evaluation, IUPAC, 1997,<sup>16</sup> there have been several studies, mostly at high resolution, of the NO<sub>2</sub> spectrum at temperatures ranging from 298 K to 220 K.<sup>3-9</sup> The most extensive study is that of Vandaele et al.,<sup>8</sup> covering the wavelength range 238-1000 nm at 220 K and 294 K. It is in excellent agreement with a number of other high resolution studies. At temperatures close to 298 K the data of  
10 Vandaele et al.,<sup>3,8</sup> Merienne et al.,<sup>1</sup> and Yoshino et al.<sup>6</sup> all lie within  $\pm 2\%$  over most of the wavelength range covered by their measurements. All of the studies appear to be less reliable at the extremes of the wavelength range covered by each of them but there is sufficient overlap for this group of studies to provide a set of reliable cross-section data for the range 300-600 nm. The study of Burrows et al.<sup>9</sup> also gives values within  
15  $\sim 2\%$  of these studies and provides reliable medium resolution data for the 300-600 nm range. At shorter wavelengths (200-300 nm) there are studies of Bass et al.,<sup>17</sup> Jenouvrier et al.,<sup>4</sup> Merienne et al.,<sup>7</sup> and Schneider et al.<sup>18</sup> The studies of Jenouvrier

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et al.,<sup>4</sup> and Merienne et al.<sup>7</sup> are in excellent agreement with the high resolution studies at longer wavelengths where they overlap and are preferred for the 200-300 nm range. There are uncertainties in the wavelength calibration of Schneider et al.,<sup>18</sup> but the older data of Bass et al.<sup>17</sup> are in reasonable agreement. Our recommended values for cross-sections are those given in the studies just described<sup>1-9</sup> and are preferred to those in the older studies of Schneider et al.,<sup>18</sup> Harwood and Jones,<sup>19</sup> and Davidson et al.,<sup>20</sup> which were the basis of our previous recommendations, IUPAC, 1997.<sup>16</sup> The recommended spectra are too detailed for cross-sections for an extensive listing here but 5 nm averaged cross-sections are given, taken from the studies of Mérienne et al.,<sup>1,7</sup> Coquart et al.,<sup>2</sup> and Jenouvrier et al.<sup>4</sup> These studies<sup>1,2,4,7</sup> suffer a little from undersampling at high resolution but are in good agreement with the recommended high resolution studies. For more detailed spectra the original papers<sup>1-9</sup> should be consulted; in most cases detailed spectra are available from the authors.

Studies at temperatures down to 220 K<sup>2,5,7,8,19</sup> have shown that the effect of lowering the temperature is to increase the sharpness of the structural features of the spectrum. There are no shifts in wavelength observed and those reported by Schneider et al.<sup>18</sup> and Davidson et al.<sup>20</sup> may have been due to small calibration errors. At 220 K the data of Vandaele et al.,<sup>8</sup> Coquart et al.<sup>2</sup> and Merienne et al.<sup>7</sup> agree to within ~ 2.5% in the regions where they overlap. The data of Harder et al.<sup>5</sup> are in good agreement with these other studies over most of their wavelength range but show large deviations at longer wavelengths (> 500 nm). The data of Harwood and Jones<sup>19</sup> are lower by between 5% and 10 % over most of their range but up to 20% lower at long wavelengths.

A significant pressure effect on the spectrum has also been observed in pure NO<sub>2</sub> (0.026-1.3 mbar)<sup>8</sup> and in highly dilute NO<sub>2</sub>/N<sub>2</sub> mixtures (6.6-790 mbar).<sup>5</sup> The publications of Vandaele et al.<sup>8</sup> and Harder et al.<sup>5</sup> should be consulted for details.

The preferred values of the quantum yields in our previous evaluation, IUPAC, 1997,<sup>16</sup> were those derived by Gardner et al.<sup>13</sup> based on their own data and a critical assessment of the earlier studies of Jones and Bayes,<sup>10</sup> Davenport,<sup>12</sup> and Harker et al.<sup>11</sup> The measurements of Roehl et al.<sup>14</sup> are in agreement with these recommendations. Since

these studies Troe<sup>21</sup> has corrected the values of Gardner et al.<sup>13</sup> and Roehl *et al.*<sup>14</sup> for small, but significant effects of secondary reactions and fluctuations of the specific rate constant. The values presented by Troe<sup>21</sup> are adopted as our preferred values.

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## NO<sub>3</sub> + hν → products

### Primary photochemical transitions

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
NO <sub>3</sub> + hν → NO + O <sub>2</sub> ( <sup>3</sup> Σ) (1)		10.8	11 080
→ NO + O <sub>2</sub> ( <sup>1</sup> Δ) (2)		105	1139
→ NO + O <sub>2</sub> ( <sup>1</sup> Σ) (3)		168	714
→ NO <sub>2</sub> + O( <sup>3</sup> P) (4)		204	587

### Absorption cross-section data

Wavelength range/nm	Reference	Comments
400-700	Sander, 1986 <sup>1</sup>	(a)

### Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(\text{NO} + \text{O}_2)$ , $\phi_4$	570-635	Orlando et al., 1993 <sup>2</sup>	(b)

### Comments

(a) Two methods were used to produce NO<sub>3</sub>. In one, NO<sub>3</sub> radicals were generated from the flash photolysis of Cl<sub>2</sub>-ClONO<sub>2</sub> mixtures, with NO<sub>3</sub> formation and ClONO<sub>2</sub> loss being monitored by UV absorption. Measurements were made at

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230, 250, and 298 K. The value of  $\sigma(\text{NO}_3)$  at 662 nm and 298 K, determined by this method ( $2.28 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ ), was preferred by the author. The cross section was observed to increase as the temperature was lowered.  $\text{NO}_3$  was also produced in a discharge flow system by the  $\text{F} + \text{HNO}_3$  reaction. The value of  $\sigma(\text{NO}_3)$  at 662 nm and 298 K determined by this method was  $1.83 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ . Values of  $\sigma(\text{NO}_3)$  were tabulated for 1 nm intervals from 400 nm to 700 nm for 298 K and 230 K.

- (b) The photodissociation of  $\text{NO}_3$  was studied at 298 K using pulsed laser photolysis, with resonance fluorescence detection of  $\text{O}(^3\text{P})$  atoms and  $\text{NO}(X^2\Pi)$ .  $\phi[\text{O}(^3\text{P})]$  was 1.0 over the range 570–585 nm, decreasing to a value of  $< 0.1$  at 635 nm.  $\phi(\text{NO})$  was  $< 0.1$  at 580 nm and about  $0.20 \pm 0.1$  at 590 nm. These data were combined with earlier results of Magnotta and Johnston<sup>3</sup> to provide quantum yields of  $\phi(\text{NO} + \text{O}_2)$  and  $\phi(4)$  as a function of wavelength (586–639 nm) and to calculate photolysis rates for overhead Sun at the earth's surface, with  $J(\text{NO}_2 + \text{O}) = 0.19 \text{ s}^{-1}$  and  $J(\text{NO} + \text{O}_2) = 0.016 \text{ s}^{-1}$ .

## Preferred Values

### Absorption cross-sections of NO<sub>3</sub> at 298 K and 230 K.

$\lambda/\text{nm}$	$10^{19} \sigma/\text{cm}^2$ 298 K	$10^{19} \sigma/\text{cm}^2$ 230 K	$\lambda/\text{nm}$	$10^{19} \sigma/\text{cm}^2$ 298 K	$10^{19} \sigma/\text{cm}^2$ 230 K	$\lambda/\text{nm}$	$10^{19} \sigma/\text{cm}^2$ 298 K	$10^{19} \sigma/\text{cm}^2$ 230 K
400	0.0	0.4	431	1.3	1.8	462	4.0	4.0
401	0.0	0.4	432	1.5	1.8	463	4.1	4.8
402	0.0	0.5	433	1.8	2.0	464	4.8	5.1
403	0.2	0.5	434	1.8	2.2	465	5.1	5.4
404	0.0	0.3	435	1.6	2.4	466	5.4	5.7
405	0.3	0.7	436	1.5	2.3	467	5.7	6.0
406	0.2	0.6	437	1.8	2.0	468	5.6	5.9
407	0.1	0.5	438	2.1	2.2	469	5.8	6.0
408	0.3	0.5	439	2.0	2.8	470	5.9	5.7
409	0.0	0.8	440	1.9	2.4	471	6.2	6.2
410	0.1	0.5	441	1.8	2.5	472	6.4	6.5
411	0.2	0.8	442	2.1	2.3	473	6.2	6.5
412	0.5	0.4	443	1.8	2.3	474	6.2	6.4
413	0.5	0.7	444	1.9	2.4	475	6.8	7.4
414	0.2	1.2	445	2.0	2.9	476	7.8	8.3
415	0.6	0.8	446	2.4	2.9	477	7.7	8.2
416	0.6	0.8	447	2.9	3.3	478	7.3	7.4
417	0.7	1.1	448	2.4	3.6	479	7.3	7.4
418	0.5	1.1	449	2.8	3.3	480	7.0	7.5
419	0.8	1.1	450	2.9	3.3	481	7.1	7.4
5 420	0.8	1.4	451	3.0	3.7	482	7.1	7.3

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$\lambda/\text{nm}$	$10^{19} \sigma/\text{cm}^2$ 298 K	$10^{19} \sigma/\text{cm}^2$ 230 K	$\lambda/\text{nm}$	$10^{19} \sigma/\text{cm}^2$ 298 K	$10^{19} \sigma/\text{cm}^2$ 230 K	$\lambda/\text{nm}$	$10^{19} \sigma/\text{cm}^2$ 298 K	$10^{19} \sigma/\text{cm}^2$ 230 K
421	0.8	1.3	452	3.3	4.0	483	7.2	7.1
422	0.9	1.3	453	3.1	3.7	484	7.7	7.4
423	1.1	1.3	454	3.6	4.0	485	8.2	8.2
424	0.9	1.4	455	3.6	4.1	486	9.1	9.5
425	0.7	1.7	456	3.6	3.6	487	9.2	9.4
426	1.4	1.6	457	4.0	4.2	488	9.5	9.2
427	1.4	1.3	458	3.7	4.7	489	9.6	10.6
428	1.2	1.6	459	4.2	4.5	490	10.3	11.2
429	1.1	1.4	460	4.0	4.6	491	9.9	10.3
430	1.7	1.7	461	3.9	4.3	492	9.9	10.6

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$\lambda/\text{nm}$	$10^{19} \sigma/\text{cm}^2$ 298 K	$10^{19} \sigma/\text{cm}^2$ 230 K	$\lambda/\text{nm}$	$10^{19} \sigma/\text{cm}^2$ 298 K	$10^{19} \sigma/\text{cm}^2$ 230 K	$\lambda/\text{nm}$	$10^{19} \sigma/\text{cm}^2$ 298 K	$10^{19} \sigma/\text{cm}^2$ 230 K
493	10.1	10.9	538	23.4	26.0	583	29.3	34.6
494	10.1	10.1	539	20.4	22.4	584	28.2	32.8
495	10.6	11.1	540	21.0	22.6	585	28.9	34.0
496	12.1	12.9	541	20.4	21.8	586	33.2	39.7
497	12.2	14.0	542	18.8	19.7	587	41.6	51.8
498	12.0	13.2	543	16.8	17.5	588	50.4	63.8
499	11.7	12.6	544	17.0	17.3	589	61.3	77.3
500	11.3	12.3	545	19.6	21.3	590	59.6	71.8
501	11.1	11.4	546	24.2	26.5	591	54.4	64.6
502	11.1	11.1	547	29.1	33.0	592	51.1	60.2
503	11.1	11.9	548	29.8	33.4	593	45.8	53.2
504	12.6	13.3	549	27.1	29.7	594	41.9	50.2
505	12.8	14.0	550	24.8	27.8	595	42.9	52.8
506	13.4	15.0	551	24.3	27.6	596	46.2	58.1
507	12.8	14.0	552	24.7	28.5	597	43.6	54.0
508	12.7	13.0	553	25.3	29.4	598	36.7	43.7
509	13.5	14.1	554	27.8	33.1	599	31.0	36.5
510	15.1	16.5	555	31.1	38.0	600	27.6	29.7
511	17.3	20.0	556	32.6	39.2	601	28.6	30.4
512	17.7	21.1	557	32.9	39.3	602	33.2	35.7
513	16.0	19.2	558	35.1	42.2	603	38.0	43.0
514	15.8	17.3	559	37.2	45.3	604	43.7	51.4
515	15.8	17.0	560	33.2	38.5	605	43.6	53.2
516	15.6	17.5	561	29.8	33.8	606	33.2	39.6

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$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$ 298 K	$10^{19}\sigma/\text{cm}^2$ 230 K	$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$ 298 K	$10^{19}\sigma/\text{cm}^2$ 230 K	$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$ 298 K	$10^{19}\sigma/\text{cm}^2$ 230 K
517	14.9	15.4	562	29.0	32.7	607	24.0	26.5
518	14.4	14.9	563	28.0	32.1	608	18.5	19.1
519	15.4	15.9	564	27.2	30.8	609	17.1	17.7
520	16.8	17.3	565	27.3	31.0	610	17.7	18.5
521	18.3	18.9	566	28.5	33.0	611	19.1	20.7
522	19.3	20.6	567	28.1	31.4	612	22.3	25.2
523	17.7	19.1	568	28.5	32.0	613	26.3	32.0
524	16.4	16.8	569	28.9	32.6	614	25.5	30.5
525	15.8	16.0	570	27.9	31.1	615	22.6	25.8
526	16.3	16.8	571	27.6	30.9	616	20.9	22.5
527	18.1	19.3	572	27.4	30.5	617	21.1	22.0
528	21.0	23.8	573	27.8	30.9	618	23.9	24.4
529	23.9	27.3	574	28.6	31.9	619	25.6	27.1
530	22.3	24.7	575	30.8	36.0	620	32.7	35.8
531	20.9	22.7	576	32.7	38.7	621	52.4	62.9
532	20.2	22.0	577	33.8	39.5	622	101.8	121.3
533	19.5	21.1	578	33.1	38.5	623	147.3	174.5
534	20.4	22.7	579	32.4	38.3	624	120.5	138.7
535	23.0	26.6	580	33.4	39.9	625	83.8	100.7
536	25.7	30.6	581	35.5	43.9	626	73.0	88.2
537	25.8	30.5	582	32.8	39.5	627	75.3	96.1

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$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$ 298 K	$10^{19}\sigma/\text{cm}^2$ 230 K	$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$ 298 K	$10^{19}\sigma/\text{cm}^2$ 230 K	$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$ 298 K	$10^{19}\sigma/\text{cm}^2$ 230 K
628	73.7	94.3	649	5.4	5.3	670	9.5	11.2
629	69.8	90.3	650	5.0	5.0	671	7.9	9.4
630	67.6	89.7	651	5.5	5.6	672	7.6	9.7
631	48.4	61.0	652	6.1	6.6	673	6.4	8.1
632	32.7	39.8	653	7.1	7.9	674	5.2	6.3
633	21.7	25.1	654	8.2	9.2	675	4.8	5.5
634	16.4	17.3	655	9.8	11.0	676	4.9	5.2
635	14.4	14.0	656	13.3	14.4	677	5.9	6.2
636	16.9	16.2	657	17.1	18.5	678	7.5	7.2
637	20.7	20.1	658	24.2	25.9	679	7.8	7.3
638	20.3	18.9	659	40.7	42.7	680	6.9	6.4
639	15.8	14.2	660	74.5	79.0	681	5.3	5.3
640	12.3	11.3	661	144.8	167.5	682	4.0	4.4
641	10.0	9.5	662	210.0	266.9	683	3.0	3.2
642	9.2	8.4	663	174.4	229.7	684	2.6	2.8
643	9.7	8.1	664	112.9	145.5	685	1.8	2.4
644	9.5	8.4	665	74.1	92.9	686	1.6	1.5
645	8.6	8.0	666	49.6	62.9	687	1.2	2.3
646	7.5	6.9	667	30.4	37.4	688	1.2	2.0
647	7.0	6.8	668	19.0	23.3	689	1.2	1.9
648	6.2	6.3	669	12.5	14.5	690	1.0	2.1

### Quantum Yields at 298 K

$\phi_4 = 1.0$  for  $\lambda \leq 587$  nm.

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The preferred values of the absorption cross-sections are based on the data of Sander<sup>1</sup> and are obtained by normalizing the experimental values of Sander<sup>1</sup> in the range 400-691 nm to the value of  $2.1 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$  for the peak value at 662 nm. This peak value is adopted from the evaluation of Wayne et al.<sup>4</sup> The measurements of Yokelson et al.,<sup>5</sup> made over the range 440-720 nm, which supersede previous data from the same laboratory,<sup>6</sup> are in good agreement with the data of Sander.<sup>1</sup>

There is also good agreement between the studies of Sander<sup>1</sup> and of Yokelson et al.<sup>5</sup> on the temperature dependence of the cross-sections, which were studied over the range 230-298 K by Sander,<sup>1</sup> and 200-298 K by Yokelson et al.<sup>5</sup> A significant increase in cross-section is found as temperature is lowered, in contrast to the findings of Cantrell et al.<sup>7</sup> who found temperature change to have little effect. To obtain the temperature dependence of the band at 662 nm, the value of  $\sigma$  at 230 K obtained by Sander<sup>1</sup> is accepted and combined with the preferred value at 298 K to give  $\sigma(T) = \{4.59 \times 10^{-17} - (8.37 \times 10^{-20}T)\} \text{ cm}^2 \text{ molecule}^{-1}$  at 662 nm.

The measurements of Orlando et al.<sup>2</sup> confirm qualitatively the wavelength dependence of  $\phi(\text{NO} + \text{O}_2)$  and  $\phi_4$  observed in the earlier room temperature measurements of Magnotta and Johnston,<sup>3</sup> and provide more accurate values for  $\phi_4$ . The earlier problem<sup>3</sup> of quantum yields in excess of 1.4 was not encountered in the work of Orlando et al.,<sup>2</sup> which confirms that  $\text{NO}_3$  radical dissociation is exclusively to  $\text{NO}_2 + \text{O}(^3\text{P})$  at wavelengths less than 587 nm.

A molecular beam study of Davis et al.<sup>8</sup> has provided considerable insight into the photodissociation of the  $\text{NO}_3$  radical. There is a very sharp threshold for channel (4) at 587 nm for cold  $\text{NO}_3$  and any dissociation at longer wavelengths via channel (4) must occur from internally excited  $\text{NO}_3$ . At  $\lambda \geq 588 \text{ nm}$  this process competes with photodissociation of  $\text{NO}_3$  to form  $\text{NO} + \text{O}_2$  via a three-centre transition state from the vibrationally excited ground state. The yield from this process falls off above 600 nm and may only occur from hot band absorption above 605 nm. These facts imply

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that the branching ratio for bulk, thermally equilibrated  $\text{NO}_3$  radicals will depend very strongly on temperature, especially near the threshold for the  $\text{NO}_2$ -forming channel, where higher temperatures will tend to favour the simple bond fission, channel (4).

Using the measured energy thresholds from the molecular beam experiments, Johnston et al.<sup>9</sup> have modelled product yields from the excited  $\text{NO}_3$  resulting from photon absorption. They have calculated values of  $\phi(\text{NO})$ ,  $\phi(\text{NO}_2)$ , and  $\phi(\text{fluorescence})$  as a function of wavelength in the range 401–690 nm at temperatures of 190, 230, and 298 K. The values at 298 K agree well with the experimental findings of Orlando et al.,<sup>2</sup> with only some departures for  $\phi(\text{NO}_2)$  in the 605–620 nm region.

On the basis of their measured quantum yields, Orlando et al.<sup>2</sup> have suggested photodissociation rates at the earth's surface, for an overhead sun, and the wavelength range 400–700 nm, of  $J(\text{NO}_2 + \text{O}) = 0.19 \text{ s}^{-1}$  and  $J(\text{NO} + \text{O}_2) = 0.016 \text{ s}^{-1}$ . These are preferred for atmospheric calculations. The experimental values of Magnotta and Johnston<sup>3</sup> are in agreement, and the calculations of Johnston et al.<sup>9</sup> also provide support for these photodissociation rates.

The information from the molecular beam experiments of Davis et al.<sup>8</sup> dictates that these values of  $J$  only apply for temperatures close to room temperature. Calculated values are available for lower temperatures, but further measurements of the quantum yields for  $\text{NO}_3$  radical photolysis in bulk samples at lower temperatures are required before recommendations can be made for atmospheric photolysis rates at stratospheric temperatures.

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## $\text{N}_2\text{O} + h\nu \rightarrow \text{products}$

### Primary photochemical transitions

Reaction		$\Delta H^\circ/\text{kJ} \cdot \text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}(^3\text{P})$	(1)	161	742
$\rightarrow \text{N}_2 + \text{O}(^1\text{D})$	(2)	351	341
$\rightarrow \text{N} + \text{NO}$	(3)	483	248
$\rightarrow \text{N}_2 + \text{O}(^1\text{S})$	(4)	568	211

### Absorption cross-section data

Wavelength range/nm	Reference	Comments
173-240	Selwyn et al., 1977 <sup>1</sup>	(a)

### Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(-\text{N}_2\text{O}) = 2.0$ $\phi(\text{NO}) = 1.0$ $\phi(\text{O}_2) = 0.5$	184.9	Greiner, 1967 <sup>2</sup>	(b)
$\phi_1 \leq 0.03$	214	Paraskevopoulos and Cvetanovic, 1969 <sup>3</sup>	(c)
$\phi_3 \leq 0.01$	185-230	Preston and Barr, 1971 <sup>4</sup>	(d)

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## Comments

- (a) Measured at five temperatures from 194 K to 302 K, with a resolution of 0.7 nm. Values were tabulated at 1nm intervals. A nine parameter fit expressing  $\sigma$  as a function of  $\lambda$  and  $T$  was also given.
- 5 (b) N<sub>2</sub>O was photolyzed at 184.9 nm in a static system at temperatures in the range 299-301 K. Analysis for N<sub>2</sub>O, NO, and O<sub>2</sub> was carried out by mass-spectrometry. No other products were observed but the analysis system was not sensitive to NO<sub>2</sub>. Pressure was varied in the range 5.3-285 mbar (4-214 Torr) of N<sub>2</sub>O. From the results obtained in this and other studies, it was concluded that  $\phi(-N_2O) = 2.0$ ,  $\phi(NO) = 1.0$ , and  $\phi(O_2) = 0.5$  over the range 138-210 nm.
- 10 (c) N<sub>2</sub>O was photolyzed at 298 K in the presence of neopentane, 1-butene, and added inert gases. The yield of O(<sup>3</sup>P) atoms was determined from the yield of addition products formed with 1-butene.
- 15 (d) N<sub>2</sub>O containing 1% <sup>15</sup>NO was photolyzed at 296 K and  $\lambda = 185$  nm, 214 nm, and 229 nm. The isotopic composition of the N<sub>2</sub> produced was measured.

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## Preferred Values

### Absorption cross-sections of N<sub>2</sub>O at 298 K

$\lambda/\text{nm}$	$10^{20}\sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20}\sigma/\text{cm}^2$
175	12.6	210	0.755
180	14.6	215	0.276
185	14.3	220	0.092
190	11.1	225	0.030
195	7.57	230	0.009
200	4.09	235	0.003
205	1.95	240	0.001

### Temperature dependence of absorption cross section

$$\ln \sigma(\lambda, T) = A_1 + A_2\lambda + A_3\lambda^2 + A_4\lambda^3 + A_5\lambda^4 + (T - 300)\exp(B_1 + B_2\lambda + B_3\lambda^2 + B_4\lambda^3)$$

where

$$\begin{aligned} A_1 &= 68.21023 & B_1 &= 123.4014 \\ A_2 &= -4.071805 & B_2 &= -2.116255 \\ A_3 &= 4.301146 \times 10^{-2} & B_3 &= 1.111572 \times 10^{-2} \\ A_4 &= -1.777846 \times 10^{-4} & B_4 &= -1.881058 \times 10^{-5} \\ A_5 &= 2.520672 \times 10^{-7} \end{aligned}$$

for  $\lambda = 173\text{--}240$  nm and  $T = 194\text{--}302$  K.

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## Quantum Yields

$\phi_2 = 1.0$  for  $\lambda = 185\text{-}230$  nm.

### *Comments on Preferred Values*

The preferred absorption cross-section and the expression for  $\ln \sigma(\lambda, T)$  are from Selwyn et al.<sup>1</sup> These cross-section values have been confirmed both at room temperature and at 208 K by the studies of Hubrich and Stuhl<sup>5</sup> and Mérienne et al.,<sup>6</sup> who also determined the temperature dependence.

The preferred value of the quantum yield is based on the studies of Greiner<sup>2</sup>, Parakevopoulos and Cvetanovic<sup>3</sup>, and Preston and Barr.<sup>4</sup> Greenblatt and Ravishankara<sup>7</sup> have also measured the quantum yield for production of  $\text{NO}(^2\Pi)$  and  $\text{N}(^4\text{S})$  atoms at 193 nm to be  $< 8 \times 10^{-3}$ .

Other relevant spectroscopic studies are those of Yoshino et al.,<sup>8</sup> who made high-resolution room temperature cross-section measurements in the 170-222 nm range, and of Lee and Suto.<sup>9</sup> who measured the photoabsorption and fluorescence cross-sections in the 106-160 nm region.

The UV absorption spectrum of the heavier isotopomers of  $\text{N}_2\text{O}$  ( $^{15}\text{N}^{14}\text{NO}$ ,  $^{14}\text{N}^{15}\text{NO}$ ,  $^{14}\text{N}^{14}\text{N}^{17}\text{O}$ ,  $^{14}\text{N}^{14}\text{N}^{18}\text{O}$ ) are slightly blue shifted due to their lower zero point energies and, as a result, are expected to be photolysed more slowly in the atmosphere. This is evident in the studies of Selwyn and Johnston<sup>10</sup> who measured the absorption spectrum of  $\text{N}_2\text{O}$  and its  $^{15}\text{N}$  isotopic forms over the wavelength range 172-197 nm and the temperature range 150-500 K. Isotopic fractionation is valuable as a means of investigating  $\text{N}_2\text{O}$  sources and sinks in the atmospheric cycle and, consequently, the isotope effect to be expected for the photolysis has been analysed by Yang and Miller,<sup>11</sup> and has been the subject a number of recent experimental studies,<sup>12-16</sup> which should be consulted for details.

State-resolved photofragment spectroscopy studies of  $\text{N}_2\text{O}$  photodissociation at 193

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nm<sup>17</sup> and 205 nm<sup>18</sup> show that 43% of the energy deposited in the molecule appears as translational energy of the O(<sup>1</sup>D) atom.

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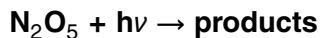
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### Primary photochemical transitions

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{N}_2\text{O}_5 + h\nu \rightarrow \text{NO}_3 + \text{NO}_2$	(1)	96	1252
$\rightarrow \text{NO}_3 + \text{NO} + \text{O}$	(2)	402	298
$\rightarrow \text{NO}_3 + \text{NO}_2^* \rightarrow \text{NO}_3 + \text{NO}_2 + h\nu$	(3)		

### Absorption cross-section data

Wavelength range/nm	Reference	Comments
200-380	Yao et al., 1982 <sup>1</sup>	(a)
240-420	Harwood et al., 1993 <sup>2</sup>	(b)
208-398	Harwood et al., 1998 <sup>3</sup>	(c)

### Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(\text{NO}_3)$	249-350	Swanson et al., 1982 <sup>4</sup>	(d)
$\phi(\text{NO}_3), \phi[\text{O}(\text{}^3\text{P})]$	290	Barker et al., 1985 <sup>5</sup>	(e)
$\phi(\text{NO}_3), \phi[\text{O}(\text{}^3\text{P})]$	248-289	Ravishankara et al., 1986 <sup>6</sup>	(f)
$\phi(\text{NO}_3)$	248, 308, 352.5	Harwood et al., 1998 <sup>3</sup>	(g)

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## Comments

- (a) Measured over the temperature range 223-300 K. For the wavelength range 200-280 nm, no temperature dependence was observed and values were tabulated at 5 nm intervals. For 285-385 nm, a pronounced temperature dependence was observed and the results were presented as an equation expressing  $\sigma$  as a function of  $\lambda$  and  $T$ .
- (b) Measurements were made over the temperature range 233-313 K using a dual beam diode array spectrometer. Absolute cross-sections were based on pressure measurements and determination of  $\text{NO}_2$  and  $\text{HNO}_3$  impurities by spectroscopic methods. For 260-380 nm, a pronounced temperature dependence was observed and the results were expressed in the form  $\log_{10}(\sigma) = A + B/T$ .
- (c) Spectra were measured using a diode array spectrograph having a resolution of  $\sim 1$  nm and were normalized to the value of  $\sigma$  at 280 nm reported by Harwood et al.<sup>2</sup> The  $\text{N}_2\text{O}_5$  was analysed to check for  $\text{HNO}_3$  impurities and found to contain  $< 1\%$ .
- (d) Pulsed laser photolysis, mostly at 249 nm, with a few experiments at 350 nm. The  $\text{NO}_3$  quantum yield was measured to be  $0.89 \pm 0.15$ . At low reactant concentration, the quantum yield approached  $1.0 \pm 0.1$ .
- (e) Pulsed laser photolysis. The quantum yield for production of  $\text{O}(^3\text{P})$  atoms was determined to be  $< 0.1$  in experiments with atomic resonance fluorescence detection of oxygen atoms. Optoacoustic techniques with added  $\text{NO}$  were used to determine  $\phi(\text{NO}_3)$  to be  $0.8 \pm 0.2$ .
- (f) Pulsed laser photolysis. The quantum yield for  $\text{NO}_3$  production at 249 nm was determined to be unity in experiments with detection of  $\text{NO}_3$  by absorption at 662 nm. The quantum yield for  $\text{O}(^3\text{P})$  production was observed to decrease from  $0.72 \pm 0.17$  at 248 nm to  $0.15 \pm 0.05$  at 289 nm.

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(g) Pulsed laser photolysis at 248 nm, 308 nm, or 352.5 nm with  $[\text{NO}_3]$  monitored by absorption at 661.9 nm. At each of the three photolysis wavelengths two different actinometric methods were used to establish the laser fluence for calculating the quantum yield. Values of  $\phi(\text{NO}_3)$  obtained were: at 248 nm ( $0.67 \pm 0.14$ ,  $0.64 \pm 0.08$ ); at 308 nm ( $0.88 \pm 0.10$ ,  $1.03 \pm 0.10$ ); at 352.5 nm ( $0.91 \pm 0.04$ ,  $1.21 \pm 0.04$ ). The quantum yields were independent of pressure over the range 197-789 mbar (150-600 Torr).

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## Preferred Values

### Absorption cross-sections of N<sub>2</sub>O<sub>5</sub> at 298 K

$\lambda/\text{nm}$	$10^{20}\sigma/\text{cm}^2$	$B/\text{K}$	$\lambda/\text{nm}$	$10^{20}\sigma/\text{cm}^2$	$B/\text{K}$
210	470		315	1.62	-0.253
215	316		320	1.21	-0.294
220	193		325	0.89	-0.338
225	128		330	0.67	-0.388
230	91		335	0.50	-0.409
235	73		340	0.38	-0.492
240	60		345	0.279	-0.530
245	51		350	0.215	-0.583
250	40		355	0.164	-0.719
255	32		360	0.124	-0.770
260	25.9	-0.091	365	0.091	-0.801
265	20.4	-0.100	370	0.072	-0.885
270	16.4	-0.104	375	0.053	-0.765
275	13.2	-0.112	380	0.041	-0.992
280	11.1	-0.112	385	0.032	-0.992
285	8.59	-0.126	390	0.0228	-0.949
290	6.71	-0.135	395	0.0171	-0.845
295	5.11	-0.152	400	0.0138	-0.966
300	3.87	-0.170	405	0.0103	-1.00
305	2.91	-0.194	410	0.0080	-1.16
310	2.17	-0.226			

Temperature dependence:  $\log_{10}\sigma_T$  ( $\text{cm}^2 \text{ molecule}^{-1}$ ) =  $\log_{10}\sigma_{298} + 1000B(1/T - 1/298)$ .

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$\lambda/\text{nm}$	$\phi(\text{NO}_3)$	$\phi(\text{O})$
248	0.8	0.72
266		0.38
287		0.21
289		0.15
300	1.0	
350	1.0	

### Comments on Preferred Values

5 The absorption cross sections reported by Harwood et al.<sup>2</sup> are in excellent agreement with the earlier data of Yao et al.<sup>1</sup> and the more recent values obtained by Harwood et al.<sup>3</sup> at wavelengths  $> 240$  nm. At wavelengths shorter than 240 nm the values obtained by Harwood et al.<sup>3</sup> are lower than those of Yao et al.,<sup>1</sup> the divergence between the two studies increasing with decreasing wavelength, so that at 210 nm the absorption cross-section obtained by Yao et al.<sup>1</sup> is  $\sim 50\%$  greater than that of Harwood et al.<sup>3</sup> The preferred values for the cross-sections at 298 K were obtained by averaging the values obtained by Yao et al.,<sup>1</sup> Harwood et al.,<sup>2</sup> and Harwood et al.<sup>3</sup> for  $\lambda \geq 240$  nm and averaging those of Yao et al.<sup>1</sup> and Harwood et al.<sup>3</sup> in the range 210-240 nm.

10 The temperature dependences of the cross-sections measured by Harwood et al.<sup>2</sup> agree well with the values obtained by Yao et al.,<sup>1</sup> except at the longer wavelengths where the results in the former study show a slightly larger dependence. Thus, using the expressions for the temperature dependence and the  $A$  values given in the two studies, the  $\sigma$  values calculated at 380 nm differ by about 30%. The preferred values of the temperature coefficients are taken from Harwood et al.<sup>2</sup>

20 The quantum yields for  $\text{NO}_3$  and O atom formation have been measured at a number of wavelengths in the range 248-352.5 nm. The preferred value of  $\phi(\text{NO}_3) = 1.0$  at 300

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nm and 350 nm are based on the results of Swanson et al.<sup>4</sup> at 350 nm, Barker et al.<sup>5</sup> at 290 nm, and Harwood et al.<sup>3</sup> at 308 nm and 352.5 nm, which agree within the fairly substantial error limits. The value of  $\phi(\text{NO}_3)$  at wavelengths below 300 nm is less certain. A quantum yield close to unity has been reported by Swanson et al.<sup>4</sup> at 249 nm and by Ravishankara et al.<sup>6</sup> over the range 248–289 nm, but the recent study of Harwood et al.<sup>3</sup> suggests a substantially lower value at 248 nm. Our preferred value of 0.8, with suggested error limits of at least 10%, reflects the findings of all of these studies.<sup>3,4,6</sup>

The preferred quantum yields for O atom production are those reported by Ravishankara et al.<sup>6</sup> Barker et al.<sup>5</sup> also report a quantum yield for O atom production of < 0.1 at 290 nm in agreement with the findings of Ravishankara et al.<sup>6</sup> that  $\phi(\text{O})$  is substantial at 248 nm but decreases with increasing wavelength, approaching zero in the neighbourhood of the thermodynamic threshold for O atom production at 298 nm.

The study of Oh et al.<sup>7</sup> indicates that electronically excited  $\text{NO}_2$  in the  ${}^2B_1$  state is produced, and photolysis induced fluorescence (PIF) quantum yield values are reported.

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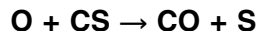
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## Appendix 4: SO<sub>x</sub> reactions



$$\Delta H^\circ = -361 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

5

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(2.06 \pm 0.14) \times 10^{-11}$	305	Slagle et al., 1975 <sup>1</sup>	DF-MS
$(2.24 \pm 0.36) \times 10^{-11}$	300	Bida et al., 1976 <sup>2</sup>	DF-UVA
$2.6 \times 10^{-10} \exp[-(760 \pm 140)/T]$	156-294	Lilenfeld and Richardson, 1977 <sup>3</sup>	DF-EPR/MS
$2.0 \times 10^{-11}$	298*		
<i>Relative Rate Coefficients</i>			
$2.2 \times 10^{-11}$	298	Hancock and Smith, 1971 <sup>4</sup>	RR (a)

### Comments

(a) Discharge flow system. O(<sup>3</sup>P) was added to CS<sub>2</sub>, and the infrared chemiluminescence from the O + CS reaction monitored. NO<sub>2</sub> was added to compete for O atoms. A rate coefficient ratio of  $k/k(\text{O} + \text{NO}_2) = 2.3$  was obtained, and placed on an absolute basis by use of  $k(\text{O} + \text{NO}_2) = 9.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation).

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### Preferred Values

$$k = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.7 \times 10^{-10} \exp(-760/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 150\text{-}300 \text{ K.}$$

### 5 Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 250 \text{ K.}$$

### 10 Comments on Preferred Values

Because of its significance in the CO chemical laser, this reaction has been the subject of a number of studies.<sup>1-4</sup> The values of  $k$  obtained at 298 K fall within a range of about 20%. The preferred value is the mean of these measurements,<sup>1-4</sup> all of which seem reliable. To obtain the preferred expression for  $k$ , the only available value of  $E/R$  is accepted<sup>3</sup> and the pre-exponential factor is adjusted to fit the preferred 298 K rate coefficient.

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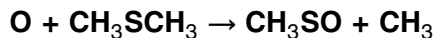
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$$\Delta H^\circ = -133 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.42 \times 10^{-11} \exp[(366 \pm 15)/T]$	268-424	Lee et al., 1976 <sup>1</sup>	FP-RF
$(4.84 \pm 0.52) \times 10^{-11}$	298		
$1.28 \times 10^{-11} \exp[(404 \pm 30)/T]$	272-472	Lee et al., 1980 <sup>2</sup>	DF-RF
$(4.83 \pm 0.46) \times 10^{-11}$	296		
$1.11 \times 10^{-11} \exp[(460 \pm 41)/T]$	296-557	Nip et al., 1981 <sup>3</sup>	(a)
$5.11 \times 10^{-11}$	297		

### Comments

(a) O(<sup>3</sup>P) atoms were generated by the mercury-photosensitized photolysis of N<sub>2</sub>O using a sinusoidally-modulated mercury lamp, and monitored by NO<sub>2</sub> chemiluminescence using a phase-shift technique.

### Preferred Values

$k = 5.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.3 \times 10^{-11} \exp(409/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270-560 K.

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## Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta(E/R) = \pm 100$  K.

5

## Comments on Preferred Values

The data of Nip et al.<sup>3</sup> are in excellent agreement, over the entire temperature range studied, with both of the studies of Lee et al.<sup>1,2</sup> The preferred values of  $k$  at 298 K and  $(E/R)$  are obtained from a least-squares fit of the data from those three studies.<sup>1-3</sup> The product study of Cvetanovic et al.<sup>4</sup> suggests that at high pressures (0.39-1.58 bar) the reaction proceeds almost entirely by addition followed by rapid fragmentation to  $\text{CH}_3 + \text{CH}_3\text{SO}$ . A broad chemiluminescence spectrum in the range 240-460 nm from this reaction at 1.3 mbar (1 Torr) pressure has been reported by Pavanaja et al.<sup>5</sup> They identified the emitting species as electronically excited HO and  $\text{SO}_2$ , and by numerical integration they showed that production of these excited species is consistent with secondary chemistry following the initial reaction to give the products shown above.

15

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$$\begin{aligned} \Delta H^\circ(1) &= -83 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta H^\circ(2) &= -348 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta H^\circ(3) &= -231 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

### Rate coefficient data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.0 \times 10^{-11} \exp[-(300 \pm 150)/T]$	305-410	Smith, 1968 <sup>1</sup>	FP-UVA
$4.2 \times 10^{-12}$	305		
$8.3 \times 10^{-11} \exp(-950/T)$	300-920	Homann et al., 1968 <sup>2</sup>	DF-MS
$3.5 \times 10^{-12}$	300		
$(2.08 \pm 0.08) \times 10^{-12}$	227	Westenberg and deHaas, 1969 <sup>3</sup>	DF-EPR/MS
$(3.0 \pm 0.3) \times 10^{-12}$	297		
$(7.8 \pm 0.3) \times 10^{-12}$	538		
$(3.7 \pm 0.3) \times 10^{-12}$	298	Callear and Hedges, 1970 <sup>4</sup>	FP-UVA
$(4.0 \pm 0.3) \times 10^{-12}$	302	Slagle et al., 1974 <sup>5</sup>	(a)

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.8 \times 10^{-11} \exp[-(650 \pm 35)/T]$	218-293	Wei and Timmons, 1975 <sup>6</sup>	DF-EPR
$(3.1 \pm 0.2) \times 10^{-12}$	293		
$(2.9 \pm 0.2) \times 10^{-12}$	249	Graham and Gutman, 1977 <sup>7</sup>	DF-MS
$(3.6 \pm 0.3) \times 10^{-12}$	273		
$(4.1 \pm 0.2) \times 10^{-12}$	295		
$(5.1 \pm 0.6) \times 10^{-12}$	335		
$(6.6 \pm 0.3) \times 10^{-12}$	376		
$(8.5 \pm 0.6) \times 10^{-12}$	431		
$(11.2 \pm 0.8) \times 10^{-12}$	500		

## Comments

(a) Studied by using crossed molecular beams with photoionization mass spectrometric detection of products.

## 5 Preferred Values

$k = 3.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 3.3 \times 10^{-11} \exp(-650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 210-500 K.

$k_1/k \geq 0.90$  over the temperature range 200-500 K.

## 10 Reliability

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$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta(E/R) = \pm 100$  K.

### Comments on Preferred Values

There are several determinations of  $k$  at 298 K using a variety of techniques, which are in good agreement. The preferred value is an average of the values of Smith,<sup>1</sup> Homann et al.,<sup>2</sup> Westenberg and deHaas,<sup>3</sup> Callear and Hedges,<sup>4</sup> Slagle et al.,<sup>5</sup> Wei and Timmons,<sup>6</sup> and Graham and Gutman.<sup>7</sup> The preferred temperature coefficient is that of Wei and Timmons,<sup>6</sup> which is in good agreement with that of Graham and Gutman.<sup>7</sup>

The reported values for the branching ratios show considerable scatter. For  $k_3/k$  values of 0.093,<sup>5</sup> 0.096,<sup>7</sup> 0.015,<sup>8</sup> 0.30<sup>9</sup> and 0.085<sup>10</sup> have been reported and for  $k_2/k$  values of 0.05-0.20,<sup>5</sup> 0.014<sup>11</sup> and 0.030.<sup>10</sup> Channel 1 is clearly the major channel but at this stage our only recommendation is that  $k_1/k \geq 0.90$ .

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<sup>1</sup> I. W. M. Smith, *Trans. Faraday Soc.*, 64, 378, 1968.

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<sup>3</sup> A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, 50, 707, 1969.

<sup>4</sup> A. B. Callear and R. E. M. Hedges, *Trans. Faraday Soc.*, 66, 605, 1970.

<sup>5</sup> I. R. Slagle, J. R. Gilbert, and D. Gutman, *J. Chem. Phys.*, 61, 704, 1974.

<sup>6</sup> C. N. Wei and R. B. Timmons, *J. Chem. Phys.*, 62, 3240, 1975.

<sup>7</sup> R. E. Graham and D. Gutman, *J. Phys. Chem.*, 81, 207, 1977.

<sup>8</sup> G. Hancock and I. W. M. Smith, *Trans. Faraday Soc.*, 67, 2586, 1971.

<sup>9</sup> R. D. Suart, P. H. Dawson, and G. H. Kimbell, *J. Appl. Phys.*, 43, 1022, 1972.

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<sup>11</sup> D. S. Y. Hsu, W. M. Shaub, T. L. Burks, and M. C. Lin, *Chem. Phys. Lett.*, 44, 143, 1979.

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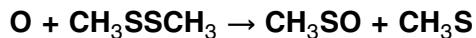
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$$\Delta H^\circ = -167 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.12 \pm 0.22) \times 10^{-10}$	270-329	Lee and Tang, 1980 <sup>1</sup>	DF-RF
$4.35 \times 10^{-11} \exp[(251 \pm 61)/T]$	298-571	Nip et al., 1981 <sup>2</sup>	(a)
$(1.0 \pm 0.3) \times 10^{-10}$	298		

### Comments

(a) O(<sup>3</sup>P) atoms were generated by the mercury-photosensitized photolysis of N<sub>2</sub>O using a sinusoidally-modulated mercury lamp, and monitored by NO<sub>2</sub> chemiluminescence using a phase-shift technique.

### Preferred Values

$k = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 6.5 \times 10^{-11} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290-570 K.

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$\Delta \log k = \pm 0.3$  at 298 K.

$\Delta(E/R) = \pm 100$  K.

5

*Comments on Preferred Values*

The data of Nip et al.<sup>2</sup> obtained using a modulated photolysis technique, are about a factor of 2 lower than the data from the earlier discharge flow-resonance fluorescence study of Lee and Tang,<sup>1</sup> who reported no temperature dependence over the rather limited range 270-329 K. The cause of the discrepancy between the two measurements is not clear. The preferred value at 298 K is an average of the values from the two studies.<sup>1,2</sup> The temperature dependence is that from Nip et al.<sup>2</sup> with the *A* factor adjusted to yield the preferred value at 298 K.

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The product study of Cvetanovic et al.<sup>3</sup> suggests that at high pressures, 0.39-1.58 bar, the reaction proceeds mainly by addition followed by rapid fragmentation to CH<sub>3</sub>S + CH<sub>3</sub>SO. A broad chemiluminescence spectrum in the range 240-460 nm from this reaction at 1.3 mbar (1 Torr) pressure has been reported by Pavanaja et al.<sup>4</sup> They identified the emitting species as electronically excited HO and SO<sub>2</sub>, and showed from a computer simulation that production of these excited species is consistent with secondary chemistry following the initial reaction to give the products shown above.

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<sup>1</sup> J. H. Lee and I. N. Tang, *J. Chem. Phys.*, 72, 5718, 1980.

<sup>2</sup> W. S. Nip, D. L. Singleton, and R. J. Cvetanovic, *J. Am. Chem. Soc.*, 103, 3526, 1981.

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<sup>3</sup> R. J. Cvetanovic, D. L. Singleton, and R. S. Irwin, *J. Am. Chem. Soc.*, 103, 3530, 1981.

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<sup>4</sup> U. B. Pavanaja, H. P. Upadhyaya, A. V. Sapre, K. V. S. Rama Rao, and J. P. Mittal, J. Chem. Soc. Faraday Trans., 90, 825, 1994.

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$$\Delta H^\circ(1) = -213 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(2) = -224 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.1 \pm 1.4) \times 10^{-15}$	298	Sullivan and Warneck, 1965 <sup>1</sup>	DF-MS
$2.0 \times 10^{-10} \exp(-2920/T)$	290-465	Hoyermann et al., 1967 <sup>2</sup>	DF-EPR
$1.2 \times 10^{-14}$	300		
$1.08 \times 10^{-10} \exp(-2770/T)$	300-1150	Homann et al., 1968 <sup>3</sup>	DF-MS
$1.1 \times 10^{-14}$	300		
$3.2 \times 10^{-11} \exp(-2280/T)$	273-808	Westenberg and deHaas, 1969 <sup>4</sup>	DF-EPR/MS
$(1.4 \pm 0.1) \times 10^{-14}$	297		
$(1.19 \pm 0.06) \times 10^{-14}$	297	Breckenridge and Miller, 1972 <sup>5</sup>	DF-MS
$1.65 \times 10^{-11} \exp[-(2165 \pm 30)/T]$	263-502	Klemm and Stief, 1974 <sup>6</sup>	FP-RF

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.2 \pm 0.1) \times 10^{-14}$	298		
$2.0 \times 10^{-11} \exp[-(2140 \pm 40)/T]$	239-404	Wei and Timmons, 1975 <sup>7</sup>	DF-EPR
$(1.35 \pm 0.13) \times 10^{-14}$	295		
$(1.39 \pm 0.14) \times 10^{-14}$	296	Manning et al., 1976 <sup>8</sup>	FP-RF
$(1.17 \pm 0.12) \times 10^{-14}$	298	Yoshida and Saito, 1978 <sup>9</sup>	DF-A (a)

## Comments

(a) SO radicals were monitored by microwave absorption at 13044 MHz.

## Preferred Values

- 5  $k = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.  
 $k = 1.6 \times 10^{-11} \exp(-2150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230-500 K.

## Reliability

- 10  $\Delta \log k = \pm 0.2$  at 298 K.  
 $\Delta(E/R) = \pm 150 \text{ K}$ .

## Comments on Preferred Values

- 15 The values obtained for  $k$  by a variety of techniques<sup>1-9</sup> are in excellent agreement over a wide range of temperatures and pressures ( $\leq 340 \text{ mbar}$ ). The available evi-

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dence suggests that at low temperatures the reaction proceeds by channel (1) and that channel (2) may only become significant at temperatures above 600 K.

Because of the possible enhancement of the rate by channel 2 at high temperatures, the recommended value of  $E/R$  is the mean of the values obtained in studies by Klemm and Stief<sup>6</sup> and Wei and Timmons<sup>7</sup> which were limited to temperatures below 502 K. The value of  $k$  at 298 K is the mean of the values in refs. 1-9, and the pre-exponential factor is adjusted to fit this value of  $k$  and the recommended value of  $E/R$ .

Approximate measurements of  $k_2/k_1$  are:  $10^{-3}$  at 298 K<sup>10</sup> and  $10^{-2}$  at 500 K.<sup>3</sup> Studies of detailed dynamics of this reaction have been reported by Hsu et al.,<sup>11</sup> Nickolaisen et al.<sup>12</sup> and Chen et al.<sup>13</sup>

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<sup>1</sup> J. O. Sullivan and P. Warneck, Ber. Bunsenges. Phys. Chem., 69, 7, 1965.

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<sup>11</sup> D. S. Y. Hsu, W. M. Shaub, T. L. Birks, and M. C. Lin, Chem. Phys., 44, 143, 1979.

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<sup>13</sup> X. Chen, F. Wu, and B. R. Weiner, Chem. Phys. Lett., 247, 313, 1995.

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$$\Delta H^\circ = -348.1 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.1 \times 10^{-32} \exp(-1009/T) [\text{Ar}]$	299-400	Atkinson and Pitts, 1978 <sup>1</sup>	FP-CL (a)
$1.05 \times 10^{-33} [\text{Ar}]$	298		
$1.37 \times 10^{-33} [\text{N}_2]$	298		

## Comments

(a) Flash photolysis technique with detection of  $\text{O}(^3\text{P})$  atoms by  $\text{NO}_2$  chemiluminescence. Relative efficiencies of  $k(\text{M}=\text{N}_2)$ :  $k(\text{M}=\text{Ar})$ :  $k(\text{M}=\text{SO}_2) = 1.0:0.77:6.9$  were determined.

## Preferred Values

$k_0 = 1.4 \times 10^{-33} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_0 = 4.0 \times 10^{-32} \exp(-1000/T) [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-400 K.

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## Reliability

$\Delta \log k_0 = \pm 0.3$  at 300 K.

$\Delta(E/R) = \pm 200$  K over the temperature range 200-400 K.

5

### Comments on Preferred Values

The preferred values are based on the absolute rate coefficient study of Atkinson and Pitts.<sup>1</sup> Because the reaction has an activation barrier, the Arrhenius form is chosen. The falloff transition to the high pressure range is expected at pressures not too far above 1 bar. However, as yet no experimental data are available in this pressure region. Based on a theoretical analysis of dissociation and recombination data, fitting a barrier of 22 kJ·mol<sup>-1</sup> for the spin-forbidden reaction O(<sup>3</sup>P) + SO<sub>2</sub> (<sup>1</sup>A<sub>1</sub>) → SO<sub>3</sub> (<sup>1</sup>A<sub>1</sub>), Troe<sup>2</sup> derived the expression  $k_0 = 1.1 \times 10^{-31} (T/1000)^{-4} \exp(-2646/T)$  [Ar] over the temperature range 250-2500 K, which agrees the Atkinson and Pitts data to within a factor of 2 at 298 K.

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<sup>2</sup> J. Troe, *Ann. Rev. Phys. Chem.*, 29, 223, 1978; D. C. Astholz, K. Glänzer, and J. Troe, *J. Chem. Phys.*, 70, 2409, 1979.

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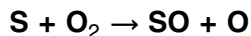
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$$\Delta H^\circ = -23.0 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.0 \pm 0.5) \times 10^{-12}$	298	Fair and Thrush, 1969 <sup>1</sup>	DF-CL
$(2.8 \pm 0.3) \times 10^{-12}$	298	Fair et al., 1971 <sup>2</sup>	FP-A
$2.2 \times 10^{-12} \exp[(0 \pm 50)/T]$	252-423	Davis et al., 1972 <sup>3</sup>	FP-RF
$(1.7 \pm 0.3) \times 10^{-12}$	298	Donovan and Little, 1972 <sup>4</sup>	FP-RA
$(1.5 \pm 0.3) \times 10^{-12}$	298	Clyne and Townsend, 1975 <sup>5</sup>	DF-RF
$1.7 \times 10^{-12} \exp[(153 \pm 108)/T]$	296-393	Clyne and Whitefield, 1979 <sup>6</sup>	DF-RF
<sup>5</sup> $(2.6 \pm 0.3) \times 10^{-12}$	298		

### Preferred Values

$k = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 250-430 K.

### Reliability

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta(E/R) = \pm 200$  K.

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All of the available measurements of  $k^{1-6}$  are in good agreement. Clyne and Whitefield<sup>6</sup> observed a small decrease in  $k$  with increasing temperature, but until more definitive measurements of  $E/R$  are made a temperature independent  $k$  is recommended with error limits encompassing the existing measured values. The preferred value at 298 K is the mean of values from refs. 1-6.

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- <sup>2</sup> R. W. Fair, A. Van Roodselaar, and O. P. Strausz, *Can J. Chem.*, 49, 1659, 1971.
- <sup>3</sup> D. D. Davis, R. B. Klemm, and M. J. Pilling, *Int. J. Chem. Kinet.*, 4, 367, 1972.
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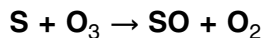
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$$\Delta H^\circ = -415 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.2 \pm 0.3) \times 10^{-11}$	298	Clyne and Townsend, 1975 <sup>1</sup>	DF-RF

### Preferred Values

$$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

### Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

### Comments on Preferred Values

The only available experimental determination<sup>1</sup> is accepted as the preferred value. The method was direct, and in the same study a number of other rate coefficients for S atom reactions were measured giving results in good agreement with other techniques.

### References

<sup>1</sup> M. A. A. Clyne and L. W. Townsend, Int. J. Chem. Kinet., Symp. 1, 73, 1975.

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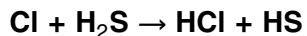
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$$\Delta H^\circ = -50.0 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(7.3 \pm 0.9) \times 10^{-11}$	298	Nesbitt and Leone, 1980 <sup>1</sup>	PLP-CL
$(4.00 \pm 0.08) \times 10^{-11}$	296	Clyne and Ono, 1983 <sup>2</sup>	DF-RF
$(5.1 \pm 0.7) \times 10^{-11}$	296	Clyne et al., 1984 <sup>3</sup>	DF-MS
$(6.29 \pm 0.46) \times 10^{-11}$	211-353	Nava et al., 1985 <sup>4</sup>	FP-RF
$3.69 \times 10^{-11} \exp[(208 \pm 24)/T]$	202-430	Nicovich et al., 1995 <sup>5</sup>	PLP-RF
$(7.4 \pm 1.1) \times 10^{-11}$	298		

### Preferred Values

$k = 7.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 3.7 \times 10^{-11} \exp(208/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-430 K.

### Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$ .

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The preferred value accepts the results of the recent study of Nicovich et al.<sup>5</sup> which was an extensive study conducted over a wide range of experimental conditions. In that study the value of  $k$  at room temperature was found to be independent of pressure over the range studied [33-800 mbar (25-600 Torr)]. The room temperature value of  $k$  reported by Nesbitt and Leone<sup>1</sup> is in excellent agreement with the preferred value. That of Nava et al.<sup>4</sup> is 15% lower, and those of Clyne and Ono<sup>2</sup> and Clyne et al.<sup>3</sup> are significantly lower. In the study of Nicovich et al.,<sup>5</sup> experimental conditions were adjusted to minimize interferences from radical-radical secondary reactions. An *ab initio* study of reactions of chlorine atoms with several reduced sulfur compounds has been reported by Wilson and Hirst.<sup>6</sup> For this reaction these results indicate that adduct formation is the dominant reaction pathway but that hydrogen atom abstraction could be significant.

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<sup>1</sup> D. J. Nesbitt and S. R. Leone, *J. Chem. Phys.*, 72, 1722, 1980.

<sup>2</sup> M. A. A. Clyne and Y. Ono, *Chem. Phys. Lett.*, 94, 597, 1983.

<sup>3</sup> M. A. A. Clyne, A. J. MacRobert, T. P. Murrells, and L. J. Stief, *J. Chem. Soc. Faraday Trans. 2*, 80, 877, 1984.

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<sup>6</sup> C. Wilson and D. M. Hirst, *J. Chem. Soc. Faraday Trans.*, 93, 2831, 1997.

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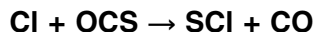
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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<1.1 \times 10^{-16}$	298	Eibling and Kaufman, 1983 <sup>1</sup>	DF-MS
$<4 \times 10^{-15}$	298	Clyne et al., 1984 <sup>2</sup>	DF-MS
$<1 \times 10^{-14}$	298	Nava et al., 1985 <sup>3</sup>	FP-RF

### 5 Preferred Values

$k < 1.0 \times 10^{-16}$  at 298 K.

### Comments on Preferred Values

10 The reaction of Cl atoms with OCS is extremely slow and only upper limits to the rate coefficient have been obtained.<sup>1-3</sup> The lowest of these upper limits (Eibling and Kaufman<sup>1</sup>) is the preferred value.

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- 15 <sup>2</sup> M. A. A. Clyne, A. J. MacRobert, T. P. Murrells, and L. J. Stief, J. Chem. Soc., Faraday Trans. 2, 80, 877, 1984.
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## Cl + CS<sub>2</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<5 \times 10^{-15}$ (Air, 400 mbar)	293	Nicovich et al., 1990 <sup>1</sup>	PLP-RF (a)
<i>Relative Rate Coefficients</i>			
$(8.3 \pm 1.7) \times 10^{-14}$ (Air, 1013 mbar)	293	Martin et al., 1987 <sup>2</sup>	RR (b)
$<4 \times 10^{-15}$ (Air, 933 mbar)	298	Wallington et al., 1991 <sup>3</sup>	RR (c)

### Comments

(a) Pulsed laser photolysis of Cl<sub>2</sub> in CS<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> mixtures over the pressure range 40-400 mbar (30-300 Torr) and the temperature range 193-258 K. [Cl] monitored by resonance fluorescence. Experiments in the absence of O<sub>2</sub> revealed reversible adduct formation and the establishment of an equilibrium between Cl, CS<sub>2</sub> and CS<sub>2</sub>Cl. The thermodynamic parameters for equilibrium were derived. The upper limit tabulated for the overall removal of CS<sub>2</sub> in the presence of O<sub>2</sub> is for all channels of the CS<sub>2</sub>Cl + O<sub>2</sub> reaction which do not lead to Cl atom formation.

(b) Steady state photolysis of Cl<sub>2</sub> in the presence of CS<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and a reference compound (CH<sub>4</sub> or CH<sub>3</sub>Cl). [CS<sub>2</sub>] and [CH<sub>4</sub>] (or [CH<sub>3</sub>Cl]) were monitored by quadrupole mass spectrometry. Constant total pressure of 1 bar. [N<sub>2</sub>]/[O<sub>2</sub>] varied. Values of  $k(\text{Cl} + \text{CH}_3\text{Cl}) = 4.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{Cl} + \text{CH}_4) = 9.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  were used.<sup>4</sup>

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(c) Steady state photolysis of  $\text{Cl}_2$  in the presence of  $\text{CS}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CHF}_2\text{Cl}$  with FTIR monitoring. Value of  $k(\text{Cl} + \text{CHF}_2\text{Cl})/k(\text{Cl} + \text{CH}_4) < 0.04$  measured in same study and combined with  $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and the measured rate coefficient ratio  $k(\text{Cl} + \text{CS}_2)/k(\text{Cl} + \text{CHF}_2\text{Cl})$  in presence of  $\text{O}_2$  to give the tabulated upper limit to  $k$ .

## Preferred Values

$k \leq 4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K in air at 1 bar.

## Comments on Preferred Values

The overall reaction of Cl with  $\text{CS}_2$  appears to be too slow to be of importance in the atmosphere. Nicovich et al.<sup>1</sup> have shown that it proceeds initially by rapid formation of the  $\text{ClCS}_2$  adduct, as suggested earlier by Martin et al.,<sup>2</sup> but the subsequent reaction of the adduct with  $\text{O}_2$  appears to be slow.

The recommended upper limit is that of Wallington et al.,<sup>3</sup> which agrees with the work of Nicovich et al.<sup>1</sup> Wallington et al.<sup>3</sup> have suggested that the value obtained by Martin et al.<sup>2</sup> was erroneously high due to complexities in their system arising from HO radical production from the reference compounds which were chosen. An ab initio study of reactions of chlorine atoms with several reduced sulfur compounds has been reported by Wilson and Hirst.<sup>5</sup> For the reaction of Cl with  $\text{CS}_2$  these results indicate an enthalpy of formation of the adduct of  $-29.3 \text{ kJ mol}^{-1}$  at 298 K.

## References

- <sup>1</sup> J. M. Nicovich, C. J. Shackelford, and P. H. Wine, J. Phys. Chem., 94, 2896, 1990.
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$$\Delta H^\circ(1) = -66.1 \text{ kJ}\cdot\text{mol}^{-1}$$

5

### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.8 \pm 0.4) \times 10^{-10}$	298	Nesbitt and Leone, 1980 <sup>1</sup>	PLP-CL
$k_2 = (4.3 \pm 1) \times 10^{-12}$	298	Nesbitt and Leone, 1981 <sup>2</sup>	PLP-CL
$(1.1 \pm 0.4) \times 10^{-10}$	298	Mellouki et al., 1988 <sup>3</sup>	DF-EPR/MS
$1.19 \times 10^{-10} \exp[(151 \pm 38)/T]$	193-430	Nicovich et al., 1995 <sup>4</sup>	PLP-RF
$(2.0 \pm 0.3) \times 10^{-10}$	298		

### 10 Preferred Values

$$k = 2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.2 \times 10^{-10} \exp(150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 190\text{-}430 \text{ K.}$$

### Reliability

15

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

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The preferred value accepts the results of the study of Nicovich et al.<sup>4</sup> which was an extensive study conducted over a wide range of experimental conditions. In that study the value of  $k$  at room temperature was found to be independent of pressure over the range studied [33-200 mbar (25-150 Torr)]. The room temperature value of  $k$  reported by Nesbitt and Leone<sup>1</sup> is in good agreement with the preferred value, but Mellouki et al.<sup>3</sup> reported value is lower by a factor of two. The results of Nesbitt and Leone<sup>2</sup> show that only about 2% of the total reaction occurs by channel (2), via abstraction from the methyl group. An ab initio study of reactions of chlorine atoms with several reduced sulfur compounds has been reported by Wilson and Hirst.<sup>5</sup> For this reaction these results indicate that formation of the adduct is rate-limiting, but that H-atom abstraction is expected to be important.

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<sup>5</sup> C. Wilson and D. M. Hirst, *J. Chem. Soc. Faraday Trans.*, 93, 2831, 1997.

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$$\Delta H^\circ(1) = -39.6 \text{ kJ}\cdot\text{mol}^{-1}$$

## 5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.8 \times 10^{-10}$ (4 mbar $\text{N}_2$ )	297	Stickel et al., 1992 <sup>1</sup>	PLP-RF
$(3.3 \pm 0.5) \times 10^{-10}$ (933 mbar $\text{N}_2$ )	297		
<i>Relative Rate Coefficients</i>			
$(3.2 \pm 0.3) \times 10^{-10}$ (1013 mbar $\text{N}_2$ )	295	Nielsen et al., 1990 <sup>2</sup>	RR (a)
$(3.61 \pm 0.21) \times 10^{-10}$ (1013 mbar $\text{N}_2$ )	298	Kinnison et al., 1996 <sup>3</sup>	RR (b)
<i>Branching Ratios</i>			
$k_1/k > 0.97$ (1.3 mbar He)	298	Butkovskaya et al., 1995 <sup>4</sup>	DF-MS
$k_1/k > 0.98$ (13-40 mbar $\text{N}_2$ )	298	Zhao et al., 1996 <sup>5</sup>	PLP-TDLS

## Comments

- (a) Photolysis of mixtures of  $\text{COCl}_2$ - $\text{CH}_3\text{SCH}_3$ -cyclohexane- $\text{N}_2$  in a Teflon chamber. [Cyclohexane] and  $[\text{CH}_3\text{SCH}_3]$  measured at intervals by GC. A rate coefficient of  $k(\text{Cl} + \text{cyclohexane}) = 3.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was used.<sup>6</sup>

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(b) Photolysis of mixtures of  $\text{COCl}_2\text{-CH}_3\text{SCH}_3 - n\text{-butane-N}_2$  in a Teflon chamber.  $[n\text{-Butane}]$  and  $[\text{CH}_3\text{SCH}_3]$  measured by GC.  $k(\text{Cl} + n\text{-butane}) = 1.94 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  used.<sup>6</sup>

### Preferred Values

5  $k = 3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and 1 bar  $\text{N}_2$ .

### Reliability

$\Delta \log k = \pm 0.15$  at 298 K and 1 bar  $\text{N}_2$ .

10

### Comments on Preferred Values

The study of this reaction by Stickel et al.<sup>1</sup> shows the reaction kinetics to have a complex dependency on temperature and pressure. The overall reaction rate is close to collisional and increases with decreasing temperature and with increasing pressure. The HCl yield (measured by TDLS) approaches unity as the pressure tends to zero but decreases to a value of  $\sim 0.5$  at 270 mbar (203 Torr)  $\text{N}_2$  and 297 K.<sup>1</sup>

15

These findings are interpreted in terms of the occurrence of two reaction channels, Cl abstraction and adduct formation. At low pressures the abstraction channel is dominant (refs. 1, 4, and 5) but with increasing pressure the adduct can be stabilized leading to an increase in the total  $k$  as pressure increases and temperature decreases.

20

Langer et al.<sup>7</sup> using a UV photolysis system with gas chromatographic detection, reported the yield of  $\text{CH}_3\text{Cl}$  formed in this reaction at 298 K and 1 bar air to be  $(1.34 \pm 0.07) \times 10^{-3}$ . The authors concluded that the most likely source is decomposition of the adduct formed in pathway (2) to give  $\text{CH}_3\text{Cl} + \text{CH}_3\text{S}$ .

25

An *ab initio* study of reactions of chlorine atoms with several reduced sulfur compounds has been reported by Wilson and Hirst.<sup>8</sup> For this reaction the structure of the

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adduct has been characterized, vibrational frequencies reported, and reaction energetics calculated.

Until the reaction is studied in more detail and a complete analysis of the temperature and pressure dependence can be made, our recommendations are limited to high pressures and 298 K. They are based on the results of Stickel et al.,<sup>1</sup> Nielsen et al.,<sup>2</sup> and Kinnison et al.,<sup>3</sup> which are in excellent agreement. There is also a value of  $2.0 \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and 1 bar  $\text{N}_2$  reported by Barnes et al.,<sup>9</sup> but no experimental details are given.

## References

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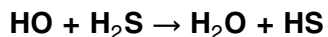
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$$\Delta H^\circ = -115.4 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.3 \times 10^{-11} \exp(-443/T)$	298-885	Westenberg and deHaas, 1973 <sup>1</sup>	DF-EPR
$(5.48 \pm 0.33) \times 10^{-12}$	298		
$(3.1 \pm 0.5) \times 10^{-12}$	298	Stuhl, 1974 <sup>2</sup>	FP-RF
$(5.2 \pm 0.5) \times 10^{-12}$	298-423	Perry et al., 1976 <sup>3</sup>	FP-RF
$6.4 \times 10^{-12} \exp[-(55 \pm 58)/T]$	245-366	Wine et al., 1981 <sup>4</sup>	FP-RF
$(5.13 \pm 0.57) \times 10^{-12}$	297		
$2.27 \times 10^{-19} T^{2.5} \exp(725/T)$	228-518	Leu and Smith, 1982 <sup>5</sup>	DF-RF
$(3.9 \pm 0.7) \times 10^{-12}$	298		
$(5.01 \pm 0.55) \times 10^{-12}$	228-437	Michael et al., 1982 <sup>6</sup>	FP-RF
$7.8 \times 10^{-12} \exp[-(146 \pm 105)/T]$	239-425	Lin, 1982 <sup>7</sup>	FP-RF
$(4.42 \pm 0.48) \times 10^{-12}$	295		
$(4.3 \pm 0.6) \times 10^{-12}$	300	Wang and Lee, 1985 <sup>8</sup>	DF-RF
$3.81 \times 10^{-19} T^{2.43} \exp(732/T)$	245-450	Lin et al., 1985 <sup>9</sup>	DF-RF
$(4.4 \pm 0.7) \times 10^{-12}$	299		
<sup>5</sup> $(4.9 \pm 0.9) \times 10^{-12}$	245	Lafage et al., 1987 <sup>10</sup>	DF-RF/LIF

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.8 \pm 0.6) \times 10^{-12}$	263		
$1.32 \times 10^{-11} \exp[-(394 \pm 190/T)]$	294-450		
$(3.3 \pm 0.5) \times 10^{-12}$	294		
<i>Relative Rate Coefficients</i>			
$(5.31 \pm 0.35) \times 10^{-12}$	$297 \pm 2$	Cox and Sheppard, 1980 <sup>11</sup>	RR (a)
$(5.5 \pm 0.9) \times 10^{-12}$	300	Barnes et al., 1986 <sup>12</sup>	RR (b)

### Comments

(a) HO radicals were generated by the photolysis of HONO-NO-air mixtures at atmospheric pressure. The decay of  $\text{H}_2\text{S}$  was measured relative to that of  $\text{C}_2\text{H}_4$  by GC, and the relative rate coefficient placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{C}_2\text{H}_4) = 8.57 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 297 K and atmospheric pressure of air.<sup>13</sup>

(b) HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO}$  in  $\text{N}_2\text{-O}_2$  mixtures at atmospheric pressure. The decay of  $\text{H}_2\text{S}$  was measured relative to that for ethene by GC, and the relative rate coefficient placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{C}_2\text{H}_4) = 8.44 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K and atmospheric pressure of air.<sup>13</sup>

### Preferred Values

$k = 4.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 6.1 \times 10^{-12} \exp(-80/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220-520 K.

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## Reliability

$\Delta \log k = \pm 0.08$  at 298 K.

5  $\Delta(E/R) = \pm 80$  K.

## Comments on Preferred Values

10 The preferred values are obtained from a unit-weighted least-squares analysis of the absolute rate constants of Perry et al.,<sup>3</sup> Wine et al.,<sup>4</sup> Leu and Smith,<sup>5</sup> Michael et al.,<sup>6</sup> Lin,<sup>7</sup> Wang and Lee,<sup>8</sup> Lin et al.,<sup>9</sup> and Lafage et al.,<sup>10</sup> which are in good agreement. The earlier studies of Westenberg and deHaas<sup>1</sup> and Stuhl<sup>2</sup> reported a significantly higher temperature dependence of the rate coefficient and a lower room temperature rate coefficient, respectively, than later studies, and the data from these studies<sup>1,2</sup> are not  
15 used in the evaluation of the preferred values. The studies of Leu and Smith,<sup>5</sup> Lin et al.<sup>9</sup> and Lafage et al.<sup>10</sup> show non-Arrhenius behavior of the rate coefficient, with a shallow minimum in the rate coefficient at  $\sim 270$ -300 K. The rate coefficient is independent of pressure<sup>5-7,9</sup> and the nature of the diluent gas.<sup>9</sup> These findings<sup>5-7,9</sup> cast some doubt upon the suggestion that the non-Arrhenius behavior is due to the occurrence of both  
20 addition and abstraction channels.

Despite the non-Arrhenius behavior of the rate coefficient  $k$  over an extended temperature range, the preferred expression is given in the Arrhenius form which is satisfactory for the temperature range covered by our recommendation.

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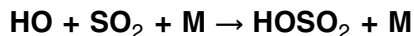
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$$\Delta H^\circ = -125 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(7.2 \pm 2.6) \times 10^{-31} [\text{N}_2]$	300	Harris and Wayne, 1975 <sup>1</sup>	DF-RF
$7.0 \times 10^{-31} (T/300)^{-2.9} [\text{N}_2]$	(a)	Erlar et al., 1975 <sup>2</sup>	DF-RF
$4.9 \times 10^{-31} [\text{N}_2]$	300	Davis, 1976 <sup>3</sup>	(b)
$(1.6 \pm 0.3) \times 10^{-31} [\text{Ar}]$	298	Atkinson et al., 1976 <sup>4</sup>	FP-RF (c)
$3.6 \times 10^{-31} [\text{N}_2]$	300	Erlar and Zellner, 1978 <sup>5</sup>	FP-RA
$(2.54 \pm 0.33) \times 10^{-31} [\text{N}_2]$	298	Leu, 1982 <sup>6</sup>	DF-RF (d)
$(7.91 \pm 0.24) \times 10^{-32}$ $\times (T/298)^{-(2.85 \pm 0.21)} [\text{He}]$	261-414		
$1.6 \times 10^{-31} [\text{N}_2]$	297	Paraskevopoulos et al., 1983 <sup>7</sup>	FP-RA (e)
$5.8 \times 10^{-31} (T/300)^{-2.6} [\text{N}_2]$	260-420	Wine et al., 1984 <sup>8</sup>	FP-RF (f)
$(2.4 \pm 0.7) \times 10^{-31} [\text{N}_2]$	298	Lee et al., 1990 <sup>9</sup>	DF-RF
$(1.1 \pm 0.3) \times 10^{-32} \exp(640/T) [\text{He}]$	280-413		

## Comments

(a) Temperature range not cited.

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(b) Measurements cited in ref. 10 in the pressure range 6.7-670 mbar (5-500 Torr), extrapolated to  $k_0$  and  $k_\infty$ .

(c) Pressure range 33-870 mbar (25-650 Torr).

(d) Measurements at pressures near 1.3 mbar (1 Torr).

(e) Pressure range 73-1013 mbar (55-760 Torr). Falloff extrapolation using Lindemann-Hinshelwood (i.e. neglecting broadening factors), and hence responsible for low value.

(f) Temperature range 260-420 K, pressure range 17-928 mbar (13-696 Torr), bath gases He, Ar, N<sub>2</sub> and SF<sub>6</sub>. Expression derived from fall-off parameterisation using  $F_c = \exp(-T/388)$ .

### Preferred Values

$k_0 = 4.5 \times 10^{-31} (T/300)^{-3.9} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 200-300 K.

### Reliability

$\Delta \log k_0 = \pm 0.3$  at 300 K.

$\Delta n = \pm 1$ .

### Comments on Preferred Values

The preferred value is that given by Wine et al.<sup>8</sup> based on a falloff analysis using  $F_c = 0.525$ . In combination with  $k_\infty$ , (see below) this expression accurately reproduces the data of Wine et al.,<sup>8</sup> Paraskevopoulos et al.,<sup>7</sup> Lee et al.<sup>9</sup> and Leu<sup>6</sup> in N<sub>2</sub> at room temperature and covers the atmospheric pressure range without any extrapolation. The

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temperature dependence of  $k_0$  was based on an analysis of data obtained in Ar, He and  $F_6$ .

## High-pressure rate coefficients

### Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.8 \times 10^{-12}$	435	Gordon and Mulac, 1975 <sup>11</sup>	(a)
$9.0 \times 10^{-13}$	300	Davis, 1976 <sup>3</sup>	(b)
$8.3 \times 10^{-13}$	300	Atkinson et al., 1976 <sup>4</sup>	FP-RF (c)
$1.2 \times 10^{-12}$	297	Paraskevopoulos et al., 1983 <sup>7</sup>	FP-RA (d)
$1.26 \times 10^{-12} (T/300)^{-0.7}$	260-420	Wine et al., 1984 <sup>8</sup>	FP-RF (e)
$1.2 \times 10^{-11} \exp(-360/T)$	220-400	Fulle et al., 1999 <sup>12</sup>	LP-LIF (f)

### Comments

(a) Pulse radiolysis in  $\text{H}_2\text{O}$  vapor at 1 bar.

(b) See comment (b) for  $k_0$ .

(c) See comment (c) for  $k_0$ .

(d) See comment (e) for  $k_0$ .

(e) See comment (f) for  $k_0$ .

(f) Pressure range 1 – 96 bar (He).

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## Preferred Values

$k_{\infty} = 1.3 \times 10^{-12} (T/300)^{-0.7}$  over the temperature range 200-300 K.

### Reliability

$\Delta \log k_{\infty} = \pm 0.3$  over the temperature range 200-300 K.

### Comments on Preferred Values

See Comments on preferred values for  $k_0$ . Falloff representation with  $F_c = 0.525$  near 250 K. The data obtained by Fulle et al.<sup>12</sup> at pressures up to 96 Bar (He) indicate a larger value for the rate coefficient at the high pressure limit (factors of 1.5 and 2.8 at 220 and 300 K, resp.), and also a barrier of  $\approx 3$  kJ/mol for the recombination process. These large values for the high pressure limit appear to be in disaccord with measured values for the rate constant for deactivation of OH ( $v=1$ ) by SO<sub>2</sub> which are more in line with the recommended values above.<sup>13</sup> Further experimental and theoretical input would be useful in resolving this discrepancy.

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- <sup>8</sup> P. H. Wine, D. H. Semmes, R. J. Thompson, C. A. Gump, A. R. Ravishankara, A. Torabi, and J. M. Nicovich, J. Phys. Chem., 88, 2095, 1984.
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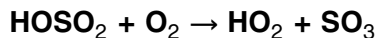
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$$\Delta H^\circ = 4 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4 \pm 2) \times 10^{-13}$	250	Margitan, 1984 <sup>1</sup>	FP-RF (a)
$(4 \pm 2) \times 10^{-13}$	298		
$(3.5 \pm 1) \times 10^{-13}$	298	Martin et al., 1986 <sup>2</sup>	DF-EPR (b)
$(4.37 \pm 0.66) \times 10^{-13}$	$297 \pm 1$	Gleason et al., 1987 <sup>3</sup>	DF-CIMS (c)
$1.34 \times 10^{-12} \exp[-(330 \pm 70)/T]$	297-423	Gleason and Howard, 1988 <sup>4</sup>	DF-CIMS (c)
$(4.37 \pm 0.66) \times 10^{-13}$	297		

### Comments

(a) The reaction was studied at 53 and 133 mbar (40 and 100 Torr) of Ar diluent at 250 and 298 K. HO radicals were removed by the  $\text{HO} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO}_2 + \text{M}$  reaction, but the addition of  $\text{O}_2$  and NO regenerated HO radicals by the reactions  $\text{HOSO}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3$  and  $\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$ . The effects of varying the amounts of  $\text{O}_2$  were studied. The same rate coefficient was measured at 250 K and 298 K, but it was suggested<sup>1</sup> that this was due to a lack of precision in the technique rather than indicating that  $k$  is temperature independent.

(b) The effects of addition of NO and  $\text{O}_2$  on the HO radical decays were studied. A system of 12 reactions was used to model the reaction system to obtain the rate

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coefficient  $k$ .

(c) HO radicals were produced by the  $\text{H} + \text{NO}_2$  reaction, and  $\text{SO}_2$  and  $\text{O}_2$  were added down-stream.  $\text{HOSO}_2$  was monitored by sampling into a flowing afterglow containing  $\text{Cl}^-$  ions.  $\text{SO}_3^-$  ions, formed by the reaction  $\text{Cl}^- + \text{HOSO}_2 \rightarrow \text{SO}_3^- + \text{HCl}$ , were detected by quadrupole MS. The  $\text{SO}_3$  product of the reaction was also detected by  $\text{Cl}^- + \text{SO}_3 + \text{M} \rightarrow (\text{ClSO}_3)^- + \text{M}$  with MS measurement of  $(\text{ClSO}_3)^-$ . The total pressure was varied over the range 2.7-10.7 mbar (2-8 Torr), and no change in  $k$  was observed, allowing an upper limit of  $3.4 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  ( $\text{M} = \text{N}_2$ ) for the rate coefficient for the reaction  $\text{HOSO}_2 + \text{O}_2 + \text{M} \rightarrow \text{HOSO}_2\text{O}_2 + \text{M}$  to be set.

### Preferred Values

$k = 4.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.3 \times 10^{-12} \exp(-330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290-420 K.

### Reliability

$\Delta \log k = \pm 0.10$  at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$ .

### Comments on Preferred Values

In the earlier studies,<sup>1,2</sup> HO radical decays due to the reaction  $\text{HO} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO}_2 + \text{M}$  were monitored in the presence of NO and  $\text{O}_2$ . The reaction sequence  $\text{HOSO}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3$  and  $\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$  then regenerates HO radicals. Modeling of the NO decay led to the rate coefficient  $k$ . This method of determining  $k$  is less direct than the more recent measurements of Gleason et al.<sup>3</sup> and Gleason and Howard,<sup>4</sup> where  $\text{HOSO}_2$  radicals were monitored by MS. We therefore

accept the temperature-dependent expression obtained by Gleason and Howard.<sup>4</sup> The earlier results,<sup>1,2</sup> though less precise, are in good agreement with the preferred values.

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## HO + OCS → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.3 \times 10^{-12} \exp[-(2300 \pm 100)/T]$ $(6 \pm 4) \times 10^{-16}$	300-517 300	Leu and Smith, 1981 <sup>1</sup>	DF-RF (a)
$1.13 \times 10^{-13} \exp[-(1200 \pm 400)/T]$ $(2.0^{+0.4}_{-0.8}) \times 10^{-15}$	255-483 300	Cheng and Lee, 1986 <sup>2</sup>	DF-RF (b)
$(1.92 \pm 0.25) \times 10^{-15}$	298	Wahner and Ravishankara, 1987 <sup>3</sup>	FP/PLP-LIF (c)

### Comments

- 5 (a) The measured HO radical decay rates were corrected for the presence of H<sub>2</sub>S in the OCS sample used ( $0.01 \pm 0.003\%$  H<sub>2</sub>S for the experiments at 300-421 K and  $0.04 \pm 0.01\%$  H<sub>2</sub>S for the experiments at 517 K). At 300 K the measured rate coefficient, uncorrected for the presence of H<sub>2</sub>S, was  $1.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- 10 (b) The purity of OCS was checked by FTIR spectroscopy, showing that H<sub>2</sub>S was present at less than 0.005%. The measured rate coefficient  $k$  was independent of pressure (1.2-7.9 mbar) and the addition of O<sub>2</sub> (up to 18% or 0.36 mbar of O<sub>2</sub>).
- (c) The rate coefficient  $k$  was independent of pressure (120-400 mbar), the nature of buffer gas, and the addition of O<sub>2</sub> (up to 48 mbar).

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## Preferred Values

$k = 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.1 \times 10^{-13} \exp(-1200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250–500 K.

5

### Reliability

$\Delta \log k = \pm 0.3$  at 298 K.

$\Delta(E/R) = \pm 500$  K.

10

### Comments on Preferred Values

The rate coefficients measured by Cheng and Lee<sup>2</sup> and Wahner and Ravishankara<sup>3</sup> are approximately a factor of 3 higher at 298 K than the earlier value of Leu and Smith.<sup>1</sup> This may be due to the corrections applied by Leu and Smith<sup>1</sup> to account for the presence of traces of H<sub>2</sub>S in their system, because in the absence of any correction to the measured rate coefficient of Leu and Smith<sup>1</sup> there is reasonable agreement between the studies.<sup>1–3</sup> Cheng and Lee<sup>2</sup> took care to keep the H<sub>2</sub>S level in their OCS very low and this, together with the confirmatory measurements of Wahner and Ravishankara,<sup>3</sup> leads us to recommend their values. These recommendations are compatible with the earlier upper limits given by Atkinson et al.<sup>4</sup> and Ravishankara et al.,<sup>5</sup> but not with the higher value obtained by Kurylo,<sup>6</sup> which may have been due to the occurrence of interfering secondary chemistry and/or excited state reactions.

20

Kurylo and Laufer<sup>7</sup> have suggested that the reaction proceeds through adduct formation, as found for the reaction of HO with CS<sub>2</sub>, followed by decomposition of the adduct to yield mainly HS + CO<sub>2</sub>. This is supported by the product study of Leu and Smith<sup>1</sup> at 517 K. However, in contrast to the HO + CS<sub>2</sub> reaction, there is no marked effect of O<sub>2</sub> on the rate coefficient. Furthermore, very little oxygen atom exchange be-

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tween H<sup>18</sup>O and OCS is found,<sup>8</sup> which may suggest that any adduct formed is weakly bound and short-lived.

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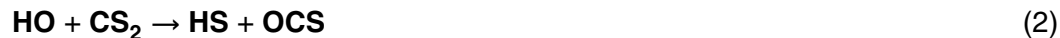
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$$\Delta H^\circ(1) = -44 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(2) = -153 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### Rate coefficient data

$k_{01}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1 \times 10^{-12}$ at 70 Torr [N <sub>2</sub> ]	247-299	Hynes et al., 1988 <sup>1</sup>	PLP-LIF (a)
$6 \times 10^{-13}$ at 30 Torr [N <sub>2</sub> ]	259-318	Murrells et al., 1990 <sup>2</sup>	PLP-LIF (b)
$5.0 \times 10^{-32}$ [He]	298	Diau and Lee, 1991 <sup>3</sup>	PLP-LIF (c)
$8.9 \times 10^{-32}$ [He]	269		
$14.7 \times 10^{-32}$ [He]	249		

### Comments

- 10 (a) Photolysis of H<sub>2</sub>O<sub>2</sub> at 248 nm in mixtures of CS<sub>2</sub> and He, N<sub>2</sub>, air, or O<sub>2</sub>. Pressure range 87-920 mbar (65-690 Torr).
- (b) Photolysis of H<sub>2</sub>O<sub>2</sub> at 248 nm or 266 nm in mixtures of CS<sub>2</sub> and He-N<sub>2</sub> or He-SF<sub>6</sub> mixtures. Pressure range 12-80 mbar (9-60 Torr). The effect of O<sub>2</sub> [0.7-20 mbar (0.5-15 Torr)] on the rate was studied.

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(c) Photolysis of H<sub>2</sub>O<sub>2</sub> at 248 nm in mixtures of CS<sub>2</sub> and added He or Ar (limited data set). Pressure range 12-360 mbar (9-270 Torr) of Ar or He. Effect of CS<sub>2</sub> on rate was studied.

### Preferred Values

5  $k_{01} = 8 \times 10^{-31} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 250-320 K.

### Reliability

10  $\Delta \log k_{01} = \pm 0.5$ , over the temperature range 250-320 K.

### Comments on Preferred Values

15 Because of the low thermal stability of HOCS<sub>2</sub>, experimental studies have to account for the re-dissociation of the adduct. After clarification of the mechanism, rate coefficients now can be specified. The preferred values are based on a combination of the data for M=N<sub>2</sub> from refs. 1 and 2, with a falloff representation. The data and a falloff representation indicates that the low pressure limit is approached within 10% only at pressures below about 27 mbar (20 Torr). The strong temperature dependence of  $k_{01}$   
20 for M = He derived in ref. 3 ( $E/R = -1610 \text{ K}$ ) is not consistent with the results from Hynes et al.<sup>1</sup> in He or Murrels et al.<sup>2</sup> in N<sub>2</sub>. Hynes et al.<sup>1</sup> did however report a strong temperature dependence at 680±20 Torr N<sub>2</sub> or O<sub>2</sub> or air ( $k = 6.9 \times 10^{-14} \exp(1150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) It appears that reaction (2) is slow, with a rate coefficient of  $k_2 < 2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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## High-pressure rate coefficients

### Rate coefficient data

$k_{\infty 1}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.8 \times 10^{-12}$ at 0.91 bar [N <sub>2</sub> ]	250-270	Hynes et al., 1988 <sup>1</sup>	PLP-LIF (a)
$3.1 \times 10^{-12}$ at 0.88 bar [N <sub>2</sub> ]	297		
$1.9 \times 10^{-12}$ at 150 Torr [Ar]	209	Bulatov et al., 1988 <sup>4</sup>	PLP-LIF (b)
$1.3 \times 10^{-12}$ at 1.01 bar [air]	295	Becker et al., 1990 <sup>5</sup>	PLP-LIF (c)

### Comments

5 (a) See comment (a) for  $k_0$ .

(b) Mixtures of O<sub>2</sub>-H<sub>2</sub>O-CS<sub>2</sub>-Ar. The rates of HOCS<sub>2</sub> formation and decomposition were measured, with an equilibrium constant of  $K_c = 2.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$ .

10 (c) H<sub>2</sub>O<sub>2</sub> photolyzed at 248 nm in mixtures of CS<sub>2</sub> and N<sub>2</sub>-O<sub>2</sub> or Ar-O<sub>2</sub>. The partial pressure of O<sub>2</sub> was in the range 0.32-1013 mbar (0.24-760 Torr), at a total pressure of 1.01 bar (760 Torr). The rate coefficient was found to increase further when more O<sub>2</sub> was added, with a value of  $2.79 \times 10^{-12} \text{ cm}^3 \text{ molecule s}^{-1}$  obtained at 747 Torr O<sub>2</sub>.

### Preferred Values

15  $k_{\infty 1} = 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 250-300 K.

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## Reliability

$\Delta \log k_{\infty 1} = \pm 0.5$  over the temperature range 250-300 K.

## Comments on Preferred Values

The preferred rate coefficient  $k_{\infty 1}$  is based on a falloff representation of the data from references 1 and 2, with high-pressure data mostly from ref. 1. The largest weight is given to the measurements near 250 K where decomposition of the adduct and the subsequent kinetics are of comparably minor influence in contrast to the room temperature experiments. A falloff curve with an estimated value of  $F_c = 0.8$  was employed for extrapolation. Experiments at 1 bar total pressure are apparently still far below the high pressure limit. An extensive discussion of the complicated mechanism is given in refs 1,2 and 6. Rate expressions combining adduct formation, dissociation, and subsequent reaction with  $O_2$  have been proposed which are not reproduced here (see also data sheets on  $HOCS_2 + M$  and  $HOCS_2 + O_2$ ). More experiments separating the individual steps are required, as are temperature dependent studies.

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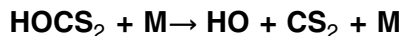
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$$\Delta H^\circ = 44.0 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0[\text{M}]/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.3 \times 10^4$ at 0.100 bar N <sub>2</sub>	255	Hynes et al., 1988 <sup>1</sup>	PLP-LIF (a)
$2.6 \times 10^4$ at 0.108 bar N <sub>2</sub>	280		
$4.3 \times 10^3$ at 0.020 bar N <sub>2</sub>	277	Murrells et al., 1990 <sup>2</sup>	PLP-LIF (b)
$3.0 \times 10^4$ at 0.032 bar N <sub>2</sub>	298		
$7.36 \times 10^{-15}$ [He]	298	Diau and Lee, 1991 <sup>3</sup>	PLP-LIF (c)
$2.14 \times 10^{-15}$ [He]	269		
$0.46 \times 10^{-15}$ [He]	249		

## Comments

(a) Photolysis at 298 K in mixtures of CS<sub>2</sub> and He, N<sub>2</sub>, air or O<sub>2</sub>. Pressure range 87-920 mbar (65-690 Torr). A value of  $K_c$  (297 K) =  $1.39 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$  was obtained for the equilibrium between HO + CS<sub>2</sub> and HOCS<sub>2</sub> as well as  $K_c$  (247 K) =  $3.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$ .

(b) Photolysis of H<sub>2</sub>O<sub>2</sub> at 248 nm and 266 nm in He-N<sub>2</sub>-CS<sub>2</sub> or He-SF<sub>6</sub>-CS<sub>2</sub> mixtures. Pressure range = 12-80 mbar (9-60 Torr). The effect of O<sub>2</sub> [0.7-20 mbar (0.5-

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15 Torr]) on the rate was studied.  $K_c$  (299 K) =  $1.7 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$ ,  $K_c$  (274 K) =  $7.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$  and  $K_c$  (249 K) =  $5.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$  were obtained for the equilibrium between HO + CS<sub>2</sub> and HOCS<sub>2</sub>.

5 (c) Photolysis of H<sub>2</sub>O<sub>2</sub> at 248 nm in mixtures of CS<sub>2</sub> and He or Ar. Pressure range 12-360 mbar (9-270) Torr of He. The effect of CS<sub>2</sub> on the rate was studied.  $K_c$  (298 K) =  $0.87 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$ ,  $K_c$  (273 K) =  $4.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$  and  $K_c$  (249 K) =  $2.6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$  were obtained for the equilibrium between HO + CS<sub>2</sub> and HOCS<sub>2</sub>.

**Preferred Values**

10  $k_0 = 4.8 \times 10^{-14} [\text{N}_2] \text{ s}^{-1}$  at 298 K.

$k_0 = 1.6 \times 10^{-6} \exp(-5160/T) [\text{N}_2] \text{ s}^{-1}$  over the temperature range 250-300 K.

*Reliability*

15  $\Delta \log k_0 = \pm 0.5$  at 298 K.

$\Delta(E/R) = \pm 500 \text{ K}$ .

*Comments on Preferred Values*

20 The preferred values are based on a falloff representation from references 1 and 2 of the data for the reverse process HO + CS<sub>2</sub> + M → HOCS<sub>2</sub> + M and the determination of the equilibrium constant from the same work. The data from ref. 3 are not consistent with this evaluation (with differences of about a factor of 2). HOCS<sub>2</sub> formation and dissociation are characterized by an equilibrium constant of  $K_c = 5.16 \times 10^{-25} \exp(5160/T) \text{ cm}^3 \text{ molecule}^{-1}$ , such as derived from the data of ref. 2.

25



## High-pressure rate coefficients

### Rate coefficient data

$k_{\infty}/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.1 \times 10^4$ at 0.907 bar [N <sub>2</sub> ]	252	Hynes et al., 1988 <sup>1</sup>	PLP-LIF (a)
$6.5 \times 10^4$ at 0.913 bar [N <sub>2</sub> ]	270		
$2.2 \times 10^5$ at 0.880 bar [N <sub>2</sub> ]	297		
$7.4 \times 10^4$	298	Bulatov et al., 1988 <sup>4</sup>	PLP-LIF (b)

### Comments

5 (a) See comment (a) for  $k_0$ .

(b) Photolysis of O<sub>3</sub> in the presence of H<sub>2</sub>O, CS<sub>2</sub> and Ar. Rate of HOCS<sub>2</sub> formation and decomposition measured and evaluated with an equilibrium constant of  $K_c = 2.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1}$ .

### Preferred Values

10  $k_{\infty} = 4.8 \times 10^5 \text{ s}^{-1}$  at 298 K.

$k_{\infty} = 1.6 \times 10^{13} \exp(-5160/T) \text{ s}^{-1}$  over the temperature range 250-300 K.

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## Reliability

$\Delta \log k_{\infty} = \pm 0.5$  at 298 K.

$\Delta(E/R) = \pm 500$  K.

5

## Comments on Preferred Values

10

The preferred values are based on the falloff extrapolation of the data for the reverse reaction and the equilibrium constant  $K_c = 5.16 \times 10^{-25} \exp(5160/T) \text{ cm}^3 \text{ molecule}^{-1}$  from ref. 2. Falloff curves are constructed with an estimated value of  $F_c = 0.8$ . The small pre-exponential factor of  $k_{\infty}$  can be explained theoretically as being due to the low bond energy of HOCS<sub>2</sub>. For discussion of the mechanism see refs. 1, 2 and 5.

## References

15

<sup>1</sup> A. J. Hynes, P. H. Wine, and J. M. Nicovich, *J. Phys. Chem.*, 92, 3846, 1988.

<sup>2</sup> T. P. Murrells, E. R. Lovejoy, and A. R. Ravishankara, *J. Phys. Chem.*, 94, 2381, 1990.

<sup>3</sup> E. W.-G. Diau and Y.-P. Lee, *J. Phys. Chem.*, 95, 379, 1991.

<sup>4</sup> V. P. Bulatov, S. G. Cheskis, A. A. Iogansen, P. V. Kulatov, O. M. Sarkisov, and E. Hassinen, *Chem. Phys. Lett.*, 153, 258, 1988.

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<sup>5</sup> E. R. Lovejoy, T. P. Murrells, A. R. Ravishankara, and C. J. Howard, *J. Phys. Chem.*, 94, 2386, 1990.

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# HOCS<sub>2</sub> + O<sub>2</sub> → products

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.4 \times 10^{-14} \exp[(217 \pm 301)/T]$	251-348	Hynes et al., 1988 <sup>1</sup>	PLP-LIF (a)
$(3.26 \pm 0.70) \times 10^{-14}$	295 ± 1		
$(2.6 \pm 1.0) \times 10^{-14}$	249-299	Murrells et al., 1990 <sup>2</sup>	PLP-LIF
$(2.4 \pm 0.4) \times 10^{-14}$	273	Lovejoy et al., 1990 <sup>3</sup>	PLP-LIF (b)
$(3.1 \pm 0.6) \times 10^{-14}$	298	Diau and Lee, 1991 <sup>4</sup>	PLP-LIF (c)

## Comments

- 5 (a) The effects of He, N<sub>2</sub>, air and O<sub>2</sub> were studied, and the total pressure was varied over the range 87-920 mbar (65-690 Torr). If the rate coefficient  $k$  is assumed to be temperature independent, the average of the measured values is  $(2.9 \pm 1.1) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 251-348 K.
- 10 (b) A rate coefficient for the reaction of the DOCS<sub>2</sub> radical with O<sub>2</sub> of  $(2.3 \pm 0.4) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 273 K was also measured,<sup>3</sup> showing no significant deuterium isotope effect and hence no evidence for a direct H-atom abstraction process.
- 15 (c) Values of  $k(\text{HOCS}_2 + \text{NO}) = (7.3 \pm 1.8) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{HOCS}_2 + \text{NO}_2) = (4.2 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K were also obtained in this work. The latter is the first measurement of the rate coefficient for the reaction with NO<sub>2</sub>. The rate coefficient for the reaction with NO is consistent with the

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values of  $k(\text{HOCS}_2 + \text{NO}) = (1.3 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 249 K and  $k(\text{HOCS}_2 + \text{NO}) = (9.1 \pm 3.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 299 K measured by Lovejoy et al.<sup>5</sup>

### Preferred Values

5  $k = 2.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 240–350 K.

### Reliability

10  $\Delta \log k = \pm 0.15$  over the temperature range 240–350 K.

### Comments on Preferred Values

15 The reaction of  $\text{HOCS}_2$  with  $\text{O}_2$  is an intermediate step in the overall reaction of the HO radical with  $\text{CS}_2$  under atmospheric conditions. The  $\text{HOCS}_2$  is formed by the addition of HO to  $\text{CS}_2$ ; once formed it may undergo dissociation back to HO and  $\text{CS}_2$  or react with  $\text{O}_2$ .

The four studies<sup>1–4</sup> of the kinetics of this reaction, all using the same general experimental technique, are in good agreement. The rate coefficients measured by Hynes et al.<sup>1</sup> over the temperature range 251–348 K could equally well be represented by either the Arrhenius expression cited in the table, with a small negative temperature dependence, or by a temperature-independent rate coefficient. The results of Murrells et al.<sup>2</sup> favor the latter. For the preferred values we assume the rate coefficient to be temperature independent over the temperature range studied and take a mean of the values of Hynes et al.,<sup>1</sup> Murrells et al.,<sup>2</sup> Lovejoy et al.<sup>3</sup> and Diau and Lee.<sup>4</sup>

25 Lovejoy et al.<sup>5,6</sup> used LP-LIF to measure an  $\text{HO}_2$  radical formation yield of  $0.95 \pm$

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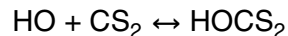
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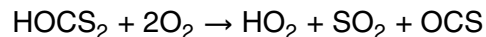
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0.15 (249-300 K) from the reaction of the HO radical with CS<sub>2</sub> in the presence of O<sub>2</sub> (by converting HO<sub>2</sub> radicals to HO radicals by reaction with NO),<sup>5</sup> and used DF-CIMS to measure an SO<sub>2</sub> yield from the HO radical reaction with CS<sub>2</sub> in the presence of O<sub>2</sub> of 0.90 ± 0.20 at 340 K.<sup>6</sup>

The main steps in the atmospheric oxidation of CS<sub>2</sub> initiated by HO are then



followed by the overall reaction

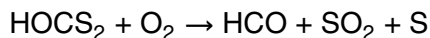


In the atmosphere, reaction of the HOCS<sub>2</sub> with O<sub>2</sub> predominates over reaction with NO or NO<sub>2</sub>. The study by Stickel et al.<sup>7</sup> has provided some further insight into the mechanism of this complex reaction. Two types of experiment were performed. In one, the reaction was initiated by pulsed laser photolysis and product concentrations monitored in real time by tunable diode laser absorption spectroscopy. In the other, continuous photolysis was used with FTIR product detection. Products observed were OCS, SO<sub>2</sub>, CO, and CO<sub>2</sub>. Both experiments gave concordant values for the yields of OCS and CO of 0.83 ± 0.08 and 0.16 ± 0.03, respectively. The yield of CO<sub>2</sub> was small (<0.01). The overall yield of SO<sub>2</sub> (1.15 ± 0.10) was made up of two components, a 'prompt' value of 0.84 ± 0.20 resulting from SO<sub>2</sub> produced in a primary channel of the reaction and a longer time component assumed due to production of SO<sub>2</sub> from reaction of O<sub>2</sub> with S or SO produced in another primary channel. The data of Stickel et al.<sup>7</sup> thus suggest two primary channels, the major one leading to OCS and SO<sub>2</sub> and a minor channel leading to CO and SO. There are a number of possible reaction channels leading directly to these species or to their precursors, which subsequently produce them on a very short time scale.

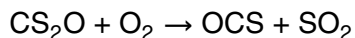
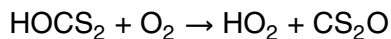
Lovejoy et al.<sup>6</sup> used DF-CIMS to investigate the products of the reaction of the H<sup>18</sup>O radical with CS<sub>2</sub> in <sup>16</sup>O<sub>2</sub> at ~340 K, and observed the formation of <sup>16</sup>OS<sup>18</sup>O with a yield

of  $0.90 \pm 0.20$ .  $S^{16}O_2$  formation was observed,<sup>6</sup> and this may be consistent with the formation of S atoms or SO radicals.<sup>7</sup>

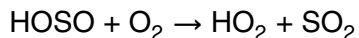
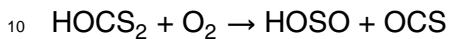
These studies suggest that the reaction pathway



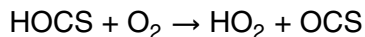
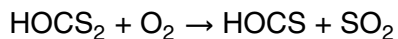
- 5 followed by reactions of HCO and S to form  $HO_2 + CO$  and  $SO_2$  accounts for ~15% of the overall reaction,<sup>7</sup> with the remainder (~85%) proceeding by<sup>6</sup>



or



or



- 15 A theoretical study of the  $HOCS_2-O_2$  intermediate<sup>8</sup> suggests that HOSO and OCS are the main dissociation products, which would then be followed by the reaction  $HOSO + O_2 \rightarrow HO_2 + SO_2$ .

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# HO + CH<sub>3</sub>SH → products

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$8.89 \times 10^{-12} \exp[(398 \pm 151)/T]$ $(3.39 \pm 0.34) \times 10^{-11}$	300-423 300	Atkinson et al., 1977 <sup>1</sup>	FP-RF
$1.15 \times 10^{-11} \exp[(338 \pm 100)/T]$ $(3.37 \pm 0.41) \times 10^{-11}$	244-366 298	Wine et al., 1981 <sup>2</sup>	FP-RF
$1.01 \times 10^{-11} \exp[(347 \pm 59)/T]$ $3.24 \times 10^{-11}$	254-430 298	Wine et al., 1984 <sup>3</sup>	FP-RF
$3.69 \times 10^{-11}$ $3.17 \times 10^{-11}$	270 300	Hynes and Wine, 1987 <sup>4</sup>	PLP-LIF (a)
<i>Relative Rate Coefficients</i>			
$(9.68 \pm 0.97) \times 10^{-11}$ $(3.72 \pm 0.37) \times 10^{-11}$	297 ± 2 300	Cox and Sheppard, 1980 <sup>5</sup> Barnes et al., 1986 <sup>6</sup>	RR (b) RR (c)
$(3.50 \pm 0.49) \times 10^{-11}$	313		

## Comments

- 5 (a) The rate coefficients were observed to be independent of total pressure and of the presence or absence of O<sub>2</sub>, up to 196 mbar O<sub>2</sub> at 270 K or 933 mbar O<sub>2</sub> at 300 K.
- (b) HO radicals were generated by the photolysis of HONO-NO-air mixtures at atmo-

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spheric pressure. The decay of  $\text{CH}_3\text{SH}$  was measured relative to that of  $\text{C}_2\text{H}_4$  by GC, and the relative rate coefficient placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{C}_2\text{H}_4) = 8.57 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 297 K and atmospheric pressure of air.<sup>7</sup>

(c) HO radicals were generated by the photolysis of  $\text{H}_2\text{O}_2$  in  $\text{N}_2$  at atmospheric pressure. The decay of  $\text{CH}_3\text{SH}$  was measured relative to that for propene by GC, and the relative rate coefficients placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{propene}) = 4.85 \times 10^{-12} \exp(504/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at atmospheric pressure of air.<sup>7</sup>

## Preferred Values

$k = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 9.9 \times 10^{-12} \exp(356/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240-430 K.

### Reliability

$\Delta \log k = \pm 0.10$  at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$ .

### Comments on Preferred Values

The preferred values are based upon a least-squares analysis of the absolute rate coefficients of Atkinson et al.,<sup>1</sup> Wine et al.,<sup>2,3</sup> and Hynes and Wine,<sup>4</sup> which are in excellent agreement. The relative rate study of Barnes et al.<sup>6</sup> shows that erroneous rate coefficient data are obtained in the presence of  $\text{O}_2$  and  $\text{NO}$ , thus accounting for the much higher value of Cox and Sheppard.<sup>5</sup>

The study of Hynes and Wine<sup>4</sup> shows that there is no observable effect of  $\text{O}_2$  on

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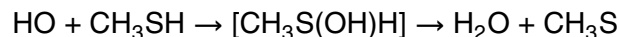
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the measured rate coefficient, and the rate coefficients at 298 K for the reactions of the HO radical with  $\text{CD}_3\text{SH}$ <sup>4</sup> and  $\text{CH}_3\text{SD}$ <sup>3</sup> are within 15% of that for  $\text{HO} + \text{CH}_3\text{SH}$ . These data indicate<sup>3,4</sup> that the reaction proceeds via initial addition of HO to form the adduct  $\text{CH}_3\text{S(OH)H}$ .<sup>3</sup> Tyndall and Ravishankara<sup>8</sup> have determined, by monitoring the  $\text{CH}_3\text{S}$  radical by LIF, a  $\text{CH}_3\text{S}$  radical yield from the reaction of the HO radical with  $\text{CH}_3\text{SH}$  of  $1.1 \pm 0.2$ . The reaction then proceeds by



Butkovskaya and Setser<sup>9</sup> concluded, from observations of the IR chemiluminescent spectra of reactions of HO and DO radicals with  $\text{CH}_3\text{SH}$  and  $\text{CH}_3\text{SD}$ , that direct H-atom abstraction from the  $\text{CH}_3$  group accounts for  $11 \pm 4\%$  of the total of the DO radical reactions and  $24 \pm 8\%$  of the total of the HO radical reactions.

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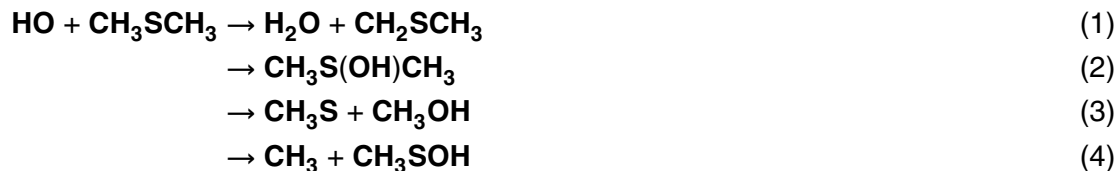
<sup>5</sup> R. A. Cox and D. Sheppard, *Nature*, **284**, 330, 1980.

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<sup>9</sup> N. I. Butkovskaya and D. W. Setser, *J. Phys. Chem. A*, **103**, 6921, 1999.



$$\Delta H^\circ(1) = -105 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) \approx -43 \text{ kJ}\cdot\text{mol}^{-1} \text{ (uses } \Delta H_f \text{ CH}_3\text{S(OH)CH}_3 = 43 \text{ kJ}\cdot\text{mol}^{-1}\text{)}^7$$

$$\Delta H^\circ(3) = -77 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(4) \approx 0 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2 + k_3 + k_4$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = 1.15 \times 10^{-11} \exp[-(338 \pm 100)/T]$	248-363	Wine et al., 1981 <sup>1</sup>	FP-RF
$k_1 = (4.26 \pm 0.56) \times 10^{-12}$	298		
$(6.28 \pm 0.10) \times 10^{-12}$ (1 bar of air)	298	Hynes et al., 1986 <sup>2</sup>	PLP-LIF (a)
$k_1 = 1.36 \times 10^{-11} \exp[-(332 \pm 96)/T]$	276-397	Hynes et al., 1986 <sup>2</sup>	FP-RF
$k_1 = 4.46 \times 10^{-12}$	298		
$k_1 = 1.18 \times 10^{-11} \exp[-(236 \pm 150)/T]$	260-393	Hsu et al., 1987 <sup>3</sup>	DF-RF (b)
$k_1 = (5.54 \pm 0.15) \times 10^{-12}$	298		
$k_1 = 1.35 \times 10^{-11} \exp[-(285 \pm 135)/T]$	297-368	Abbatt et al., 1992 <sup>4</sup>	DF-LIF (c)

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = (4.98 \pm 0.46) \times 10^{-12}$	$297 \pm 2$		
$k_1 = (4.95 \pm 0.35) \times 10^{-12}$	298	Barone et al., 1996 <sup>5</sup>	PLP-LIF
<i>Branching Ratios</i>			
$k_1/k = 0.84 \pm 0.15$	298	Stickel et al., 1993 <sup>6</sup>	(d)
$k_1/k = 0.84 \pm 0.26$	298	Turnipseed et al., 1996 <sup>7</sup>	(e)
$k_3/k < 0.04$	298	Turnipseed et al., 1996 <sup>7</sup>	(f)
$k_4/k < 0.07$	298	Zhao et al., 1996 <sup>8</sup>	(g)

## Comments

- (a) Detection of HO, with the effects of O<sub>2</sub> being investigated over the temperature range 261-321 K. The measured rate coefficient was observed to depend on the O<sub>2</sub> concentration, and the rate coefficient given in the table is that measured at 1 bar (750 Torr) total pressure of air. The rate coefficient measured in the absence of O<sub>2</sub> is ascribed to reaction (1), with the adduct formed in (2) rapidly dissociating back to the reactants. In the presence of O<sub>2</sub> this adduct reacts rapidly with O<sub>2</sub>, and hence the measured rate coefficient increases with the O<sub>2</sub> concentration.
- (b) Rate coefficient not affected by the addition of up to 1.3 mbar (1 Torr) of O<sub>2</sub>.
- (c) HO generated from the H + NO<sub>2</sub> reaction. The total pressure was varied over the range 14.1-130 mbar (10.6-97.5 Torr) of N<sub>2</sub>. The measured rate coefficient was invariant to the total pressure over this range.
- (d) For the reaction DO + CH<sub>3</sub>SCH<sub>3</sub>, HDO was monitored by tunable diode laser absorption spectroscopy, and the branching ratio obtained by assuming a unit

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HDO yield from the DO radical reaction with *n*-hexane and cyclohexane. The branching ratio was independent of total pressure of N<sub>2</sub> [13–40 mbar (10–30 Torr)], temperature (298–348 K) and replacement of 13 mbar (10 Torr) total pressure of N<sub>2</sub> by 13 mbar total pressure of O<sub>2</sub>. From the temporal profiles of the HDO signals, rate coefficients *k*<sub>1</sub> for the reaction of the DO radical with CH<sub>3</sub>SCH<sub>3</sub> of (5.4 ± 0.4) × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K and 13 mbar (10 Torr) N<sub>2</sub>, (5.8 ± 1.9) × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K and 40 mbar (30 Torr) N<sub>2</sub>, and (4.4 ± 1.0) × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 348 K and 13 mbar (10 Torr) N<sub>2</sub> were also obtained, in agreement with the rate coefficients for the HO radical reaction.

(e) Indirect measurement of CH<sub>3</sub>SCH<sub>2</sub> by addition of O<sub>2</sub> and NO and measuring CH<sub>3</sub>S formation by LIF.

(f) Direct detection of CH<sub>3</sub>S by LIF

(g) Direct detection of CH<sub>3</sub> using TDLAS

### Preferred Values

$k_1 = 1.13 \times 10^{-11} \exp(-253/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240–400 K.

$k_2 = 1.0 \times 10^{-39} [\text{O}_2] \exp(5820/T) / \{1 + 5.0 \times 10^{-30} [\text{O}_2] \exp(6280/T)\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240–360 K.

### Reliability

$\Delta \log k_1 = \pm 0.10$  at 298 K.

$\Delta(E/R) = \pm 150 \text{ K}$ .

$\Delta \log k_2 = \pm 0.3 \text{ K}$  and 1 bar of air.

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It is now recognized<sup>25,9–11</sup> that this reaction proceeds via the two reaction steps (1) and (2). The  $\text{CH}_3\text{S}(\text{OH})\text{CH}_3$  adduct radical decomposes sufficiently rapidly such that in the absence of  $\text{O}_2$  only the rate coefficient  $k_1$  is measured. In the presence of  $\text{O}_2$  the  $\text{CH}_3\text{S}(\text{OH})\text{CH}_3$  radical reacts by  $\text{CH}_3\text{S}(\text{OH})\text{CH}_3 + \text{O}_2 \rightarrow$  products. Hence only in the presence of  $\text{O}_2$  is the addition channel (2) observed, with the rate coefficient being dependent on the  $\text{O}_2$  concentration (but, to at least a first approximation, not on the concentration of other third bodies such as  $\text{N}_2$ , Ar or  $\text{SF}_6$ ).<sup>2</sup>  $\text{HO}_2$  is formed at  $\approx 50\%$  yield in the reaction of  $\text{CH}_3\text{S}(\text{OH})\text{CH}_3$  with  $\text{O}_2$

The relative rate study of Wallington et al.<sup>11</sup> showed that previous relative studies carried out in the presence of NO are dubious. The most recent absolute rate coefficients<sup>1–5</sup> measured in the absence of  $\text{O}_2$  confirm that the earlier absolute rate coefficients of Atkinson et al.<sup>14</sup> and Kurylo<sup>15</sup> are erroneously high, and those of MacLeod et al.<sup>16</sup> were in error because of wall reactions. The preferred rate coefficients  $k_1$  for the abstraction channel (1) are based on the studies of Wine et al.,<sup>1</sup> Hynes et al.,<sup>2</sup> Hsu et al.,<sup>3</sup> Abbatt et al.<sup>4</sup> and Barone et al.<sup>5</sup> and the rate coefficient for the HO radical addition channel (2) utilizes the data of Hynes et al.<sup>2</sup> and Williams et al.<sup>17</sup> The expression for  $k_2$  reproduces the  $\text{O}_2$  and T dependence of  $k_{obs}$  ( $k_{obs} = k_1 + k_2 + k_3 + k_4 \equiv k_1 + k_2$ ) of Hynes et al.<sup>2</sup> and Williams et al.<sup>17</sup> at pressures close to one atmosphere (where the rate coefficients for HO addition to  $\text{CH}_3\text{SCH}_3$  and the reverse dissociation step may be in the falloff region). This equation fits the room temperature data obtained at pressures of air from 0.07 to 0.93 bar, though there are large differences in measured values of  $k$  at 100 Torr and 760 Torr at low temperatures.<sup>2,5,17</sup>

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# HO + CH<sub>3</sub>SSCH<sub>3</sub> → products

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.9 \times 10^{-11} \exp[(380 \pm 160)/T]$ $(1.98 \pm 0.18) \times 10^{-10}$	249-367 298	Wine et al., 1981 <sup>1</sup>	FP-RF
$6.2 \times 10^{-11} \exp[(410 \pm 210)/T]$ $(2.39 \pm 0.30) \times 10^{-10}$ $(2.4 \pm 0.9) \times 10^{-10}$	297-366 297 298	Abbatt et al., 1992 <sup>2</sup> Dominé and Ravishankara, 1992 <sup>3</sup>	DF-LIF (a)
<i>Relative Rate Coefficients</i>			
$(2.40 \pm 0.86) \times 10^{-10}$	297 ± 2	Cox and Sheppard, 1980 <sup>4</sup>	RR (b)

## Comments

- (a) Discharge-flow system with photoionization-MS detection of CH<sub>3</sub>SOH and CH<sub>3</sub>S product species. The temporal profiles of these product species yielded the cited rate coefficient. The CH<sub>3</sub>S radical formation yield from the HO radical reaction with CH<sub>3</sub>SSCH<sub>3</sub> was measured to be 0.28 ± 0.20 using a pulsed laser photolysis system with LIF detection of CH<sub>3</sub>S. The photolysis of CH<sub>3</sub>SSCH<sub>3</sub> at 266 nm was used to normalize the CH<sub>3</sub>S radical signal, with the CH<sub>3</sub>S radical formation yield from the photolysis of CH<sub>3</sub>SSCH<sub>3</sub> being 1.8 ± 0.2 at 248 nm.<sup>5</sup>
- (b) A rate coefficient ratio of  $k(\text{HO} + \text{CH}_3\text{SSCH}_3)/k(\text{HO} + \text{ethene}) = 28 \pm 10$  was measured by GC analyses of CH<sub>3</sub>SSCH<sub>3</sub> and ethene in irradiated HONO-CH<sub>3</sub>SSCH<sub>3</sub>-ethene-air mixtures at atmospheric pressure. The measured rate coefficient ratio

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is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{ethene}) = 8.57 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 297 K and atmospheric pressure of air.<sup>6</sup>

### Preferred Values

$k = 2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 7.0 \times 10^{-11} \exp(350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250-370 K.

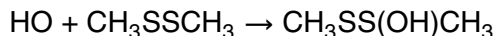
### Reliability

$\Delta \log k = \pm 0.10$  at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$ .

### Comments on Preferred Values

The absolute rate coefficients of Wine et al.,<sup>1</sup> Abbatt et al.,<sup>2</sup> and Dominé and Ravishankara<sup>3</sup> are in excellent agreement. The preferred values are derived from a least-squares analysis of the absolute rate coefficients of Wine et al.<sup>1</sup> and Abbatt et al.<sup>2</sup> The magnitude of the rate coefficient and the negative temperature dependence indicates that the reaction proceeds by initial HO radical addition to the S atoms:



Dominé and Ravishankara<sup>3</sup> measured a  $\text{CH}_3\text{S}$  yield of  $0.28 \pm 0.20$ , independent of pressure (73-640 mbar) and diluent gas ( $\text{N}_2$  and  $\text{SF}_6$ ) at 298 K, indicating that products other than  $\text{CH}_3\text{S}$  and  $\text{CH}_3\text{SOH}$  are formed in this reaction. Butkovskaya and Setser,<sup>7</sup> from a study of the IR chemiluminescence from the reactions of HO and DO radicals with  $\text{CH}_3\text{SSCH}_3$ , concluded that the major reaction pathway is that to form  $\text{CH}_3\text{SH}$  (or  $\text{CH}_3\text{SD}$ ) +  $\text{CH}_3\text{SO}$ , with these products dominating by a factor of  $\geq 3$  over formation of

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$\text{CH}_3\text{S} + \text{CH}_3\text{SOH}$ .<sup>7</sup> Hence the studies of Dominé and Ravishankara<sup>3</sup> and Butkovskaya and Setser<sup>7</sup> are not inconsistent.

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## HO<sub>2</sub> + H<sub>2</sub>S → products

### Rate coefficient data

<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
(5 ± 1) × 10 <sup>-12</sup>	298	Bulatov et al., 1990 <sup>1</sup>	FP-A (a)
<3 × 10 <sup>-15</sup>	298	Mellouki and Ravishankara, 1994 <sup>2</sup>	DF-LMR

### Comments

- 5 (a) HO<sub>2</sub> radicals were monitored by intracavity laser absorption in the near IR.

### Preferred Values

$k < 3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

#### *Comments on Preferred Values*

- 10 This upper limit is taken from the study of Mellouki and Ravishankara.<sup>2</sup> It is consistent with the upper limits reported for the corresponding reactions of HO<sub>2</sub> with CH<sub>3</sub>SH and CH<sub>3</sub>SCH<sub>3</sub>. This upper limit is three orders of magnitude lower than the value reported by Bulatov et al.<sup>1</sup> from a flash photolysis study using intracavity laser absorption in the  
15 near infrared to monitor HO<sub>2</sub>. The results of the more direct study<sup>2</sup> are preferred.

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## HO<sub>2</sub> + SO<sub>2</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(1.0 \pm 0.2) \times 10^{-15}$	300	Payne et al., 1973 <sup>1</sup>	RR (a)
$\leq 1 \times 10^{-18}$	300	Graham et al., 1979 <sup>2</sup>	RR (b)
$\leq 4.3 \times 10^{-17}$	~298	Burrows et al., 1979 <sup>3</sup>	RR (c)

### Comments

- 5 (a) Photolysis of H<sub>2</sub>O-CO-<sup>18</sup>O<sub>2</sub>-N<sub>2</sub> mixtures at 184.9 and 253.7 nm, with formation of C<sup>16</sup>O<sub>2</sub> and C<sup>16,18</sup>O<sub>2</sub> being monitored by MS.  $k/k^{1/2}(\text{HO}_2 + \text{HO}_2)$  was determined. The value tabulated here was calculated using the effective value of  $k(\text{HO}_2 + \text{HO}_2)$  in this system of  $3.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this review).
- 10 (b) Thermal decomposition of HO<sub>2</sub>NO<sub>2</sub> monitored by IR absorption. Upper limit to  $k$  derived from the absence of a detectable effect of added SO<sub>2</sub> on the HO<sub>2</sub>NO<sub>2</sub> decay rate.
- (c) DF-LMR study.  $k/k(\text{HO} + \text{H}_2\text{O}_2)$  was determined. Value tabulated here was calculated using  $k(\text{HO} + \text{H}_2\text{O}_2) = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this review).

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## Preferred Values

$k < 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### *Comments on Preferred Values*

The most recent determination<sup>3</sup> confirms that the reaction is slower than some earlier results<sup>1</sup> had suggested and supports the even lower upper limit set by Graham et al.<sup>2</sup> which we take as the preferred value.

## References

<sup>1</sup> W. A. Payne, L. J. Stief, and D. D. Davis, *J. Am. Chem. Soc.*, 95, 7614, 1973.

<sup>2</sup> R. A. Graham, A. M. Winer, R. Atkinson, and J. N. Pitts, Jr., *J. Phys. Chem.*, 83, 1563, 1979.

<sup>3</sup> J. P. Burrows, D. I. Cliff, G. W. Harris, B. A. Thrush, and J. P. T. Wilkinson, *Proc. R. Soc. (London)* A368, 463, 1979.

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## HO<sub>2</sub> + CH<sub>3</sub>SH → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<4 \times 10^{-15}$	298	Mellouki and Ravishankara, 1994 <sup>1</sup>	DF-LMR

### 5 Preferred Values

$k < 4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Comments on Preferred Values

10 This upper limit is taken from the study of Mellouki and Ravishankara.<sup>1</sup> It is consistent with the upper limits reported for the corresponding reactions of HO<sub>2</sub> with H<sub>2</sub>S and CH<sub>3</sub>SCH<sub>3</sub>. It is also consistent with results noted in the Barnes et al.<sup>2</sup> study of the reactions of the HO radical with various sulfur compounds. In that publication<sup>2</sup> the authors stated that previous experiments in that laboratory had shown that the rate  
15 coefficients for reactions of HO<sub>2</sub> with thiols were  $<1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

### References

<sup>1</sup> A. Mellouki and A. R. Ravishankara, Int. J. Chem. Kinet., 26, 355, 1994.

<sup>2</sup> I. Barnes, V. Bastian, K. H. Becker, E. H. Fink, and W. Nelsen, J. Atmos. Chem., 4, 445, 1986.

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## HO<sub>2</sub> + CH<sub>3</sub>SCH<sub>3</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<5 \times 10^{-15}$	298	Mellouki and Ravishankara, 1994 <sup>1</sup>	DF-LMR

### Preferred Values

5  $k < 5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

#### *Comments on Preferred Values*

10 This upper limit is taken from the study of Mellouki and Ravishankara.<sup>1</sup> It is consistent with the upper limits reported for the corresponding reactions of the HO<sub>2</sub> radical with H<sub>2</sub>S and CH<sub>3</sub>SH. It is also consistent with unpublished results of Niki, who in a study of the decay of CH<sub>3</sub>SCH<sub>3</sub> in the presence of HO<sub>2</sub> in 1 bar air showed the reaction of HO<sub>2</sub> with CH<sub>3</sub>SCH<sub>3</sub> to be very slow with  $k < 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (reported in Mellouki and Ravishankara<sup>1</sup> as a private communication from H. Niki).

### 15 References

<sup>1</sup> A. Mellouki and A. R. Ravishankara, Int. J. Chem. Kinet., 26, 355, 1994.

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## NO<sub>3</sub> + H<sub>2</sub>S → products

### Rate coefficient data

<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
≤ 3 × 10 <sup>-14</sup>	298 ± 2	Wallington et al., 1986 <sup>1</sup>	FP-A
< 8 × 10 <sup>-16</sup>	298	Dlugokencky and Howard, 1988 <sup>2</sup>	F-LIF
<i>Relative Rate Coefficients</i>			
< 2.5 × 10 <sup>-14</sup>	298	Cantrell et al., 1987 <sup>3</sup>	RR (a)

### Comments

- 5 (a) NO<sub>3</sub> radicals were generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub>, and the rate coefficient placed on an absolute basis by use of an equilibrium constant for the NO<sub>3</sub> + NO<sub>2</sub> ↔ N<sub>2</sub>O<sub>5</sub> reactions of 2.90 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> at 298 K.<sup>4</sup>

### Preferred Values

$k < 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Comments on Preferred Values

The preferred upper limit to the rate coefficient is based upon the absolute rate coefficient study of Dlugokencky and Howard.<sup>2</sup>

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<sup>1</sup> T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem., 90, 5393, 1986.

<sup>2</sup> E. J. Dlugokencky and C. J. Howard, J. Phys. Chem., 92, 1188, 1988.

<sup>3</sup> C. A. Cantrell, J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert, J. Phys. Chem., 91, 6017, 1987.

<sup>4</sup> IUPAC (2001). <http://www.iupac-kinetic.ch.cam.ac.uk/>

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## NO<sub>3</sub> + CS<sub>2</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<4 \times 10^{-16}$	298	Burrows et al., 1985 <sup>1</sup>	MM-A
<i>Relative Rate Coefficients</i>			
$<1.1 \times 10^{-15}$	297 ± 2	Mac Leod et al., 1986 <sup>2</sup>	RR (a)

### Comments

- 5 (a) NO<sub>3</sub> radicals were generated by thermal decomposition of N<sub>2</sub>O<sub>5</sub> at atmospheric pressure of air. The decay rates of CS<sub>2</sub> and propene were monitored by FTIR absorption spectroscopy. The upper limit to the rate coefficient was obtained by use of a rate coefficient of  $k(\text{NO}_3 + \text{propene}) = 9.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 297 K.<sup>3</sup>

### 10 Preferred Values

$k < 4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

#### *Comments on Preferred Values*

- 15 The preferred value is based upon the absolute study of Burrows et al.,<sup>1</sup> which is consistent with the slightly higher upper limit derived by Mac Leod et al.<sup>2</sup>

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- <sup>1</sup> J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, *J. Phys. Chem.*, 89, 4848, 1985.
- <sup>2</sup> H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., *J. Geophys. Res.*, 91, 5338, 1986.
- <sup>3</sup> R. Atkinson, *J. Phys. Chem. Ref. Data*, 26, 215, 1997.

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## NO<sub>3</sub> + OCS → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$<4.6 \times 10^{-17}$	$297 \pm 2$	Mac Leod et al., 1986 <sup>1</sup>	RR (a)

### Comments

- 5 (a) NO<sub>3</sub> radicals were generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub> at atmospheric pressure of air. The decay rates of OCS and propene were monitored by FTIR absorption spectroscopy. The upper limit to the rate coefficient is obtained by use of a rate coefficient of  $k(\text{NO}_3 + \text{propene}) = 9.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 297 K.<sup>2</sup>

### 10 Preferred Values

$k < 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

#### *Comments on Preferred Values*

- 15 The preferred value is based upon the sole study of Mac Leod et al.<sup>1</sup> with a somewhat higher upper limit than reported.

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<sup>1</sup> H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., *J. Geophys. Res.*, 91, 5338, 1986.

<sup>2</sup> R. Atkinson, *J. Phys. Chem. Ref. Data*, 26, 215, 1997.

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## NO<sub>3</sub> + SO<sub>2</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<4 \times 10^{-16}$	298	Burrows et al., 1985 <sup>1</sup>	MM-A
$\leq 4 \times 10^{-16}$	298 ± 2	Wallington et al., 1986 <sup>2</sup>	FP-A
$<1 \times 10^{-17}$	295 ± 2	Canosa-Mas et al., 1988 <sup>3</sup>	DF-A
$<1.2 \times 10^{-17}$	473	Canosa-Mas et al., 1988 <sup>4</sup>	DF-A
$<1 \times 10^{-15}$	298	Dlugokencky and Howard, 1988 <sup>5</sup>	F-LIF
<i>Relative Rate Coefficients</i>			
$<7 \times 10^{-21}$	303	Daubendiek and Calvert, 1975 <sup>6</sup>	RR (a)

### Comments

- <sup>5</sup> (a) Derived from the lack of observation of SO<sub>3</sub> formation in N<sub>2</sub>O<sub>5</sub>-SO<sub>2</sub>-O<sub>3</sub> mixtures, using IR absorption spectroscopy to measure the concentrations of SO<sub>3</sub>.

### Preferred Values

$k < 1 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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The preferred value is based upon the relative rate study of Daubendiek and Calvert,<sup>6</sup> with a much higher upper limit. This preferred upper limit to the 298 K rate coefficient is consistent with the upper limits measured in the absolute rate coefficient studies of Burrows et al.,<sup>1</sup> Wallington et al.,<sup>2</sup> Canosa-Mas et al.,<sup>3,4</sup> and Dlugokencky and Howard.<sup>5</sup>

## References

<sup>1</sup> J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, *J. Phys. Chem.*, 89, 4848, 1985.

<sup>2</sup> T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.*, 90, 5393, 1986.

<sup>3</sup> C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, 84, 247, 1988.

<sup>4</sup> C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, 84, 263, 1988.

<sup>5</sup> E. J. Dlugokencky and C. J. Howard, *J. Phys. Chem.*, 92, 1188, 1988.

<sup>6</sup> R. L. Daubendiek and J. G. Calvert, *Environ. Lett.*, 8, 103, 1975.

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## NO<sub>3</sub> + CH<sub>3</sub>SH → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.0 \times 10^{-13} \exp[(600 \pm 400)/T]$	280-350	Wallington et al., 1986 <sup>1</sup>	FP-A
$(8.1 \pm 0.6) \times 10^{-13}$	298		
$(7.7 \pm 0.5) \times 10^{-13}$	298	Rahman et al., 1988 <sup>2</sup>	DF-MS
$1.09 \times 10^{-12} \exp[(0 \pm 50)/T]$	254-367	Dlugokencky and Howard, 1988 <sup>3</sup>	F-LIF
$(1.09 \pm 0.13) \times 10^{-12}$	298*		
<i>Relative Rate Coefficients</i>			
$(1.00 \pm 0.22) \times 10^{-12}$	297 ± 2	Mac Leod et al., 1986 <sup>4</sup>	RR (a)

### Comments

- 5 (a) NO<sub>3</sub> radicals were generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub> in N<sub>2</sub>O<sub>5</sub>-NO<sub>2</sub>-air mixtures at atmospheric pressure. The decay rates of CH<sub>3</sub>SH and *trans*-2-butene were monitored by FTIR and GC respectively, and the measured rate coefficient ratio of  $k(\text{NO}_3 + \text{CH}_3\text{SH})/k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 2.57 \pm 0.55$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 3.89 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>5</sup>
- 10

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## Preferred Values

$k = 9.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 250–370 K.

### 5 *Reliability*

$\Delta \log k = \pm 0.15$  at 298 K.

$\Delta(E/R) = \pm 400$  K.

### 10 *Comments on Preferred Values*

The preferred value at 298 K is the mean of the four studies carried out to date,<sup>1–4</sup> which are in reasonably good agreement. Although a significant negative temperature dependence is indicated by the absolute rate coefficient study of Wallington et al.,<sup>1</sup> this is due to the rate coefficient measured at 350 K, and the rate coefficients at 280 and 298 K are identical.<sup>1</sup> The temperature independence of the rate coefficient determined by Dluogokencky and Howard<sup>3</sup> is accepted. The experimental data indicate that there is no pressure dependence of the rate coefficient, at least over the range  $\sim 0.0013$ –1 bar.

20 The magnitude of the rate coefficient and the lack of a temperature dependence of the rate coefficient shows that this reaction proceeds by initial addition, followed by decomposition of the adduct to yield  $\text{CH}_3\text{S}$  radicals (see also the data sheet on the  $\text{NO}_3 + \text{CH}_3\text{SCH}_3$  reaction)



25 This conclusion is consistent with the product studies carried out by Mac Leod et al.<sup>4</sup> and Jensen et al.<sup>6</sup> Jensen et al.<sup>6</sup> identified  $\text{CH}_3\text{SO}_3\text{H}$  (methanesulfonic acid),  $\text{SO}_2$ ,  $\text{HCHO}$ ,  $\text{CH}_3\text{ONO}_2$ ,  $\text{CH}_3\text{SNO}$ , and  $\text{HNO}_3$  as products of the  $\text{NO}_3$  radical reaction with

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CH<sub>3</sub>SH at 295 ± 2 K and 0.99 ± 0.01 bar (740 ± 10 Torr) total pressure of purified air.

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<sup>1</sup> T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.*, 90, 5393, 1986.

<sup>2</sup> M. M. Rahman, E. Becker, Th. Benter, and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.*, 92, 91, 1988.

<sup>3</sup> E. J. Dlugokencky and C. J. Howard, *J. Phys. Chem.*, 92, 1188, 1988.

<sup>4</sup> H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., *J. Geophys. Res.*, 91, 5338, 1986.

<sup>5</sup> R. Atkinson, *J. Phys. Chem. Ref. Data*, 26, 215, 1997.

<sup>6</sup> N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, *J. Atmos. Chem.*, 14, 95, 1992.

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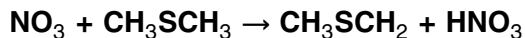
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$$\Delta H^\circ = -35 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.0 \pm 0.2) \times 10^{-12}$	278-318	Tyndall et al., 1986 <sup>1</sup>	MM-A
$(9.9 \pm 3.5) \times 10^{-13}$	298		
$(7.5 \pm 0.5) \times 10^{-13}$	298 ± 2	Wallington et al., 1986 <sup>2</sup>	FP-A
$4.7 \times 10^{-13} \exp[(170 \pm 130)/T]$	280-350	Wallington et al., 1986 <sup>3</sup>	FP-A
$(8.1 \pm 1.3) \times 10^{-13}$	298 ± 2		
$1.79 \times 10^{-13} \exp[(530 \pm 40)/T]$	256-376	Dlugokencky and Howard, 1988 <sup>4</sup>	F-LIF
$(1.06 \pm 0.13) \times 10^{-12}$	298		
$(1.3 \pm 0.3) \times 10^{-12}$	298 ± 1	Daykin and Wine, 1990 <sup>5</sup>	PLP-A
<i>Relative Rate Coefficients</i>			
$(9.92 \pm 0.20) \times 10^{-13}$	296 ± 2	Atkinson et al., 1984 <sup>6</sup>	RR (a)

### Comments

(a)  $\text{NO}_3$  radicals were generated by the thermal decomposition of  $\text{N}_2\text{O}_5$  in air at 1 atmosphere total pressure. The concentrations of  $\text{CH}_3\text{SCH}_3$  and *trans*-2-butene were measured by GC, and the measured rate coefficient ratio of  $k(\text{NO}_3 + \text{CH}_3\text{SCH}_3)/k(\text{NO}_3 + \textit{trans}-2-butene) =  $2.55 \pm 0.05$  is placed on an absolute basis by use of$

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a rate coefficient of  $k(\text{NO}_3 + \text{trans-2-butene}) = 3.89 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K.<sup>7</sup>

### Preferred Values

$k = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.9 \times 10^{-13} \exp(520/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250-380 K.

### Reliability

$\Delta \log k = \pm 0.15$  at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$ .

### Comments on Preferred Values

The absolute<sup>1-5</sup> and relative<sup>6</sup> rate coefficient studies are in reasonable agreement, although the data of Wallington et al.<sup>2,3</sup> are ~20% lower than the other data.<sup>1,4-6</sup> The absolute rate coefficients measured by Tyndall et al.,<sup>1</sup> Dlugokencky and Howard<sup>4</sup> and Daykin and Wine<sup>5</sup> and the relative rate coefficient of Atkinson et al.<sup>6</sup> have been fitted to an Arrhenius expression to obtain the preferred values. The experimental data show that the rate coefficient is independent of total pressure over the range ~0.0013-1 bar.

The magnitude of the rate constant and the negative temperature dependence indicates that this reaction proceeds by initial addition of the  $\text{NO}_3$  radical to the S atom. The kinetic data of Daykin and Wine<sup>5</sup> and Jensen et al.<sup>8</sup> for  $\text{CH}_3\text{SCH}_3$  and  $\text{CD}_3\text{SCD}_3$  show that the rate determining step involves H- (or D-) atom abstraction, indicating that the reaction is



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This conclusion is consistent with the product studies of Jensen et al.<sup>8,9</sup> and Butkovskaya and Le Bras.<sup>10</sup> Butkovskaya and Le Bras<sup>10</sup> used a DF-MS technique to show that the alternative reaction pathway yielding  $\text{CH}_3\text{SONO}_2 + \text{CH}_3$  accounts for <2% of the overall reaction at 298 K and 1.3 mbar total pressure.

## References

<sup>1</sup> G. S. Tyndall, J. P. Burrows, W. Schneider, and G. K. Moortgat, *Chem. Phys. Lett.*, 130, 463, 1986.

<sup>2</sup> T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.*, 90, 4640, 1986.

<sup>3</sup> T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.*, 90, 5393, 1986.

<sup>4</sup> E. J. Dlugokencky and C. J. Howard, *J. Phys. Chem.*, 92, 1188, 1988.

<sup>5</sup> E. P. Daykin and P. H. Wine, *Int. J. Chem. Kinet.*, 22, 1083, 1990.

<sup>6</sup> R. Atkinson, J. N. Pitts, Jr., and S. M. Aschmann, *J. Phys. Chem.*, 88, 1584, 1984.

<sup>7</sup> R. Atkinson, *J. Phys. Chem. Ref. Data*, 26, 215, 1997.

<sup>8</sup> N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, *J. Atmos. Chem.*, 14, 95, 1992.

<sup>9</sup> N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, *Atmos. Environ.*, 25A, 1897, 1991.

<sup>10</sup> N. I. Butkovskaya and G. Le Bras, *J. Phys. Chem.*, 98, 2582, 1994.

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## NO<sub>3</sub> + CH<sub>3</sub>SSCH<sub>3</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.9 \times 10^{-13} \exp[(290 \pm 50)/T]$ $(4.9 \pm 0.8) \times 10^{-13}$	280-350 298 ± 2	Wallington et al., 1986 <sup>1</sup>	FP-A
$7.4 \times 10^{-13} \exp[(0 \pm 200)/T]$ $(7.4 \pm 1.5) \times 10^{-13}$	334-382 298*	Dlugokencky and Howard, 1988 <sup>2</sup>	F-LIF
<i>Relative Rate Coefficients</i>			
(see comment)	297 ± 2	Mac Leod et al., 1986 <sup>3</sup>	RR (a)

### 5 Comments

(a) NO<sub>3</sub> radicals were generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub> in N<sub>2</sub>O<sub>5</sub>-NO<sub>2</sub>-air mixtures at atmospheric pressure. The relative decay rates of CH<sub>3</sub>SSCH<sub>3</sub> and *trans*-2-butene were monitored by FTIR spectroscopy and GC, respectively. However, the more recent study of Atkinson et al.<sup>4</sup> has shown that reliable rate coefficient data cannot be obtained from the chemical system used by Mac Leod et al.<sup>3</sup>

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## Preferred Values

$k = 7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range ~300-380 K.

### 5 *Reliability*

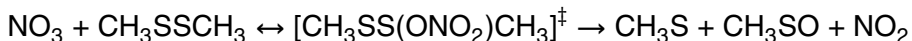
$\Delta \log k = \pm 0.3$  at 298 K.

$\Delta(E/R) = \pm 500$  K.

### 10 *Comments on Preferred Values*

The two absolute studies<sup>1,2</sup> are in reasonable agreement with respect to the room temperature rate coefficient. While the reported rate coefficient from the relative rate study<sup>3</sup> was an order of magnitude lower than the absolute data, the recent study of  
15 Atkinson et al.<sup>4</sup> shows that this was due to complexities in the experimental system used. Accordingly, the preferred values are based upon the absolute rate studies, and mainly on the data of Dlugokencky and Howard,<sup>2</sup> with the error limits being sufficient to encompass the data of Wallington et al.<sup>1</sup>

As for the NO<sub>3</sub> radical reactions with CH<sub>3</sub>SH and CH<sub>3</sub>SCH<sub>3</sub>, the NO<sub>3</sub> radical reaction  
20 with CH<sub>3</sub>SSCH<sub>3</sub> is expected to proceed by initial addition, followed by decomposition of the addition adduct<sup>3,5</sup>



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1 T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem., 90,  
25 5393, 1986.

2 E. J. Dlugokencky and C. J. Howard, J. Phys. Chem., 92, 1188, 1988.

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<sup>4</sup> R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., *J. Geophys. Res.*, 93, 7125, 1988.

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## HS + O<sub>2</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<4 \times 10^{-17}$	298	Black, 1984 <sup>1</sup>	PLP-LIF
$\leq 1 \times 10^{-17}$	298	Fiedl et al., 1985 <sup>2</sup>	DF-LIF
$<1 \times 10^{-14}$	298	Schoenle et al., 1987 <sup>3</sup>	DF-MS
$<4 \times 10^{-19}$	298	Stachnik and Molina, 1987 <sup>4</sup>	PLP-UVA
$<1.5 \times 10^{-17}$	295	Wang et al., 1987 <sup>5</sup>	DF-LMR

### Preferred Values

<sup>5</sup>  $k < 4 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Comments on Preferred Values

<sup>10</sup> The reaction of HS with O<sub>2</sub> is so slow that attempts to measure the rate coefficient have yielded only upper limits that fall in the range  $4 \times 10^{-19}$  to  $4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. The preferred value is from the study of Stachnik and Molina,<sup>4</sup> which gives the lowest upper limit and appears reliable.

<sup>15</sup> In a theoretical study by Goumri et al.,<sup>6</sup> the kinetics of the reaction HS + O<sub>2</sub> → HSOO were analyzed using RRKM theory with Gaussian-2 (G2) theory being used to calculate the thermochemistry. Under atmospheric conditions the rate constant is close to the low-pressure limit  $k_0 = 9.2 \times 10^{-34} (T/298)^{-1.69} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for  $T = 200$ – $400$  K. The low value of the S-O bond dissociation energy (91.5 kJ·mol<sup>-1</sup>) implies that

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H<sub>2</sub>SO<sub>4</sub> formation is unimportant in the atmosphere.

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- <sup>2</sup> R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem., 89, 5505, 1985.
- <sup>3</sup> G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem., 91, 66, 1987.
- <sup>4</sup> R. A. Stachnik and M. J. Molina, J. Phys. Chem., 91, 4603, 1987.
- <sup>5</sup> N. S. Wang, E. R. Lovejoy, and C. J. Howard, J. Phys. Chem., 91, 5743, 1987.
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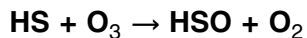
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$$\Delta H^\circ = -290 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.2 \pm 1.0) \times 10^{-12}$	298	Friedl et al., 1985 <sup>1</sup>	DF-LIF
$(2.9 \pm 0.6) \times 10^{-12}$	298	Schoenle et al., 1987 <sup>2</sup> ; Schindler and Benter, 1988 <sup>3</sup>	DF-MS (a)
$1.1 \times 10^{-11} \exp[(-280 \pm 50)/T]$	296-431	Wang and Howard, 1990 <sup>4</sup>	DF-LMR
$(4.39 \pm 0.88) \times 10^{-12}$	298		

### Comments

(a) The value published in Schoenle et al.<sup>2</sup> was corrected in the Erratum by Schindler and Benter,<sup>3</sup> to the value given in the table.

### Preferred Values

<sup>10</sup>  $k = 3.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.  
 $k = 9.5 \times 10^{-12} \exp(-280/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290-440 K.

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## Reliability

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta(E/R) = \pm 250$  K.

5

### Comments on Preferred Values

The values<sup>1,3,4</sup> of  $k$  at 298 K agree reasonably well. A mean of the values from the three studies<sup>1,3,4</sup> is taken as the preferred value. There is only one measurement of the temperature coefficient,<sup>4</sup> which is the basis of the recommended expression, with the pre-exponential factor chosen to fit the recommended value of  $k$  at 298 K.

10

Since there is only one determination of the temperature dependence of  $k$ , and in view of the complexity of the secondary chemistry in these systems, substantial error limits are assigned.

15

## References

<sup>1</sup> R. R. Friedl, W. H. Brune, and J. G. Anderson, *J. Phys. Chem.*, 89, 5505, 1985.

<sup>2</sup> G. Schoenle, M. M. Rahman, and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.*, 91, 66, 1987.

<sup>3</sup> R. N. Schindler and Th. Benter, *Ber. Bunsenges. Phys. Chem.*, 92, 558, 1988.

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<sup>4</sup> N. S. Wang and C. J. Howard, *J. Phys. Chem.*, 94, 8787, 1990.

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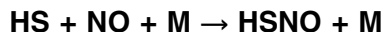
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$$\Delta H^\circ = -139 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients

### 5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.7 \times 10^{-31} (T/300)^{-2.48} [\text{N}_2]$	250-445	Black et al., 1984 <sup>1</sup>	PLP-LIF (a)
$(1.4 \pm 0.13) \times 10^{-30} [\text{Ar}]$	293	Bulatov et al., 1985 <sup>2</sup>	PLP (b)

## Comments

(a) HS formed by photolysis of  $\text{H}_2\text{S}$  at 193 nm and detected at 354.5 nm. The pressure dependence was studied over the range 40-1013 mbar (50–750 Torr). The falloff curve was represented with  $F_c = 0.6$  and  $k_\infty = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Theoretical modeling with the given  $\Delta H^\circ$ .

(b) Intracavity laser spectroscopic detection of HSO radicals at 583 nm in photolyzed  $\text{H}_2\text{S-NO-NO}_2\text{-Ar}$  mixtures, with HSO radicals being formed from the reaction  $\text{HS} + \text{NO}_2$ . Measurements were carried out at 16 mbar (12 Torr) total pressure.

### 15 Preferred Values

$k_0 = 2.4 \times 10^{-31} (T/300)^{-2.5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250-300 K.

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## Reliability

$\Delta \log k_0 = \pm 0.3$  at 298 K.

5  $\Delta n = \pm 1$ .

## Comments on Preferred Values

10 The temperature-dependent measurements from ref. 1 give a consistent picture for the association reaction. Previous work<sup>3</sup> at low pressures did not identify the termolecular nature of the reaction and yielded significantly higher rate coefficients ( $5.6 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  at 10 Torr Ar and 298 K).

## High-pressure rate coefficients

### Rate coefficient data

$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
( $2.7 \pm 0.5$ ) $\times 10^{-11}$	250-300	Black et al., 1984 <sup>1</sup>	PLP-LIF (a)

## Comments

(a) See comment (a) for  $k_0$ .

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## Preferred Values

$k_{\infty} = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 250-300 K.

### 5 *Reliability*

$\Delta \log k_{\infty} = 0.5$  over the temperature range 250-300 K.

### *Comments on Preferred Values*

10

The falloff extrapolation with  $F_c = 0.6$  of ref. 1 towards  $k_{\infty}$  appears less certain than to  $k_0$ . The preferred values are based on the data of Black et al.<sup>1</sup>

## References

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- <sup>2</sup> V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim Fiz., 4, 1353, 1985.
- <sup>3</sup> J. J. Tiee, F. B. Wampler, R. C. Oldenburg and W. W. Rice, Chem. Phys. Lett., 82, 80, 1981.

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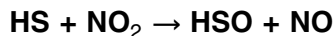
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$$\Delta H^\circ = -90 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.5 \pm 0.4) \times 10^{-11}$	298	Black, 1984 <sup>1</sup>	PLP-LIF
$(2.4 \pm 0.2) \times 10^{-11}$	293	Bulatov et al., 1984 <sup>2</sup>	PLP-A (a)
$(3.0 \pm 0.8) \times 10^{-11}$	298	Fiedl et al., 1985 <sup>3</sup>	DF-LIF
$(8.6 \pm 0.9) \times 10^{-11}$	298	Schoenle et al., 1987 <sup>4</sup>	DF-MS (b)
$4.8 \pm 1.0) \times 10^{-11}$	298	Stachnik and Molina, 1987 <sup>5</sup>	PLP-UVA
$2.9 \times 10^{-11} \exp(237/T)$	221-415	Wang et al., 1987 <sup>6</sup>	DF-LMR
<sup>5</sup> $(6.7 \pm 1.0) \times 10^{-11}$	298		

### Comments

- (a) HSO radical product was monitored by intracavity laser absorption at 583 nm.
- (b) Measured both HS decay and HSO formation by MS. If the HS decay data are taken alone the rate coefficient (once corrected according to erratum paper) increases to  $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

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## Preferred Values

$k = 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 2.9 \times 10^{-11} \exp(240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220-420 K.

### 5 *Reliability*

$\Delta \log k = \pm 0.3$  at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$ .

### 10 *Comments on Preferred Values*

There is considerable scatter in the measured values of  $k^{1-6}$  with no obvious correlation with the conditions used or the technique. The presence of H atoms in the system is known to lead to complicating secondary chemistry, and some of the differences may be due to this, particularly where HS has been generated by photolysis of H<sub>2</sub>S. In more recent studies,<sup>5,6</sup> care has been taken to eliminate or model such effects, but significant differences still persist. The study of Wang et al.<sup>6</sup> represents the only dataset in which different sources of HS have been employed to get the same result, and the only study in which data was obtained in the absence of H<sub>2</sub>S. Wang et al.<sup>6</sup> also showed that the reaction DS + NO<sub>2</sub> has the same rate coefficient as HS + NO<sub>2</sub>. In a further study, using C<sub>2</sub>H<sub>4</sub>S as DS source, Fenter and Anderson<sup>7</sup> obtained  $k(273-373 \text{ K}) = (3.4 \pm 0.8) \times 10^{-11} \exp[(210 \pm 70)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reaction of DS with NO<sub>2</sub>. This is in good agreement with the result of Wang et al.<sup>6</sup> The preferred value at 298 K and the temperature coefficient are taken from the study of Wang et al.<sup>6</sup> The absence of any pressure effect on the rate constant at pressures up to 0.96 bar<sup>1,5</sup> indicates that any addition channel is unimportant up to these pressures.

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- <sup>2</sup> V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz., 3, 1300, 1984.
- <sup>3</sup> R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem., 89, 5505, 1985.
- <sup>4</sup> G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem., 91, 66, 1987, revised by R. N. Schindler and Th. Benter, Ber. Bunsenges. Phys. Chem., 92, 558, 1988.
- <sup>5</sup> R. A. Stachnik and M. J. Molina, J. Phys. Chem., 91, 4603, 1987.
- <sup>6</sup> N. S. Wang, E. R. Lovejoy, and C. J. Howard, J. Phys. Chem., 91, 5743, 1987.
- <sup>7</sup> F. F. Fenter and J. G. Anderson, Int. J. Chem. Kin., 26, 801, 1994.

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## HSO + O<sub>2</sub> → products

### Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 2.0 \times 10^{-17}$	296	Lovejoy et al., 1987 <sup>1</sup>	DF-LMR

### Preferred Values

<sup>5</sup>  $k \leq 2.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K.

#### *Comments on Preferred Values*

The reaction is slow and only an upper limit to  $k$  is available.<sup>1</sup>

### <sup>10</sup> References

<sup>1</sup> E. R. Lovejoy, N. S. Wang and C. J. Howard, J. Phys. Chem., 91, 5749, 1987.

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$$\Delta H^\circ(1) = 4 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -95 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -361 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2 + k_3$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_3 = 1 \times 10^{-12} \exp(-1000/T)$	296-404	Wang and Howard, 1990 <sup>1</sup>	(a,b)
$k_3 = (3.5 \pm 1.5) \times 10^{-14}$	296		
$k_3 = 2.1 \times 10^{-12} \exp[(-1120 \pm 320)/T]$	273-423	Lee et al., 1994 <sup>2</sup>	DF-LIF/A
$k_3 = (4.7 \pm 1.0) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$k_1 = 7 \times 10^{-14}$	297	Wang and Howard, 1990 <sup>1</sup>	DF-LMR (c)
$k_1 = 2.7 \times 10^{-13} \exp(-400/T)$	297-405		(b)
$1.1 \times 10^{-13}$	298	Fiedl et al., 1985 <sup>3</sup>	(d)

### Comments

(a) DF-LMR. Monitoring HSO decay gives the sum of all reaction channels apart from (1). However, OH is not detected (see below) and in the absence of further information on other reaction channels we equate this to reaction 3.

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(b) No error limits given as only a very limited data set obtained.

(c) Value obtained by numerical fitting to HS profile in excess of O<sub>3</sub>. Value of rate coefficient for HS + O<sub>3</sub> used in simulation ( $4.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) was taken from the same study. Use of the recommended value for  $k(\text{HS} + \text{O}_3)$  will reduce the value obtained for  $k_1$ .

(d) Discharge flow system. The HS + O<sub>3</sub> reaction was studied with HS radicals being monitored by LIF. Addition of O<sub>3</sub> gave an initial decrease in [HS], which finally attained a steady state indicating regeneration of HS, postulated to be by the HSO + O<sub>3</sub> reaction. A rate coefficient ratio of  $k/k(\text{HS} + \text{O}_3) = 0.031$  was obtained and placed on an absolute basis by use of  $k(\text{HS} + \text{O}_3) = 3.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

### Preferred Values

$k = 1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_1 = 6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_3 = 5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Reliability

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta \log k_1 = \pm 0.3$  at 298 K.

$\Delta \log k_3 = \pm 0.3$  at 298 K.

### Comments on Preferred Values

In the recent study by Lee et al.<sup>2</sup> the rate coefficient measured is that for HSO removal by all channels other than channel 1 giving HS as a product, which subsequently

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regenerates HSO by reaction with the O<sub>3</sub> present. However, in our recommendations the rate coefficients measured by Lee et al.<sup>2</sup> are assigned to channel 3 on the grounds that Friedl et al.<sup>3</sup> could not detect HO production (channel 2); some further support for channel 3 comes from the work of Lovejoy et al.<sup>4</sup> who found that HSO<sub>2</sub> is readily formed by the HSO + NO<sub>2</sub> reaction.

Both Wang and Howard<sup>1</sup> and Lee et al.<sup>2</sup> measured a similar temperature coefficient for  $k_3$ , the preferred values are only given at 298 K until further studies are made on the effects of temperature on all of the rate coefficients.

## References

<sup>1</sup> N. S. Wang and C. J. Howard, J. Phys. Chem., 94, 8787, 1990.

<sup>2</sup> Y.-Y. Lee, Y.-P. Lee, and N. S. Wang, J. Chem. Phys., 100, 387, 1994.

<sup>3</sup> R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem., 89, 5505, 1985.

<sup>4</sup> E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem., 91, 5749, 1987.

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## HSO + NO → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.6 \pm 0.4) \times 10^{-14}$	293	Bulatov et al., 1985 <sup>1</sup>	PLP-A (a)
$\leq 1.0 \times 10^{-15}$	298	Lovejoy et al., 1987 <sup>2</sup>	DF-LMR

### Comments

- 5 (a) HSO radicals monitored by intra-cavity laser absorption at 583 nm.

### Preferred Values

$k < 1.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Comments on Preferred Values

10

The only two available measurements of  $k$  differ by at least a factor of 26. This is unlikely to be due to the higher pressures used in the Bulatov et al.<sup>1</sup> study, but may arise from secondary chemistry in their HSO source which employed relatively large H<sub>2</sub>S concentrations. Provisionally, the upper limit to the rate coefficient reported by

15 Lovejoy et al.<sup>2</sup> is preferred.

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## References

- <sup>1</sup> V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, *Khim. Fiz.*, 4, 1353, 1985.  
<sup>2</sup> E. R. Lovejoy, N. S. Wang, and C. J. Howard, *J. Phys. Chem.*, 91, 5749, 1987.

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## HSO + NO<sub>2</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4 \times 10^{-12}$	293	Bulatov et al., 1984 <sup>1</sup>	PLP-A (a)
$(9.6 \pm 2.4) \times 10^{-12}$	298	Lovejoy et al., 1987 <sup>2</sup>	DF-LMR

### Comments

- 5 (a) HSO radicals monitored by intracavity laser absorption at 583 nm.

### Preferred Values

$k = 9.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Reliability

10

$\Delta \log k = \pm 0.3$  at 298 K.

### Comments on Preferred Values

15

The only two measurements of  $k$  differ by at least a factor of 2. Lovejoy et al.<sup>2</sup> have suggested that the relatively high H<sub>2</sub>S concentrations used by Bulatov et al.<sup>1</sup> may have led to side reactions regenerating HSO. The value of Lovejoy et al.<sup>2</sup> is preferred, but wide error limits are assigned awaiting confirmatory studies. HO<sub>2</sub> was observed as a

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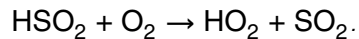
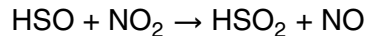
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product of the reaction by Lovejoy et al.,<sup>2</sup> which they suggest arises from the reaction sequence:



## 5 References

<sup>1</sup> V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, *Khim. Fiz.*, 3, 1300, 1984.

<sup>2</sup> E. R. Lovejoy, N. S. Wang, and C. J. Howard, *J. Phys. Chem.*, 91, 5749, 1987.

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## HSO<sub>2</sub> + O<sub>2</sub> → products

### Rate coefficient data

<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
3.0 x 10 <sup>-13</sup>	296	Lovejoy et al., 1987 <sup>1</sup>	DF-LMR

### Preferred Values

5 *k* = 3.0 x 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K.

### Reliability

Δlog *k* = ±0.8 at 298 K.

10

### Comments on Preferred Values

There is only one study of this reaction.<sup>1</sup> The method used to obtain the rate coefficient was indirect, and this leads us to suggest substantial error limits despite the high quality of the experimental work.

15

### References

<sup>1</sup> E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem., 91, 5749, 1987.

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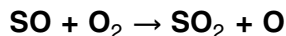
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$$\Delta H^\circ = -52.6 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.07 \pm 0.16) \times 10^{-16}$	298	Black et al., 1982 <sup>1</sup>	(a)
$2.4 \times 10^{-13} \exp[-(2370_{-250}^{+200})/T]$	230-420	Black et al., 1982 <sup>2</sup>	(a)
$8.4 \times 10^{-17}$	298		
$1.00 \times 10^{-13} \exp[-(2180 \pm 117)/T]$	262-363	Goede and Schurath, 1983 <sup>3</sup>	(b)
$6.7 \times 10^{-17}$	298		
$2.2 \times 10^{-13} \exp[-(2340 \pm 90)/T]$	250-585	Garland, 1998 <sup>4</sup>	(c)
$8.6 \times 10^{-17}$	298		

### Comments

(a) Pulsed laser photolysis of SO<sub>2</sub> at 193 nm, with SO radicals being detected by chemiluminescence from the SO + O<sub>3</sub> reaction. Pseudo-first-order decays of SO were monitored in the presence of excess O<sub>2</sub>. Total pressure = 133-667 mbar (100-500 Torr) of O<sub>2</sub> + He.

(b) SO produced from the O + OCS reaction in a flow system. Controlled admission of SO radicals to a static volume where the pseudo-first-order decay of SO in excess O<sub>2</sub> was followed by SO + O<sub>3</sub> chemiluminescence. Total pressure =

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0.0013–0.27 mbar (1–200 mTorr) O<sub>2</sub>. Only an Arrhenius expression was given with no individual rate coefficients at the temperatures studied.

(c) PLP of DMSO at 222 nm coupled with LIF detection of SO at 236.35 nm at 2 x 10<sup>-3</sup> mbar of DMSO, up to 13.3 mbar of O<sub>2</sub> and 27 mbar total pressure of Ar in a flowing gas experiment. The measurements were performed under pseudo-first order conditions in the range 450–585 K and resulted in the Arrhenius expression displayed in the table when combined with the data of Black et al.<sup>2</sup>

### Preferred Values

$k = 7.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.6 \times 10^{-13} \exp(-2280/T)$  over the temperature range 230–420 K.

### Reliability

$\Delta \log k = \pm 0.15$  at 298 K.

$\Delta(E/R) = \pm 500$  K.

### Comments on Preferred Values

This reaction is very slow and measurement of the rate coefficient  $k$  is subject to errors due to impurities. For this reason, Black et al.<sup>1,2</sup> favour their lower value of  $k$  at 298 K obtained in the temperature dependence study.<sup>2</sup> The Goede and Schurath<sup>3</sup> values are systematically about 35% lower than those from reference 2, but appear to have less experimental uncertainty at temperatures <300 K. The preferred value for the rate coefficient  $k$  at 298 K and for the temperature dependence are from Black et al.<sup>2</sup> and Goede and Schurath.<sup>3</sup> The  $A$ -factor has been adjusted to give the preferred 298 K rate coefficient.

## References

- <sup>1</sup> G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett., 90, 55, 1982.
- <sup>2</sup> G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett., 93, 598, 1982.
- <sup>3</sup> H.-J. Goede and U. Schurath, Bull. Soc. Chim. Belg., 92, 661, 1983.
- <sup>4</sup> N. L. Garland, Chem. Phys. Lett., 290, 385, 1998.

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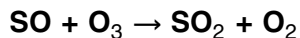
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$$\Delta H^\circ = -444.5 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.5 \times 10^{-12} \exp[-(1057 \pm 202)/T]$	223-300	Halstead and Thrush, 1966 <sup>1</sup>	DF-CL
$7.2 \times 10^{-14}$	298		
$(8.7 \pm 1.6) \times 10^{-14}$	$296 \pm 4$	Robertshaw and Smith, 1980 <sup>2</sup>	PLP-CL
$(1.06 \pm 0.16) \times 10^{-13}$	298	Black et al., 1982 <sup>3</sup>	(a)
$4.8 \times 10^{-12} \exp[-(1170^{+80}_{-120})/T]$	230-420	Black et al., 1982 <sup>4</sup>	(a)
$9.46 \times 10^{-14}$	298		

### Comments

(a) Pulsed laser photolysis of SO<sub>2</sub>-O<sub>3</sub> mixtures at 193 nm with SO<sub>2</sub> being monitored by CL from the SO + O<sub>3</sub> reaction. Excess O<sub>3</sub> was determined by UV absorption. The total pressure = 267 mbar (200 Torr) of He.

### Preferred Values

$k = 8.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 4.5 \times 10^{-12} \exp(-1170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230-420 K.

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## Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

5  $\Delta(E/R) = \pm 150$  K.

## Comments on Preferred Values

10 The studies of Halstead and Thrush,<sup>1</sup> Robertshaw and Smith<sup>2</sup> and Black et al.<sup>3,4</sup> are in general agreement. The preferred 298 K rate coefficient is the mean of these measurements.<sup>1-4</sup> The temperature dependence of Black et al.<sup>4</sup> is accepted since this study covered a much larger temperature range than the earlier study of Halstead and Thrush,<sup>1</sup> which nevertheless gave a value of  $E/R$  within the experimental error of the later study.<sup>4</sup>

## 15 References

<sup>1</sup> C. J. Halstead and B. A. Thrush, Proc. R. Soc. London Ser. A, 295, 380, 1966.

<sup>2</sup> J. S. Robertshaw and I. W. M. Smith, Int. J. Chem. Kinet., 12, 729, 1980.

<sup>3</sup> G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett., 90, 55, 1982.

<sup>4</sup> G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett., 93, 598, 1982.

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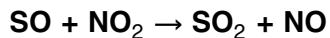
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$$\Delta H^\circ = -244.5 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
<sup>5</sup> $(1.37 \pm 0.07) \times 10^{-11}$	210-363	Brunning and Stief, 1986 <sup>1</sup>	DF-MS

### Preferred Values

$k = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 210-360 K.

### <sup>10</sup> Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$ .

### <sup>15</sup> Comments on Preferred Values

The measurements of Brunning and Stief<sup>1</sup> are the only available temperature dependent study of the rate coefficient, and indicate no measurable change in the rate coefficient  $k$  over the temperature range 210-363 K. This finding is the basis for our present recommendation for the rate coefficient, which agrees with three previous studies performed at ambient temperature.<sup>2-4</sup>

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- <sup>2</sup> M. A. A. Clyne and A. J. MacRobert, Int. J. Chem. Kinet., 12, 79, 1980.
- <sup>3</sup> G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett., 90, 55, 1982.
- <sup>4</sup> M. A. A. Clyne, C. J. Halstead, and B. A. Thrush, Proc. Roy. Soc. London, Ser. A, 295, 355, 1966.

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## SO<sub>3</sub> + H<sub>2</sub>O → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$9 \times 10^{-13}$	300	Castleman et al., 1974 <sup>1</sup>	F-MS
$\leq(5.7 \pm 0.9) \times 10^{-15}$	298	Wang et al., 1989 <sup>2</sup>	(a)
$\leq 2.4 \times 10^{-15}$	~298	Reiner and Arnold, 1993 <sup>3</sup>	(b)
$(1.2 \pm 0.2) \times 10^{-15}$	298	Reiner and Arnold, 1994 <sup>4</sup>	(b)
Complex mechanism	295	Kolb et al., 1994 <sup>5</sup>	(c)
Complex mechanism	250-360	Lovejoy et al., 1996 <sup>6</sup>	(d)
Complex mechanism	283-370	Jayne et al., 1997 <sup>7</sup>	(e)

### Comments

- 5 (a) Flow system with He and N<sub>2</sub> as carrier gases and H<sub>2</sub>O in large excess over SO<sub>3</sub>. SO<sub>3</sub> was monitored by the photodissociation of SO<sub>3</sub> at 147 nm and detection of SO<sub>2</sub> fluorescence at 300-390 nm. A halocarbon wall coating of the flow tube was used.
- 10 (b) Fast flow system at pressures of 31 to 260 mbar of synthetic air, using CIMS to detect SO<sub>3</sub>, H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub>. Small corrections for wall reactions were applied.
- (c) Atmospheric pressure turbulent flow reactor using N<sub>2</sub> as a carrier gas in the pressure range 133-1013 mbar (100-760 Torr) and CIMS detection. Both the decrease in SO<sub>3</sub> as well as the increase in H<sub>2</sub>SO<sub>4</sub> were monitored. The rate law was found to be first-order in [SO<sub>3</sub>] and second-order in [H<sub>2</sub>O]. Rate constants ranging from

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$2 \times 10^{-10}$  to  $1.4 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> were estimated based on H<sub>2</sub>O dimers and the SO<sub>3</sub>-H<sub>2</sub>O adduct, respectively.

(d) Laminar flow reactor with detection by CIMS. The observations were consistent with rapid association of SO<sub>3</sub> with H<sub>2</sub>O to form the adduct H<sub>2</sub>O-SO<sub>3</sub>, which then reacts with water to form H<sub>2</sub>SO<sub>4</sub>.

(e) Details at (c). The pressure-independent first-order loss rate coefficient for SO<sub>3</sub> may be expressed as  $k = (3.9 \pm 0.8) \times 10^{-41} \exp(6830/T)[\text{H}_2\text{O}]^2 \text{s}^{-1}$  over the range 283 to 370 K. The onset of H<sub>2</sub>SO<sub>4</sub> homogeneous nucleation was observed at  $[\text{SO}_3] > 10^{12}$  molecule cm<sup>-3</sup>.

## Preferred Values

$k = 5.7 \times 10^4 \text{ s}^{-1}$  at 298 K and 50% relative humidity.

### *Comments on Preferred Values*

No recommendation was made on the basis of the work of Castleman et al.,<sup>1</sup> due to the likely interference of wall reactions in their work. The studies of Wang et al.,<sup>2</sup> Reiner and Arnold<sup>3,4</sup> and Kolb et al.<sup>5</sup> have now confirmed that suspicion. Wang et al.<sup>2</sup> obtained an upper limit to the rate coefficient which is more than two orders of magnitude lower than the value of Castleman et al.<sup>1</sup> by treatment of the flow tube walls to reduce wall effects, and the studies of Reiner et al.,<sup>3,4</sup> using the laminar flow tube method, obtain the lowest values for the rate constant.<sup>3,4</sup> The flow studies of Kolb et al.,<sup>5</sup> Lovejoy et al.<sup>6</sup> and Jayne et al.<sup>7</sup> arrive at a rate law first order in SO<sub>3</sub> and second order in H<sub>2</sub>O.

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- <sup>2</sup> X. Wang, Y. G. Yin, M. Suto, L. C. Lee, and H. E. O'Neal, J. Chem. Phys., 89, 4853, 1989.
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- <sup>4</sup> T. Reiner and F. Arnold, J. Chem. Phys., 101, 7399, 1994.
- <sup>5</sup> C. E. Kolb, J. T. Jayne, D. R. Worsnop, M. J. Molina, R. F. Meads, and A. A. Viggiano, J. Am. Chem. Soc., 116, 10314, 1994.
- <sup>6</sup> E. R. Lovejoy, D. R. Hanson, and L. G. Huey, J. Phys. Chem., 100, 19911, 1996.
- <sup>7</sup> J. T. Jayne, U. Pöschl, Y. Chen, D. Dai, L. T. Molina, D. R. Worsnop, C. E. Kolb and M. J. Molina, J. Phys. Chem. A, 101, 10000, 1997.

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## SO<sub>3</sub> + NH<sub>3</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.9 \pm 1.5) \times 10^{-11}$	298	Shen et al., 1990 <sup>1</sup>	(a)
$(2.0 \pm 0.6) \times 10^{-11}$	295	Lovejoy and Hanson, 1996 <sup>2</sup>	(b)
$(1.8 \pm 0.5) \times 10^{-11}$	300	Lovejoy, 1997 <sup>3</sup>	(c)

### Comments

- (a) Flow system with NH<sub>3</sub> in large excess. [SO<sub>3</sub>] monitored by observation of SO<sub>2</sub> fluorescence in range 280-390 nm from photofragmentation of SO<sub>3</sub> by 147 nm radiation. He carrier gas at 1.3-2.7 mbar (1-2 Torr) total pressure.
- (b) Laminar flow reactor study with N<sub>2</sub> as the carrier gas in the pressure range 13-533 mbar (10-400 Torr), using CIMS detection. Both the decrease of SO<sub>3</sub> as well as the formation of SO<sub>3</sub>·NH<sub>3</sub> were monitored. The rate constant was pressure dependent with  $k_0 = (3.9 \pm 0.8) \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  and  $k_\infty = (4.7 \pm 1.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 295 K.
- (c) Experimental details in (b) except for a reduced pressure range of 27-106 mbar (20-80 Torr) of N<sub>2</sub> and a temperature range of 280-340 K. The rate constant is pressure dependent with  $k_0^{300} = (3.6 \pm 0.4) \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  and  $k_\infty^{300} = (4.3 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . A third law determination of the reaction enthalpy for SO<sub>3</sub> + NH<sub>3</sub> ↔ H<sub>3</sub>NSO<sub>3</sub> resulted in  $\Delta H_{298}^0 = 100.4 \pm 4.2 \text{ kJ mol}^{-1}$ .

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## Preferred Values

$k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and 1 atm.

### Reliability

5

$\Delta \log k = \pm 0.2$  at 298 K.

### Comments on Preferred Values

10

The preferred value is given for one atmosphere from the work of Lovejoy and Hanson in view of the extended pressure range used.<sup>2</sup> The extrapolation of  $k$  to 1 atm has been performed following the Troe formalism. The more recent work<sup>2,3</sup> showed the product of the reaction to be the association complex  $\text{NH}_3 \cdot \text{SO}_3$ , sulfamic acid.

## References

15

<sup>1</sup> G. Shen, M. Suto, and L. C. Lee, J. Geophys. Res., 95, 13981, 1990.

<sup>2</sup> E. Lovejoy and D. R. Hanson, J. Phys. Chem., 100, 4459, 1996.

<sup>3</sup> E. R. Lovejoy, J. Phys. Chem. A 101, 4950, 1997.

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$$\Delta H^\circ(1) = -378 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(2) = -165 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_2 = (4.5 \pm 1.7) \times 10^{-19}$	293	Richardson, 1975 <sup>1</sup>	(a)
$k_2 = (5.9 \pm 1.3) \times 10^{-18}$	495		
$(2.9 \pm 0.4) \times 10^{-19}$	298	Black et al., 1983 <sup>2</sup>	(b)
<i>Branching Ratios</i>			
$k_2/k_1 = 1.2$	298	Wood and Heicklen, 1971 <sup>3</sup> , 1973/74 <sup>4</sup>	(c)
$k_2/k_1 = 1.2$	341-415	Wood and Heicklen, 1971 <sup>5</sup>	(d)

### 10 Comments

(a) Discharge flow system used. CS radicals were produced by a discharge through CS<sub>2</sub>, CS, SO<sub>2</sub>, CO and OCS were measured by MS. A very slow linear flow rate ( $\sim 100 \text{ cm s}^{-1}$ ) was necessary to observe the reaction. SO<sub>2</sub>, a product formed via channel (1), was at least one order of magnitude lower in concentration than CO and OCS.

15 (b) CS radicals were produced by pulsed laser photolysis of CS<sub>2</sub> in He bath gas [32 mbar (24 Torr)], and were monitored by LIF at 257.7 nm.

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(c) Photolysis of CS<sub>2</sub>-O<sub>2</sub> mixtures, with analysis of CO, OCS, SO<sub>2</sub> and S<sub>2</sub>O products by GC. Light of wavelength 313 nm was used in ref. 3, which has insufficient energy to dissociate the CS<sub>2</sub>, but CS was postulated to have been formed by reaction of electronically excited CS<sub>2</sub> with O<sub>2</sub>. In the later study,<sup>4</sup>  $\lambda = 213.9$  nm was used which can photodissociate CS<sub>2</sub>.

(d) Explosion limits of CS<sub>2</sub>-O<sub>2</sub> mixtures were determined by GC. The [CO]/[OCS] ratio was relatively unaffected by pressure and temperature changes, and the value of 0.84 found for this ratio is the same as that observed in photochemical studies.<sup>3,4</sup> The explosion limits were modeled on the basis of an assumed mechanism of eight reactions, and a computer fit to the data yielded the value for  $k_2/k_1$ .

**Preferred Values**

$k = 2.9 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

*Reliability*

$\Delta \log k = \pm 0.6$  at 298 K.

*Comments on Preferred Values*

The reaction of CS with O<sub>2</sub> is slow at 298 K and difficult to study. The technique used by Black et al.<sup>2</sup> seems the most suitable for avoiding the difficulties associated with the slowness of the reaction, and their rate coefficient at 298 K is preferred.

The relative importance of the two possible reaction channels is in dispute. Evidence from the photochemical and explosion limit studies<sup>3-5</sup> indicate a comparable importance of channels (1) and (2), but in the more direct flow<sup>1</sup> system study,  $k_1$  was found to be at least an order of magnitude less than  $k_2$ . However, the value of  $k_2$  obtained

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in the fast flow study<sup>1</sup> appears to be unacceptably high. We make no recommendation for the branching ratio.

The one available measurement of  $k$  at higher temperatures,<sup>1</sup> when combined with the 298 K values, leads to an Arrhenius expression with an extremely low pre-exponential factor. No recommendation is hence made for the temperature dependence.

## References

<sup>1</sup> R. J. Richardson, J. Phys. Chem., 79, 1153, 1975.

<sup>2</sup> G. Black, L. E. Jusinski, and T. G. Slanger, Chem. Phys. Lett., 102, 64, 1983.

<sup>3</sup> W. P. Wood and J. Heicklen, J. Phys. Chem., 75, 854, 1971.

<sup>4</sup> W. P. Wood and J. Heicklen, J. Photochem., 2, 173, 1973/74.

<sup>5</sup> W. P. Wood and J. Heicklen, J. Phys. Chem., 75, 861, 1971.

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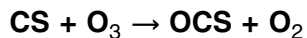
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$$\Delta H^\circ(1) = -557 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
<sup>5</sup> $(3.0 \pm 0.4) \times 10^{-16}$	298	Black et al., 1983 <sup>1</sup>	(a)

### Comments

(a) CS radicals were produced by pulsed laser photolysis of CS<sub>2</sub> at 193 nm, with He as the buffer gas at a total pressure of 67-400 mbar (50-300 Torr). CS radicals were monitored by LIF at 257.7 nm.

### Preferred Values

$$k = 3.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

### Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

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## Comments on Preferred Values

The only available measurement of the rate coefficient  $k$  is that of Black et al.<sup>1</sup> Their value is accepted, with substantial error limits.

### 5 References

<sup>1</sup> G. Black, L. E. Jusinski, and T. G. Slanger, Chem. Phys. Lett., 102, 64, 1983.

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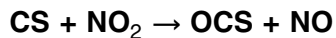
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$$\Delta H^\circ = -357 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
<sup>5</sup> $(7.6 \pm 1.1) \times 10^{-17}$	298	Black et al., 1983 <sup>1</sup>	(a)

### Comments

(a) CS radicals were produced by pulsed laser photolysis of CS<sub>2</sub> at 193 nm and monitored by LIF at 257.7 nm. He [32 mbar (24 Torr) total pressure] was used as the buffer gas.

### Preferred Values

$$k = 7.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

### Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

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The only available measurement of  $k$  is that of Black et al.<sup>1</sup> Their value is accepted, but with substantial error limits.

## References

- <sup>1</sup> G. Black, L. E. Jusinski, and T. G. Slanger, Chem. Phys. Lett., 102, 64, 1983.

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## CH<sub>2</sub>SH + O<sub>2</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.5 \pm 1.0) \times 10^{-12}$	298	Anastasi et al., 1992 <sup>1</sup>	(a)
$(4.6 \pm 1.9) \times 10^{-12}$	298	Rahman et al., 1992 <sup>2</sup>	(b)

### Comments

5 (a) Pulsed radiolysis of CH<sub>3</sub>SH-O<sub>2</sub>-SF<sub>6</sub> mixtures at 1 bar total pressure. CH<sub>2</sub>SH and CH<sub>3</sub>S radicals were generated by reactions of the radiolytically produced F atoms with CH<sub>3</sub>SH. [CH<sub>2</sub>SH] was monitored by UV absorption over range 220-380 nm.

10 (b) Fast flow discharge study. CH<sub>2</sub>SH radicals were generated by reaction of F atoms with CH<sub>3</sub>SH, and [CH<sub>2</sub>SH] was monitored by mass spectrometry. The source reactions were simulated to check consumption of F atoms. The total pressure was 3 mbar.

### Preferred Values

$k = 6.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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## Reliability

$\Delta \log k = \pm 0.3$  at 298 K.

### 5 *Comments on Preferred Values*

The only two measurements of  $k$  differ by almost a factor of 2. The values of  $k(\text{CH}_2\text{SH} + \text{NO}_2)$  measured in these two studies also differ, although the error limits are large enough to encompass the two results. Until further studies are carried out,  
10 a mean of the two values is recommended, with substantial error limits.

## References

<sup>1</sup> C. Anastasi, M. Broomfield, O. J. Nielsen, and P. Pagsberg, *J. Phys. Chem.*, 96, 696, 1992.

<sup>2</sup> M. M. Rahman, E. Becker, U. Wille, and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.*, 96, 783, 1992.  
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## CH<sub>2</sub>SH + O<sub>3</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.5 \pm 1.2) \times 10^{-11}$	298	Rahman et al., 1992 <sup>1</sup>	(a)

### Comments

- 5 (a) Fast-flow discharge study. CH<sub>2</sub>SH radicals were generated by the reaction of F atoms with CH<sub>3</sub>SH, and monitored by MS. Source reactions were simulated to check consumption of F atoms. The total pressure was 3 mbar.

### Preferred Values

$$k = 3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

### Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

### Comments on Preferred Values

15 The only available determination<sup>1</sup> of  $k$  is accepted, but with substantial error limits until confirmatory studies can be made.

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<sup>1</sup> M. M. Rahman, E. Becker, U. Wille, and R. N. Schindler, Ber. Bunsenges. Phys. Chem., 96, 783, 1992.

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## CH<sub>2</sub>SH + NO → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.5 \pm 0.2) \times 10^{-11}$	298	Anastasi et al., 1992 <sup>1</sup>	(a)

### Comments

- 5 (a) Pulsed radiolysis of CH<sub>3</sub>SH-O<sub>2</sub>-SF<sub>6</sub> mixtures at 1 bar total pressure. CH<sub>2</sub>SH and CH<sub>3</sub>S radicals were generated by reactions of the radiolytically produced F atoms with CH<sub>3</sub>SH, and [CH<sub>2</sub>SH] was monitored by UV absorption over the wavelength range 220-380 nm.

### Preferred Values

- 10  $k = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

#### *Reliability*

$\Delta \log k = \pm 0.3$  at 298 K.

- 15 *Comments on Preferred Values*

The only available determination<sup>1</sup> of  $k$  is accepted, but with substantial error limits until confirmatory studies are made.

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<sup>1</sup> C. Anastasi, M. Broomfield, O. J. Nielsen, and P. Pagsberg, J. Phys. Chem., 96, 696, 1992.

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## CH<sub>2</sub>SH + NO<sub>2</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.8 \pm 1.0) \times 10^{-11}$	298	Anastasi et al., 1992 <sup>1</sup>	(a)
$(6.9 \pm 4) \times 10^{-11}$	298	Rahman et al., 1992 <sup>2</sup>	(b)

### Comments

(a) Pulsed radiolysis of CH<sub>3</sub>SH-O<sub>2</sub>-SF<sub>6</sub> mixtures at 1 bar total pressure. CH<sub>2</sub>SH and CH<sub>3</sub>S radicals were generated by reactions of the radiolytically produced F atoms with CH<sub>3</sub>SH, and [CH<sub>2</sub>SH] was monitored by UV absorption over the wavelength range 220-380 nm.

(b) Fast flow discharge study. CH<sub>2</sub>SH radicals were generated by the reaction of F atoms with CH<sub>3</sub>SH and were monitored by MS. Source reactions were simulated to check consumption of F atoms. The total pressure was 3 mbar.

### Preferred Values

$k = 4.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

#### Reliability

$\Delta \log k = \pm 0.5$  at 298 K.

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## Comments on Preferred Values

The only two measurements<sup>1,2</sup> of  $k$  differ substantially but because the error limits are large enough to encompass the two results it is difficult to know whether the difference is significant. In the same two studies the values obtained for  $k(\text{CH}_2\text{SH} + \text{O}_2)$  differed to the same degree with much smaller error limits.

Until further studies are carried out, we recommend a weighted mean of the two values and substantial error limits.

## References

<sup>1</sup> C. Anastasi, M. Broomfield, O. J. Nielsen, and P. Pagsberg, J. Phys. Chem., 96, 696, 1992.

<sup>2</sup> M. M. Rahman, E. Becker, U. Wille, and R. N. Schindler, Ber. Bunsenges. Phys. Chem., 96, 783, 1992.

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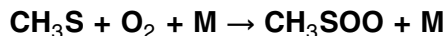
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$$\Delta H^\circ = -48.9 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<2 \times 10^{-17}$	298	Balla et al., 1986 <sup>1</sup>	PLP-LIF
$<1 \times 10^{-16}$	298	Black and Jusinski, 1986 <sup>2</sup>	PLP-LIF
$<2.5 \times 10^{-18}$	298	Tyndall and Ravishankara, 1989 <sup>3</sup>	PLP-LIF
$(1.81 \pm 0.28) \times 10^{-13}$ 107 mbar He	216	Turnipseed et al., 1992 <sup>4</sup>	(a)
$(1.55 \pm 0.23) \times 10^{-13}$ 107 mbar He	222		
$(1.05 \pm 0.20) \times 10^{-13}$ 107 mbar He	233		
$(9.0 \pm 1.6) \times 10^{-14}$ 107 mbar He	237		
$(8.62 \pm 0.84) \times 10^{-14}$ 107 mbar He	242		
$(7.0 \pm 2.0) \times 10^{-14}$ 107 mbar He	250		
<i>Relative Rate Coefficients</i>			
$2 \times 10^{-14}$	298	Hatakeyama and Akimoto, 1983 <sup>5</sup>	RR (b)
$3 \times 10^{-17}$	298	Grosjean, 1984 <sup>6</sup>	RR (c)
$>2.3 \times 10^{-16}$	296	Balla and Heicklen, 1985 <sup>7</sup>	RR (d)

### Comments

(a) Pulsed laser photolysis system with LIF detection of  $\text{CH}_3\text{S}$  radicals. The measured rate coefficients were observed to vary with the total pressure and the dilu-

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ent gas. An upper limit to the rate coefficient for the reaction of the  $\text{CH}_3\text{SOO}$  radical with  $\text{O}_2$  of  $4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 258 K was also derived. The  $\text{CH}_3\text{S-OO}$  bond energy was determined to be  $49 \text{ kJ mol}^{-1}$  at 298 K from measurements of the equilibrium constant over the temperature range 216–258 K, with  $\Delta H_f(\text{CH}_3\text{SOO}) = 75.7 \pm 4.2 \text{ kJ mol}^{-1}$  at 298 K.

(b) Photolysis of  $\text{CH}_3\text{SSCH}_3\text{-RONO-NO}$ -air mixtures. The products were analyzed by FTIR and GC-MS and the yields of  $\text{SO}_2$  and  $\text{CH}_3\text{SNO}$  measured. From an assumed mechanism, the rate coefficient ratio  $k(\text{CH}_3\text{S} + \text{NO})/k = 2 \times 10^3$  was derived. A rate coefficient of  $k(\text{CH}_3\text{S} + \text{NO}) = 4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was used to obtain the rate coefficient given in the table.

(c) Environmental chamber study using the oxidation of organo-sulfur compounds in air by natural sunlight. Major products were  $\text{SO}_2$ ,  $\text{CH}_3\text{SO}_3\text{H}$  and  $\text{HCHO}$ . Production of  $\text{SO}_2$  and sulphur were related to an unidentified compound (assumed to be  $\text{CH}_3\text{SNO}_2$ ) formed from  $\text{CH}_3\text{S} + \text{NO}_2$ . A rate coefficient ratio of  $k(\text{CH}_3\text{S} + \text{NO}_2)/k = 2 \times 10^6$  was derived, and placed on an absolute basis by use of  $k(\text{CH}_3\text{S} + \text{NO}_2) = 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (this evaluation).

(d) From the photolysis of  $(\text{CH}_3\text{S})_2\text{-O}_2\text{-N}_2$  mixtures at 253.7 nm, with product analysis by GC and MS. The  $\text{SO}_2$  yield was measured as a function of  $[(\text{CH}_3\text{S})_2]$ ,  $[\text{O}_2]$  and light intensity. From an assumed mechanism, a value of  $k^2/2k(\text{CH}_3\text{S} + \text{CH}_3\text{S}) > 6 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was derived. A rate coefficient of  $k(\text{CH}_3\text{S} + \text{CH}_3\text{S}) = 4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (from Graham et al.<sup>8</sup>) was used to obtain the rate coefficient given in the table.

### Preferred Values

The data of Turnipseed et al.<sup>4</sup> given in the above Table are preferred. These data at 107 mbar He are described by  $k(210 - 250 \text{ K}) = 1.2 \times 10^{-16} \exp(1580/T) \text{ cm}^3$

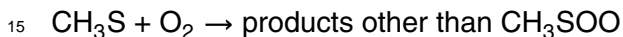
molecule<sup>-1</sup> s<sup>-1</sup>.

### Reliability

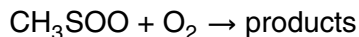
- 5  $\Delta \log k = \pm 0.3$  over the temperature range 216-250 K at 107 mbar He.

### Comments on Preferred Values

10 The study of Turnipseed et al.<sup>4</sup> was the first to observe addition of O<sub>2</sub> to the CH<sub>3</sub>S radical to form CH<sub>3</sub>SOO [and not CH<sub>3</sub>S(O)O], because the reaction was observed to be reversible leading to equilibrium between CH<sub>3</sub>S radicals, O<sub>2</sub> and CH<sub>3</sub>SOO radicals.<sup>4</sup> Previous studies<sup>1-3</sup> of the reaction of CH<sub>3</sub>S radicals with O<sub>2</sub> at 298 K did not observe the equilibrium addition of O<sub>2</sub> to CH<sub>3</sub>S radicals, and the rate coefficients measured correspond to upper limits to the rate coefficients for the reactions



and/or



20 The reaction of CH<sub>3</sub>S radicals with O<sub>2</sub> to form the CH<sub>3</sub>SOO radical, and the reverse reaction, result in ~33% of CH<sub>3</sub>S radicals being present as the CH<sub>3</sub>SOO adduct at 298 K and ground level,<sup>4</sup> with the [CH<sub>3</sub>SOO]/[CH<sub>3</sub>S] ratio being strongly temperature dependent.<sup>4</sup>

### References

- <sup>1</sup> R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys., 109, 101, 1986.  
<sup>2</sup> G. Black and L. E. Jusinski, J. Chem. Soc. Faraday Trans. 2, 82, 2143, 1986.

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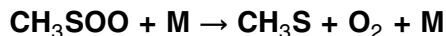
- <sup>3</sup> G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem., 93, 2426, 1989.
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- <sup>7</sup> R. J. Balla and J. Heicklen, J. Photochem., 29, 297, 1985.
- <sup>8</sup> D. M. Graham, R. L. Mieville, R. H. Pallen, and C. Sivertz, Can. J. Chem., 42, 2250, 1964.

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$$\Delta H^\circ = 48.9 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.99 \pm 0.74) \times 10^3$ at 107 mbar He	216	Turnipseed et al., 1992 <sup>1</sup>	(a)
$(3.20 \pm 0.80) \times 10^3$ at 107 mbar He	222		
$(9.1 \pm 2.6) \times 10^3$ at 107 mbar He	233		
$(1.00 \pm 0.12) \times 10^4$ at 107 mbar He	237		
$(1.28 \pm 0.12) \times 10^4$ at 107 mbar He	242		
$(2.4 \pm 0.4) \times 10^4$ at 107 mbar He	250		
<sup>5</sup> $>3.5 \times 10^4$ at 107 mbar He	258		

### Comments

(a) Pulsed laser photolysis system with LIF detection of  $\text{CH}_3\text{S}$  radicals. The formation and decay rate coefficients of  $\text{CH}_3\text{SOO}$  radicals were derived from the observed time-concentration profiles of  $\text{CH}_3\text{S}$  radicals in the presence of  $\text{O}_2$ . The measured rate coefficients for the reactions  $\text{CH}_3\text{S} + \text{O}_2 \rightarrow \text{CH}_3\text{SOO}$  were observed to vary with total pressure and with the diluent gas.

(b) See Comments on Preferred Values.

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## Preferred Values

The data of Turnipseed et al.<sup>1</sup> given in above table are preferred. These data at 107 mbar He are described by:  $k(216 - 250 \text{ K}) = 3.5 \times 10^{10} \exp(-3560/T) \text{ s}^{-1}$ .

### Reliability

5

$\Delta \log k = \pm 0.3$  at 107 mbar He over the temperature range 216-250 K.

### Comments on Preferred Values

10

The data presented by Turnipseed et al.<sup>1</sup> were the first reported for the dissociation of the CH<sub>3</sub>SOO radical (see also the data sheet in this evaluation for the reverse reaction CH<sub>3</sub>S + O<sub>2</sub> + M → CH<sub>3</sub>SOO + M). In the atmosphere, ~33% of CH<sub>3</sub>S radicals will be present as the CH<sub>3</sub>SOO adduct at 298 K at ground level,<sup>1</sup> with the [CH<sub>3</sub>SOO]/[CH<sub>3</sub>S] ratio being strongly temperature dependent.<sup>1</sup>

15

## References

<sup>1</sup> A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem., 96, 7502, 1992.

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## CH<sub>3</sub>S + O<sub>3</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<8 \times 10^{-14}$	298	Black and Jusinski, 1986 <sup>1</sup>	PLP-LIF
$(4.1 \pm 2.0) \times 10^{-12}$	298	Tyndall and Ravishankara, 1989 <sup>2</sup>	PLP-LIF
$(5.7 \pm 1.4) \times 10^{-12}$	300	Dominé et al., 1992 <sup>3</sup>	(a)
$1.98 \times 10^{-12} \exp[(290 \pm 40)/T]$	295-359	Turnipseed et al., 1993 <sup>4</sup>	(b)
$5.16 \times 10^{-12}$	298		
$1.02 \times 10^{-12} \exp[(432 \pm 77)/T]$	259-381	Martinez et al., 2000 <sup>5</sup>	(c)
$(4.6 \pm 0.6) \times 10^{-12}$	298		

### Comments

- 5 (a) Discharge flow study. CH<sub>3</sub>S radicals were generated by reaction of Cl with CH<sub>3</sub>SH. Photoionization mass spectrometry was used to monitor CH<sub>3</sub>S radicals. C<sub>2</sub>F<sub>3</sub>Cl was added to scavenge OH radicals and hence suppress OH radical-initiated chain reaction which regenerates CH<sub>3</sub>S. Some curvature was observed on [CH<sub>3</sub>S] logarithmic decay plots in excess O<sub>3</sub>. The initial slope was used to calculate  $k$ .
- 10 (b) Pulsed laser photolysis of (CH<sub>3</sub>)<sub>2</sub>S-O<sub>3</sub>-O<sub>2</sub>-He (193 nm) mixtures. [CH<sub>3</sub>S] was monitored by LIF. Pressure range 27-267 mbar (20-200 Torr).
- (c) Pulsed laser photolysis of CH<sub>3</sub>SCH<sub>3</sub>/O<sub>3</sub> mixtures at 193 nm in the range 33-400 mbar He and 259-381 K. [CH<sub>3</sub>S] was monitored by LIF leading to the pressure-independent  $k$  with a slight negative activation energy. No regeneration of CH<sub>3</sub>S

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was observed under the chosen experimental conditions (5-15% O<sub>2</sub> impurity relative to [O<sub>3</sub>], observation of CH<sub>3</sub>S over up to 7-10 lifetimes).

### Preferred Values

$k = 4.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

5  $k = 1.15 \times 10^{-12} \exp [430/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250-390 K.

### Reliability

10  $\Delta \log k = \pm 0.2$  at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$ .

### Comments on Preferred Values

15 It is difficult to study this reaction because in some conditions rapid chain processes involving the reaction products occur to regenerate CH<sub>3</sub>S radicals.<sup>2-4</sup> This complication appears to be absent in the most recent studies of Turnipseed et al.<sup>4</sup> and Martinez et al.<sup>5</sup> under the conditions used for rate coefficient determinations. Their value of  $k$  at 298 K is in good agreement with other studies in which care was taken to allow for this complication.<sup>2,3</sup> The mean of the values from the two most recent studies<sup>4,5</sup> is taken  
20 as our recommended value at 298 K.

There are two studies of the temperature dependence of  $k$ .<sup>4,5</sup> The rate parameters resulting from the most recent study covering the widest temperature range are accepted once the pre-exponential factor is adjusted to yield the recommended value of  
25  $k$  at 298 K.

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- <sup>1</sup> G. Black and L. E. Jusinski, J. Chem. Soc. Faraday Trans. 2, 82, 2143, 1986.
- <sup>2</sup> G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem., 93, 4707, 1989.
- <sup>3</sup> F. Dominé, A. R. Ravishankara, and C. J. Howard, J. Phys. Chem., 96, 2171, 1992.
- <sup>4</sup> A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem., 97, 5926, 1993.
- <sup>5</sup> E. Martinez, J. Albaladejo, A. Notario and E. Jimenez, Atm. Env., 34, 5295, 2000.

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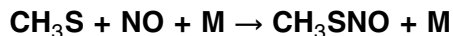
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## Low-pressure rate coefficients

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.24 \pm 0.36) \times 10^{-29} [\text{N}_2]$	295	Balla et al., 1986 <sup>1</sup>	(a)
$(1.43 \pm 0.36) \times 10^{-29} [\text{N}_2]$	351		
$(1.13 \pm 0.20) \times 10^{-29} [\text{N}_2]$	397		
$(5.84 \pm 0.66) \times 10^{-30} [\text{N}_2]$	453		

### 5 Comments

(a) Pulsed laser photolysis of  $(\text{CH}_3\text{S})_2\text{-NO-N}_2$  (or  $\text{SF}_6$ ) mixtures at 266 nm, with  $\text{CH}_3\text{S}$  being monitored by LIF. Lower part of the falloff curves were measured over the pressure range 2-400 mbar (1.5-300 Torr) of  $\text{N}_2$ . Falloff extrapolations were carried out with fitted values of  $F_c$  of 0.6, 0.86, 0.77, and 0.94 at 295, 351, 397, and 10 453 K, respectively.

### Preferred Values

$k_0 = 3.3 \times 10^{-29} (T/300)^{-4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290-450 K. This value was obtained by fitting to the pressure and temperature dependent data in  $\text{N}_2$  using a temperature independent values of  $F_c = 0.54$  and  $k_\infty$  derived from

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data in SF<sub>6</sub> (see below).

### Reliability

- 5  $\Delta \log k_0 = 0.3$  at 298 K.  
 $\Delta n = \pm 2$ .

### Comments on Preferred Values

- 10 The preferred values are based on the data of Balla et al.<sup>1</sup> A further determination in N<sub>2</sub> at a single temperature and pressure (298 K and 25 Torr) by Turnipseed et al.<sup>2</sup> is in good agreement. Although the falloff extrapolations in reference 1 were made with a theoretically improbable temperature coefficient of  $F_C$ , the low-pressure rate coefficients are much less influenced by this extrapolation than the high-pressure rate coefficients.

## 15 High-pressure rate coefficients

### Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.81 \times 10^{-12} \exp(900/T)$	295-453	Balla et al., 1986 <sup>1</sup>	(a)
$(3.97 \pm 0.44) \times 10^{-11}$ in 300 Torr SF <sub>6</sub>	295		

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## Comments

(a) See comment (a) for  $k_0$ . High-pressure limit was obtained from measurements at 267 and 400 mbar (200 and 300 Torr) of SF<sub>6</sub>.

## Preferred Values

5  $k_\infty = 4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 290-450 K.

### *Reliability*

10  $\Delta \log k_\infty = \pm 0.5$  over the temperature range 290-450 K.

### *Comments on Preferred Values*

15 The negative temperature coefficient of  $k_\infty$  reported in ref. 1 is most probably due to an increasing underestimate of the falloff corrections with increasing temperature. We recommend the use of the extrapolated  $k_\infty$  value at 298 K over large temperature ranges together with  $F_c = 0.54$ . Along with the values recommended for  $k_0$  above, this parameterisation accurately reproduces all the data in N<sub>2</sub>.

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## Intermediate Falloff Range

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	P/mbar	M	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>					
$(1.69 \pm 0.04) \times 10^{-11}$	28	He	227	Turnipseed et al., 1993 <sup>3</sup>	(a)
$(1.30 \pm 0.09) \times 10^{-11}$	25	He	242		
$(1.89 \pm 0.08) \times 10^{-11}$	25	He	242		

### Comments

- 5 (a)  $\text{CH}_3\text{S}$  radicals were generated by either photolysis of dimethyl sulfide at 193 nm or photolysis of dimethyl disulfide at 248 nm. The decay of  $\text{CH}_3\text{S}$  radical concentrations was followed by LIF. Experiments were performed under slow gas flow conditions.

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- 10 <sup>1</sup> R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys., 109, 101, 1986.  
<sup>2</sup> A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem., 100, 14 703, 1996.  
<sup>3</sup> A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem., 97, 5926, 1993.

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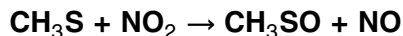
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$$\Delta H^\circ = -135 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$8.3 \times 10^{-11} \exp[(80 \pm 60)/T]$	295-511	Balla et al., 1986 <sup>1</sup>	PLP-LIF
$9.8 \times 10^{-11}$	295		
$(6.10 \pm 0.90) \times 10^{-11}$	298	Tyndall and Ravishankara, 1989 <sup>2</sup>	PLP-LIF
$(5.1 \pm 0.9) \times 10^{-11}$	297	Dominé et al., 1990 <sup>3</sup>	DF-MS
$2.1 \times 10^{-11} \exp[(320 \pm 40)/T]$	242-350	Turnipseed et al., 1993 <sup>4</sup>	(a)
$(6.28 \pm 0.28) \times 10^{-11}$	298		
$3.8 \times 10^{-11} \exp[(160 \pm 22)/T]$	263-381	Martinez, et al., 1999 <sup>5</sup>	PLP-LIF (b)
$(6.52 \pm 0.65) \times 10^{-11}$	298		
$4.3 \times 10^{-11} \exp[(241 \pm 62)/T]$	222-420	Chang et al., 2000 <sup>6</sup>	PLP-LIF (c)
$(10.1 \pm 0.5) \times 10^{-11}$	297		

### Comments

(a) Pulsed laser photolysis at 193 nm or 248 nm of  $(\text{CH}_3)_2\text{S}-\text{NO}_2$  or  $(\text{CH}_3)_2\text{S}_2-\text{NO}_2$  mixtures in bath gas of He,  $\text{N}_2$  or  $\text{SF}_6$ .  $[\text{CH}_3\text{S}]$  was monitored by LIF. Pressure varied over the range of 27-267 mbar (20-200 Torr) He.

(b) Pulsed laser photolysis of  $\text{CH}_3\text{SCH}_3$  (193 nm) or  $\text{CH}_3\text{SSCH}_3$  (248 nm) mixed with  $\text{NO}_2$  in 30-300 Torr He bath gas, detection of  $\text{CH}_3\text{S}$  by LIF. Addition of up to 5 Torr

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O<sub>2</sub> (as scavenger of CH<sub>3</sub> formed in photolysis of CH<sub>3</sub>SCH<sub>3</sub>) had no influence on the rate coefficient.

(c) Pulsed laser photolysis of CH<sub>3</sub>SSCH<sub>3</sub> (248 nm) mixed with NO<sub>2</sub> in 55-202 Torr He bath gas, detection of CH<sub>3</sub>S by LIF.

**Preferred Values**

$k = 6.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 3.0 \times 10^{-11} \exp(210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240-350 K.

*Reliability*

$\Delta \log k = \pm 0.15$  at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$ .

*Comments on Preferred Values*

The recommended value at 298 K is the mean of the studies of Tyndall and Ravishankara,<sup>2</sup> Dominé et al.,<sup>3</sup> Turnipseed et al.,<sup>4</sup> and Martínez et al.,<sup>5</sup> which are in good agreement. There are four studies<sup>1,4-6</sup> of the temperature dependence of  $k$ , all giving a negative value of  $E/R$  but differing significantly in magnitude. Two studies, Balla et al.<sup>1</sup> and Chang et al.<sup>6</sup> obtained values of  $k$  nearly twice as large as those found in the other studies. It has been suggested<sup>2</sup> that this could arise from secondary chemistry arising from the higher radical concentrations used in the work of Balla et al.,<sup>1</sup> though this argument does not apply to Chang et al.<sup>6</sup> The temperature dependent expression for  $k$  is derived by fitting to the data of Turnipseed et al.<sup>4</sup> and Martínez et al.<sup>5</sup> and the recommended value of  $k$  at 298 K.

The lack of pressure dependence of  $k$  found in the recent<sup>4-6</sup> and earlier studies<sup>1,2</sup>

is consistent with the major pathway for the reaction proceeding directly to NO and CH<sub>3</sub>SO rather than by addition to give CH<sub>3</sub>SNO<sub>2</sub>. The CH<sub>3</sub>SO yield has been determined by Dominé et al.<sup>3</sup> to be 1.07 ± 0.15, the yield of NO was determined by Tyndall and Ravishankara<sup>2</sup> to be 0.8 ± 0.2. End product studies<sup>7</sup> are in agreement with this conclusion.

## References

<sup>1</sup> R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys., 109, 101, 1986.

<sup>2</sup> G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem., 93, 2426, 1989.

<sup>3</sup> F. Dominé, T. P. Murrells, and C. J. Howard, J. Phys. Chem., 94, 5839, 1990.

<sup>4</sup> A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem., 97, 5926, 1993.

<sup>5</sup> E. Martínez, J. Albaladejo, E. Jiménez, A. Notario, and A. Aranda, Chem. Phys. Lett., 308, 37, 1999.

<sup>6</sup> P.-F. Chang, T. T. Wang, N. S. Wang, Y.-L. Hwang and Y.-P. Lee J. Phys. Chem., 104, 5525, 2000.

<sup>7</sup> I. Barnes, V. Bastian, K. H. Becker, and H. Niki, Chem. Phys. Lett., 140, 451, 1987.

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## CH<sub>3</sub>SO + O<sub>3</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1 \times 10^{-12}$	298	Tyndall and Ravishankara, 1989 <sup>1</sup>	PLP-LIF
$(6.0 \pm 3.0) \times 10^{-13}$	300	Dominé et al., 1992 <sup>2</sup>	(a)

### Comments

- 5 (a) Discharge flow study. Photoionization mass spectrometry was used to monitor CH<sub>3</sub>SO radicals. The reaction of O(<sup>3</sup>P) + C<sub>2</sub>H<sub>5</sub>SCH<sub>3</sub> was used as a source of CH<sub>3</sub>SO radicals. The rate coefficient obtained was considered preliminary.

### Preferred Values

$$k = 6.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

### Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

### Comments on Preferred Values

15 The measurement of  $k$  by Dominé et al.<sup>2</sup> is more direct than the previous study of Tyndall and Ravishankara<sup>1</sup> in which the rate coefficient was derived by a complex

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analysis of the reaction system. However, there are still a number of uncertainties in the study by Dominé et al.<sup>2</sup> who consider their quoted value of  $k$  to be preliminary. This value<sup>2</sup> is accepted but substantial error limits are recommended.

## References

- 5 <sup>1</sup> G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem., 93, 4707, 1989.  
<sup>2</sup> F. Dominé, A. R. Ravishankara, and C. J. Howard, J. Phys. Chem., 96, 2171, 1992.

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## CH<sub>3</sub>SO + NO<sub>2</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3 \pm 2) \times 10^{-11}$	298	Mellouki et al., 1988 <sup>1</sup>	DF-MS
$(8 \pm 5) \times 10^{-12}$	298	Tyndall and Ravishankara, 1989 <sup>2</sup>	PLP-LIF
$(1.2 \pm 0.25) \times 10^{-11}$	298	Dominé et al., 1990 <sup>3</sup>	DF-MS
$(1.5 \pm 0.4) \times 10^{-11}$	300	Kukui et al., 2000 <sup>4</sup>	(a) PLP-LIF, DF-LIF

### Comment

- 5 (a) PLP of CH<sub>3</sub>S<sub>2</sub>CH<sub>3</sub>-NO<sub>2</sub> mixtures at 248 nm relative to CH<sub>3</sub>I-NO<sub>2</sub> at 351 nm in the range 16-814 mbar He at 300 K. The temporal profile of CH<sub>3</sub>O was monitored using LIF and fit to obtain  $k$  which was independent of pressure. Supporting measurements on absolute CH<sub>3</sub> yields in the range 243-33 K in 16-814 mbar He have been performed, and branching ratios of the methyl forming rate constant to the total rate constant, and absolute SO<sub>2</sub> yields at 1.3 mbar He have been measured.
- 10

### Preferred Values

$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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## Reliability

$\Delta \log k = \pm 0.2$  at 298 K.

### 5 *Comments on Preferred Values*

The measured values<sup>1-3</sup> of  $k$  at 298 K agree within their error limits, some of which are substantial. The preferred value is that of Dominé et al.,<sup>3</sup> which lies between the other two values, both of which have much larger error limits. The rate coefficient for this reaction is difficult to measure because of the lack of a clean primary source of CH<sub>3</sub>SO radicals and the complexity of the secondary chemistry. The two most recent  
10 determinations<sup>3,4</sup> agree well with each other.

## References

<sup>1</sup> A. Mellouki, J. L. Jourdain, and G. Le Bras, Chem. Phys. Lett., 148, 231, 1988.

<sup>2</sup> G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem., 93, 2426, 1989.

<sup>3</sup> F. Dominé, T. P. Murrells, and C. J. Howard, J. Phys. Chem., 94, 5839, 1990.

<sup>4</sup> A. Kukui, V. Bossoutrot, G. Laverdet and G. Le Bras, J. Phys. Chem. A, 104, 935, 2000.

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## CH<sub>3</sub>SOO + O<sub>3</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$< 8 \times 10^{-13}$	227	Turnipseed et al., 1993 <sup>1</sup>	(a)

### Comments

- 5 (a) Pulsed laser photolysis of (CH<sub>3</sub>)<sub>2</sub>S-O<sub>2</sub>-O<sub>3</sub> mixtures at 193 nm in bath gas of He, N<sub>2</sub>, or SF<sub>6</sub>. CH<sub>3</sub>S + O<sub>2</sub> ↔ CH<sub>3</sub>SOO equilibrium established. [CH<sub>3</sub>S] was monitored by LIF. [CH<sub>3</sub>S] temporal profiles were simulated to obtain  $k$ .  $k(\text{CH}_3\text{S} + \text{O}_3)$  obtained in the same study was used in the fitting procedure.

### Preferred Values

- 10  $k < 8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 227 K.

### Comments on Preferred Values

- 15 The single study of the rate of this reaction<sup>1</sup> has provided only an upper limit to  $k$  at 227 K, which is accepted as the preferred value.

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<sup>1</sup> A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem., 97, 5926, 1993.

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## CH<sub>3</sub>SOO + NO → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.10 \pm 0.38) \times 10^{-11}$	227-256	Turnipseed et al., 1993 <sup>1</sup>	(a)

### Comments

- 5 (a) Pulsed laser photolysis of (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub>-O<sub>2</sub>-NO mixtures at 248 nm with He or SF<sub>6</sub> as the bath gas. Only a limited pressure range could be studied [21-28 mbar (16-21 Torr) He, 25 mbar (19 Torr) SF<sub>6</sub>], but no effect of pressure on  $k$  was observed. [CH<sub>3</sub>S] was monitored by LIF and the temporal profile simulated to obtain  $k$ .

### Preferred Values

- 10  $k = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 227-256 K.

### Reliability

- 15  $\Delta \log k = \pm 0.3$  over the range 227-256 K.

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## Comments on Preferred Values

The value of  $k$  obtained in the only study of this reaction<sup>1</sup> is accepted but substantial error limits are assigned until confirmatory studies are made.

### 5 References

<sup>1</sup> A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, *J. Phys. Chem.*, 97, 5926, 1993.

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## CH<sub>3</sub>SOO + NO<sub>2</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.2 \pm 0.6) \times 10^{-11}$	227-246	Turnipseed et al., 1993 <sup>1</sup>	(a)

### Comments

- 5 (a) Pulsed laser photolysis of (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub>-O<sub>2</sub>-NO<sub>2</sub> mixtures at 248 nm in He [107-467 mbar (80-350 Torr)] or SF<sub>6</sub> [87 mbar (65 Torr)]. [CH<sub>3</sub>S] was monitored and the temporal profile simulated to obtain  $k$ . No variation of  $k$  with pressure or temperature was observed.

### Preferred Values

- 10  $k = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 227-246 K.

### Reliability

- 15  $\Delta \log k = \pm 0.3$  over the range 227-246 K.

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## Comments on Preferred Values

The value of  $k$  obtained in the only study<sup>1</sup> of this reaction is accepted but substantial error limits are assigned until confirmatory studies are made.

### 5 References

<sup>1</sup> A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem., 97, 5926, 1993.

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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 1 \times 10^{-15}$	300	Kukui et al., 2000 <sup>1</sup>	(a)

### Comments

- 5 (a) Discharge flow of Cl-CH<sub>3</sub>SH-NO<sub>2</sub> reaction mixtures using MS/LIF detection at 13 mbar He and 300 K. The fluorescence of both CH<sub>3</sub>O and SO<sub>2</sub> were recorded as a function of time and the temporal profiles were fitted to obtain  $k$  using an upper limit of 50 s<sup>-1</sup> for the lifetime of CH<sub>3</sub>SO<sub>2</sub> with respect to dissociation into CH<sub>3</sub> + SO<sub>2</sub>.

### 10 Preferred Values

$$k \leq 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K.}$$

#### *Comments on Preferred Values*

- 15  $k$  is independent of pressure whose upper limit depends on the lifetime of CH<sub>3</sub>SO<sub>2</sub> and on the absolute yield of SO<sub>2</sub> approaching unity at long reaction times.

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<sup>1</sup> A. Kukui, V. Bossoutrot, G. Laverdet and G. Le Bras, J. Phys. Chem. A, 104, 935, 2000.

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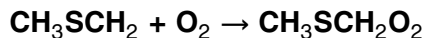
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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.7 \pm 0.4) \times 10^{-12}$ (1 bar)	298	Wallington et al., 1993 <sup>1</sup>	(a)
$2.3 \times 10^{-13}$ (1 Torr He)	298	Butkovskaya and Le Bras, 1994 <sup>2</sup>	(b)
$1.9 \times 10^{-13}$ (1 Torr He)	298		

### Comments

(a) Pulsed radiolysis of  $\text{SF}_6\text{-CH}_3\text{SCH}_3\text{-O}_2$  mixtures.  $\text{CH}_3\text{SCH}_2$  radicals were generated by reaction of F atoms with  $\text{CH}_3\text{SCH}_3$ , and monitored in absorption at 290 nm. The total pressure was approximately 1 bar.

(b) Discharge flow study of the  $\text{NO}_3\text{-CH}_3\text{SCH}_3\text{-Br}_2\text{-O}_2$  system at 1.3 mbar (1 Torr) He.  $\text{NO}_3$  radicals were produced by  $\text{F} + \text{HNO}_3$  reaction added to  $\text{CH}_3\text{SCH}_3$  to give  $\text{CH}_3\text{SCH}_2$ . Subsequent addition of  $\text{Br}_2\text{-O}_2$  mixtures allowed monitoring of competition between  $\text{O}_2$  and  $\text{Br}_2$  for  $\text{CH}_3\text{SCH}_2$ . Competition followed by mass spectrometric measurement of  $[\text{CH}_3\text{SCH}_2\text{Br}]$  profile. Modeling of profile gives  $k = 2.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Similar study of  $\text{Cl-Cl}_2\text{-CH}_3\text{SCH}_3\text{-O}_2$  system in which  $\text{CH}_3\text{SCH}_2$  was produced by  $\text{Cl} + \text{CH}_3\text{SCH}_3$  reaction gave  $k = 1.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

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## Preferred Values

$k = 5.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and 1 bar.

### *Reliability*

5  $\Delta \log k = \pm 0.4$  at 298 K and 1 bar.

### *Comments on Preferred Values*

10 The preferred value of  $k$  is taken from the study of Wallington et al.<sup>1</sup> Until confirmatory studies are made we confine our recommendations to 1 bar and assign substantial error limits.

## References

- <sup>1</sup> T. J. Wallington, T. Ellermann, and O. J. Nielsen, *J. Phys. Chem.*, 97, 8442, 1993.  
15 <sup>2</sup> N. I. Butkovskaya and G. Le Bras, *J. Phys. Chem.*, 98, 2582, 1994.

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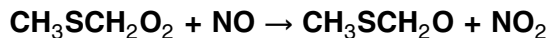
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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.9 \pm 0.6) \times 10^{-11}$	298	Wallington et al., 1993 <sup>1</sup>	(a)
$(8.0 \pm 3.1) \times 10^{-12}$	298	Turnipseed et al., 1996 <sup>2</sup>	(b)
$4.9 \times 10^{-12} \exp[(263 \pm 132)/T]$	261-400	Urbanski et al., 1997 <sup>3</sup>	(c)
$(1.14 \pm 0.05) \times 10^{-11}$	298		

### Comments

- 5 (a) Pulse radiolysis of  $\text{CH}_3\text{SCH}_3\text{-SF}_6\text{-O}_2\text{-NO}$  mixtures. Generation of  $\text{CH}_3\text{SCH}_2\text{O}_2$  radicals occurred by  $\text{F} + \text{CH}_3\text{SCH}_3 \rightarrow \text{CH}_3\text{SCH}_2 + \text{HF}$ , followed by  $\text{CH}_3\text{SCH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{O}_2$ .  $[\text{NO}_2]$  was monitored at 400 nm. Yield of  $\text{NO}_2$  compared with yield of F atoms suggested that 80% of the reaction leads to  $\text{NO}_2$  production.
- 10 (b) Derived from pulsed laser photolysis of  $\text{H}_2\text{O}_2\text{-NO-CH}_3\text{SCH}_3\text{-O}_2$  mixtures at 29 mbar total pressure, with monitoring of the temporal profiles of HO and  $\text{CH}_3\text{S}$  radicals by LIF. The cited rate coefficient was obtained from numerical modeling using a 34 step mechanism and assuming that  $\text{CH}_3\text{SCH}_2\text{O}_2 + \text{CH}_3\text{SCH}_2\text{O}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{O} + \text{CH}_3\text{SCH}_2\text{O} + \text{O}_2$  followed by decomposition of the  $\text{CH}_3\text{SCH}_2\text{O}$  radical to  $\text{HCHO} + \text{CH}_3\text{S}$ .
- 15 (c)  $\text{CH}_3\text{SCH}_2\text{O}_2$  radicals were generated by the 248 nm pulsed laser photolysis of  $\text{C(O)Cl}_2\text{-CH}_3\text{SCH}_3\text{-O}_2\text{-N}_2$  mixtures at 13 mbar total pressure, and the rate of formation of the product HCl was monitored in the presence of varying concentra-

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tions of NO by TDLAS. Secondary reactions were shown to be unimportant, and a HCHO yield of  $1.04 \pm 0.13$  was measured, with the HCHO arising from decomposition of  $\text{CH}_3\text{SCH}_2\text{O}$  radicals.

### Preferred Values

5  $k = 4.9 \times 10^{-12} \exp(260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 260-400 K.

$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Reliability

10

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$ .

### Comments on Preferred Values

15

The three studies carried out to date<sup>1-3</sup> result in room temperature rate coefficients varying by a factor of 2.4. In the study of Wallington et al.,<sup>1</sup> the formation rate of  $\text{CH}_3\text{SCH}_2\text{O}_2$  radicals was not much faster than the loss rate by reaction with NO.<sup>3</sup> The Turnipseed et al.<sup>2</sup> study was more indirect and subject to significant uncertainties. Accordingly, the preferred value of the rate coefficient is based on the most direct study of Urbanski et al.<sup>3</sup> The  $\text{CH}_3\text{SCH}_2\text{O}$  radical decomposes rapidly to form HCHO +  $\text{CH}_3\text{S}$ .<sup>3</sup>

20

### References

<sup>1</sup> T. J. Wallington, T. Ellermann, and O. J. Nielsen, J. Phys. Chem., 97, 8442, 1993.

<sup>2</sup> A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem., 100, 14 703,

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1996.

<sup>3</sup> S. P. Urbanski, R. E. Stickel, Z. Zhao, and P. H. Wine, J. Chem. Soc. Faraday Trans., 93, 2813, 1997.

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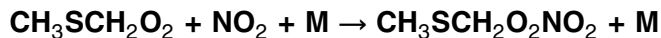
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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	P/mbar	M	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>					
$(9.2 \pm 0.9) \times 10^{-12}$	1000	SF6	296	Nielsen et al., 1995 <sup>1</sup>	(a)
$(7.1 \pm 0.9) \times 10^{-12}$	300	SF6	296		

### Comments

- 5 (a) Pulse radiolysis of SF<sub>6</sub>-CH<sub>3</sub>SCH<sub>3</sub>-O<sub>2</sub>-NO<sub>2</sub> mixtures with measurement of the rate of decay of NO<sub>2</sub> via its absorption at 400 nm. Insufficient data to obtain  $k_0$  or  $k_\infty$ , although the reaction was measured near the high-pressure limit.

### Preferred Values

$k = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 1 bar and 298 K.

#### Reliability

$\Delta \log k = \pm 0.5$  at 1 bar and 298 K.

#### Comments on Preferred Values

The preferred value is based on the sole study of Nielsen et al.<sup>1</sup> Until further studies confirm this value, we assign large error limits.

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- <sup>1</sup> O. J. Nielsen, J. Sehested, and T. J. Wallington, Chem. Phys. Lett., 236, 385, 1995.

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### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 7.9 \times 10^{-12}$	298	Wallington et al., 1993 <sup>1</sup>	(a)
$(1.2 \pm 0.5) \times 10^{-11}$	298	Urbanski et al., 1997 <sup>2</sup>	(b)

### Comments

(a)  $k$  is defined by  $-d[\text{CH}_3\text{SCH}_2\text{O}_2]/dt = 2k[\text{CH}_3\text{SCH}_2\text{O}_2]^2$ . Pulse radiolysis study of  $\text{CH}_3\text{SCH}_3\text{-O}_2\text{-SF}_6$  mixtures with monitoring of  $\text{CH}_3\text{SCH}_2\text{O}_2$  radical concentrations by UV absorption with  $\sigma_{250} = (4.3 \pm 0.7) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . The observed value of  $k_{obs} = (7.9 \pm 1.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is an upper limit to  $k$  because of the possibility of secondary reactions giving rise to an increasing decay rate of  $\text{CH}_3\text{SCH}_2\text{O}_2$  radicals.

(b)  $\text{CH}_3\text{SCH}_2\text{O}_2$  radicals were generated by the 248 nm pulsed laser photolysis of  $\text{C(O)Cl}_2\text{-CH}_3\text{SCH}_3\text{-O}_2\text{-N}_2$  mixtures at 27 mbar total pressure, and the products HCl and HCHO were monitored by TDLAS. The importance of secondary reactions (including from photolysis products of  $\text{CH}_3\text{SCH}_3$ ) was investigated experimentally and by computer modeling, and a yield of HCHO from the self-reaction of  $\text{CH}_3\text{SCH}_2\text{O}_2$  radicals of  $0.97 \pm 0.08$  was obtained by extrapolation to zero  $\text{CH}_3\text{SCH}_3$  concentration. The cited value of the rate coefficient was obtained from numerical modeling. It was concluded that the reaction leads to formation of

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CH<sub>3</sub>SCH<sub>2</sub>O radicals via pathway (2), with the CH<sub>3</sub>SCH<sub>2</sub>O radical rapidly decomposing to form HCHO (and CH<sub>3</sub>S).

### Preferred Values

$k = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

5  $k_2/k = 1.0$  at 298 K.

### Reliability

$\Delta \log k = \pm 0.3$  at 298 K.

10  $\Delta(k_2/k) = \pm 0.3$  at 298 K.

### Comments on Preferred Values

15 The preferred value is an average of the measured overall rate coefficients of Wallington et al.<sup>1</sup> and Urbanski et al.<sup>2</sup> The product data of Urbanski et al.<sup>2</sup> show that the reaction proceeds by channel (2), and that the alkoxy radical CH<sub>3</sub>SCH<sub>2</sub>O decomposes: CH<sub>3</sub>SCH<sub>2</sub>O → CH<sub>3</sub>S + HCHO. Reaction of the CH<sub>3</sub>S radical with the CH<sub>3</sub>SCH<sub>2</sub>O<sub>2</sub> radical could lead to an enhanced decay rate of the CH<sub>3</sub>SCH<sub>2</sub>O<sub>2</sub> radicals, and hence the preferred value of the rate coefficient is rigorously an upper limit.

### References

20 <sup>1</sup> T. J. Wallington, T. Ellermann, and O. J. Nielsen, J. Phys. Chem., 97, 8442, 1993.

<sup>2</sup> S. P. Urbanski, R. E. Stickel, Z. Zhao, and P. H. Wine, J. Chem. Soc. Faraday Trans., 93, 2813, 1997.

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## CH<sub>3</sub>SS + O<sub>3</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.6 \pm 1.1) \times 10^{-13}$	300	Dominé et al., 1992 <sup>1</sup>	(a)

### Comments

- 5 (a) Discharge-flow study. Photoionization mass spectrometry was used to monitor CH<sub>3</sub>SS radicals. CH<sub>3</sub>S radicals were generated by Cl + CH<sub>3</sub>SH, and CH<sub>3</sub>SS was observed to be formed in the CH<sub>3</sub>S source and thought to be due to the CH<sub>3</sub>S + S<sub>2</sub> reaction on walls. [CH<sub>3</sub>SS] was monitored in the presence of excess O<sub>3</sub> to obtain  $k$ .

### 10 Preferred Values

$k = 4.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### *Reliability*

- 15  $\Delta \log k = \pm 0.3$  at 298 K.

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## Comments on Preferred Values

The only available measurement<sup>1</sup> of  $k$  is accepted but substantial error limits are assigned until confirmatory studies are made.

### 5 References

<sup>1</sup> F. Dominé, A. R. Ravishankara, and C. J. Howard, J. Phys. Chem., 96, 2171, 1992.

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## CH<sub>3</sub>SS + NO<sub>2</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.8 \pm 0.3) \times 10^{-11}$	297	Dominé et al., 1990 <sup>1</sup>	(a)

### Comments

- 5 (a) Fast-flow discharge study. CH<sub>3</sub>SS radicals were produced as a by-product of CH<sub>3</sub>S radical production. CH<sub>3</sub>S radicals were produced by the Cl + CH<sub>3</sub>SH reaction. CH<sub>3</sub>SS was observed to be formed in the CH<sub>3</sub>S source and thought to be due to the CH<sub>3</sub>S + S<sub>2</sub> reaction on walls. [CH<sub>3</sub>SS] was monitored by photoionization mass spectrometry in excess NO<sub>2</sub>.

### 10 Preferred Values

$$k = 1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

### *Reliability*

- 15  $\Delta \log k = \pm 0.3$  at 298 K.

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## Comments on Preferred Values

The study of Dominé et al.<sup>1</sup> has provided the only available value for the rate coefficient of this reaction. This value is accepted but with substantial error limits until  
5 confirmatory studies are made.

## References

<sup>1</sup> F. Dominé, T. P. Murrells, and C. J. Howard, J. Phys. Chem., 94, 5839, 1990.

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## CH<sub>3</sub>SSO + NO<sub>2</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.5 \pm 1.2) \times 10^{-12}$	297	Dominé et al., 1990 <sup>1</sup>	(a)

### Comments

- 5 (a) Fast-flow discharge system with photoionization mass spectrometric detection of products. CH<sub>3</sub>SSO radicals were produced by CH<sub>3</sub>SS + NO<sub>2</sub> → CH<sub>3</sub>SSO + NO. Mass 47 peak was monitored in excess NO<sub>2</sub> and the contributions from CH<sub>3</sub>S and CH<sub>3</sub>SSO (from CH<sub>3</sub>SSO + hν → CH<sub>3</sub>S<sup>+</sup> + e<sup>-</sup> + SO) were separated by modeling using data from other mass peaks.

### 10 Preferred Values

$k = 4.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### *Reliability*

- 15  $\Delta \log k = \pm 0.3$  at 298 K.

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## Comments on Preferred Values

The study of Dominé et al.,<sup>1</sup> has provided the only available value for the rate coefficient of this reaction. This value is accepted but with substantial error limits until  
5 confirmatory studies are made.

## References

<sup>1</sup> F. Dominé, T. P. Murrells, and C. J. Howard, *J. Phys. Chem.*, 94, 5839, 1990.

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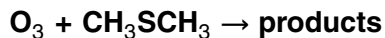
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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$<8.3 \times 10^{-19}$	296	Martinez and Herron, 1978 <sup>1</sup>	(a)

### Preferred Values

<sup>5</sup>  $k < 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Comments on Preferred Values

<sup>10</sup> The preferred upper limit to the rate coefficient is based upon the sole study of Martinez and Herron.<sup>1</sup>

### References

<sup>1</sup> R. I. Martinez and J. T. Herron, Int. J. Chem. Kinet., 10, 433, 1978.

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## ClO + CH<sub>3</sub>SCH<sub>3</sub> → products

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.9 \pm 0.5) \times 10^{-14}$	298	Barnes et al., 1989 <sup>1</sup>	DF-MS
$(9.5 \pm 2.0) \times 10^{-15}$	298 ± 1	Barnes et al., 1991 <sup>2</sup>	DF-MS

### Preferred Values

5  $k = 9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Reliability

$\Delta \log k = \pm 0.5$  at 298 K.

10

### Comments on Preferred Values

15

The two available measurements<sup>1,2</sup> of this rate coefficient are from the same laboratory using basically the same technique. In the earlier study,<sup>1</sup> wall effects were evident and it was recognized that the rate coefficient  $k$  obtained was likely to be an upper limit. Better control of wall effects was obtained in the later study,<sup>2</sup> and the rate coefficient obtained was preferred.<sup>2</sup> The reaction is usually assumed to produce CH<sub>2</sub>S(O)CH<sub>3</sub> + Cl but, although the sulfoxide has been detected,<sup>1</sup> no yields have been measured.

20

In view of the potential for heterogeneous wall reactions (as evident from the discrepancies between the two studies of Barnes et al.<sup>1,2</sup>) the preferred value is based on the

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rate coefficient reported in the most recent study of Barnes et al.,<sup>2</sup> but with substantial uncertainty limits. Clearly, further studies of this reaction as a function of temperature and pressure are required.

## References

- <sup>1</sup> I. Barnes, K. H. Becker, D. Martin, P. Carrier, G. Mouvier, J. L. Jourdain, G. Laverdet, and G. Le Bras, "Biogenic Sulfur in the Environment," edited by E. S. Saltzman and W. J. Cooper, ACS Symposium Series, No. 393, p. 464, 1989.
- <sup>2</sup> I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, *Int. J. Chem. Kinet.*, **23**, 579, 1991.

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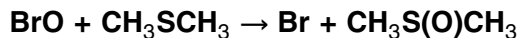
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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.65 \pm 0.65) \times 10^{-13}$	298	Barnes et al., 1989 <sup>1</sup>	DF-MS
$(2.7 \pm 0.5) \times 10^{-13}$	298 ± 1	Barnes et al., 1991 <sup>2</sup>	DF-MS
$1.5 \times 10^{-14} \exp[(845 \pm 175)/T]$	246-320	Bedjanian et al., 1996 <sup>3</sup>	DF-MS (a)
$(2.7 \pm 0.2) \times 10^{-13}$	297		
$(4.40 \pm 0.66) \times 10^{-13}$	295 ± 2	Ingham et al., 1999 <sup>4</sup>	PLP-A (b)

### Comments

- 5 (a)  $\text{CH}_3\text{S(O)CH}_3$  was observed as a reaction product, with a measured formation yield at 320 K and 1.3 mbar (1 Torr) total pressure of  $0.94 \pm 0.11$ .
- 10 (b) BrO radicals were generated by the reaction of  $\text{O}(^3\text{P})$  atoms (formed from 248 nm photolysis of  $\text{O}_3$ ) with  $\text{Br}_2$ , and detected by absorption at 338.3 nm. Experiments were carried out at 80, 133 and 267 mbar total pressure, with measured rate coefficients of  $(4.40 \pm 0.60) \times 10^{-13}$ ,  $(4.40 \pm 0.66) \times 10^{-13}$  and  $(4.36 \pm 0.65) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. Formation of  $\text{CH}_3\text{S(O)CH}_3$  was observed, with a formation yield of  $1.17 \pm 0.34$ .

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## Preferred Values

$k = 4.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Reliability

$\Delta \log k = \pm 0.3$  at 298 K.

### Comments on Preferred Values

The most recent measurement of the rate coefficient by Ingham et al.<sup>4</sup> was carried out total pressures of 80-267 mbar, compared to the earlier measurements of Barnes et al.<sup>1,2</sup> and Bedjanian et al.,<sup>3</sup> which were carried out at 0.5-6.8 mbar pressure. The higher rate coefficient of Ingham et al.<sup>4</sup> may then reflect a pressure dependence of the rate coefficient at pressures below ~80 mbar. The preferred value of the rate coefficient at 298 K is taken from the more atmospherically relevant study of Ingham et al.<sup>4</sup> The uncertainty is sufficient to encompass the reported room temperature rate coefficients.<sup>1-4</sup> Until further confirmation of the room temperature rate coefficient is obtained, no temperature dependence is recommended.

The reaction produces  $\text{CH}_3\text{S}(\text{O})\text{CH}_3 + \text{Br}$  as the dominant, if not only, products under the experimental conditions employed.<sup>3,4</sup> The reaction is postulated<sup>3,4</sup> to proceed by:



## References

<sup>1</sup> I. Barnes, K. H. Becker, D. Martin, P. Carlier, G. Mouvier, J. L. Jourdain, G. Laverdet, and G. Le Bras, "Biogenic Sulfur in the Environment," E. S. Saltzman and W. J. Cooper, Eds., ACS Symposium Series, No. 393, p. 464, 1989.

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- <sup>2</sup> I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, *Int. J. Chem. Kinet.*, 23, 579, 1991.
- <sup>3</sup> Y. Bedjanian, G. Poulet, and G. Le Bras, *Int. J. Chem. Kinet.*, 28, 383, 1996.
- <sup>4</sup> T. Ingham, D. Bauer, R. Sander, P. J. Crutzen, and J. N. Crowley, *J. Phys. Chem. A*, 103, 7199, 1999.
- <sup>5</sup>

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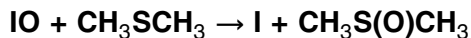
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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.0 \pm 1.5) \times 10^{-11}$	$296 \pm 2$	Barnes et al., 1987 <sup>1</sup>	(a)
$(1.5 \pm 0.5) \times 10^{-11}$	298	Martin et al., 1987 <sup>2</sup>	DF-MS
$\leq 3.5 \times 10^{-14}$	$298 \pm 2$	Daykin and Wine, 1990 <sup>3</sup>	PLP-A (b)
$(1.5 \pm 0.2) \times 10^{-14}$	298	Maguin et al., 1991 <sup>4</sup>	DF-MS
$(8.8 \pm 2.1) \times 10^{-15}$	$298 \pm 1$	Barnes et al., 1991 <sup>5</sup>	DF-MS
$(1.6 \pm 0.1) \times 10^{-14}$	298	Knight and Crowley, 2001 <sup>6</sup>	DF-MS

### Comments

- 5 (a) Photolysis of  $\text{NO}_2\text{-I}_2\text{-CH}_3\text{SCH}_3\text{-N}_2$  mixtures. Photolytic production of  $\text{O}(^3\text{P})$  atoms from  $\text{NO}_2$  formed IO radicals via the reaction  $\text{O}(^3\text{P}) + \text{I}_2 \rightarrow \text{IO} + \text{I}$ . The concentrations of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CH}_3\text{SCH}_3$ , and  $\text{CH}_3\text{SOCH}_3$  were followed as a function of time by FTIR absorption spectroscopy. A computer fit of the measured product yields to a 16-step reaction mechanism yielded the cited rate coefficient.
- 10 (b) IO radicals were monitored by long-pathlength absorption at 427 nm.

### Preferred Values

$k = 1.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

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$\Delta \log k = \pm 0.2$  at 298 K.

5 *Comments on Preferred Values*

In the earlier studies of this reaction by Barnes et al.<sup>1</sup> and Martin et al.,<sup>2</sup> erroneously high values were obtained which are now believed to have been due to features of the secondary chemistry and heterogeneous processes occurring under the conditions used. The three most recent studies,<sup>4–6</sup> using basically the same technique, give much lower values but differ from each other by almost a factor of two. Support for these lower values comes from the laser photolysis study by Daykin and Wine,<sup>3</sup> where an upper limit to the rate coefficient was obtained which is some three orders of magnitude lower than those derived in the earlier studies of Barnes et al.<sup>1</sup> and Martin et al.<sup>2</sup> In the most recent study of Knight and Crowley,<sup>6</sup> the initial IO radical concentrations were about an order of magnitude lower than employed by Maguin et al.<sup>4</sup> and Barnes et al.,<sup>5</sup> and corrections for the concurrent self-reaction of IO radicals were not required in the data analysis.<sup>6</sup>

20  $\text{CH}_3\text{S}(\text{O})\text{CH}_3$  has been detected in a number of studies,<sup>1,2,4–6</sup> and a semi-quantitative measurement of the yield by Barnes et al.<sup>5</sup> gave a yield of  $0.84 \pm 0.40$ . The preferred value is the mean of the rate coefficients of Maguin et al.,<sup>4</sup> Barnes et al.<sup>5</sup> and Knight and Crowley,<sup>6</sup> with the uncertainty being sufficient to encompass the rate coefficients measured in all three studies. A temperature-dependent study of this reaction is needed.

## References

25 <sup>1</sup> I. Barnes, K. H. Becker, P. Carlier, and G. Mouvier, *Int. J. Chem. Kinet.*, 19, 489, 1987.

<sup>2</sup> D. Martin, J. L. Jourdain, G. Laverdet, and G. Le Bras, *Int. J. Chem. Kinet.*, 19, 503,

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1987.

<sup>3</sup> E. P. Daykin and P. H. Wine, *J. Geophys. Res.*, 95, 18 547, 1990.

<sup>4</sup> F. Maguin, A. Mellouki, G. Laverdet, G. Poulet, and G. Le Bras, *Int. J. Chem. Kinet.*, 23, 237, 1991.

<sup>5</sup> I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, *Int. J. Chem. Kinet.*, 23, 579, 1991.

<sup>6</sup> G. P. Knight and J. N. Crowley, *Phys. Chem. Chem. Phys.*, 3, 393, 2001.

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## OCS + hν → products

### Primary photochemical processes

Reaction		$\Delta H^\circ / \text{kJ mol}^{-1}$	$\lambda_{\text{threshold}} / \text{nm}$
OCS + hν → CO + S( <sup>3</sup> P)	(1)	308	388
→ CO + S( <sup>1</sup> D)	(2)	419	286

### Absorption cross-section data

Wavelength range/nm	Reference	Comments
185-300	Molina et al., 1981 <sup>1</sup>	(a)

### Quantum yield data ( $\phi = \phi_1 + \phi_2$ )

Measurement	Wavelength/nm	Reference	Comments
$\phi_1/\phi_2 = 0.055$	222	Nan et al., 1993 <sup>2</sup>	(b)
$\phi = 1.04 \pm 0.09$	248	Zhao et al., 1995 <sup>3</sup>	(c)

### Comments

(a) At a spectral resolution of 0.2 nm at temperatures of 295 and 225 K. Data were given in figures and tables showing values averaged over 1 nm and averaged

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over wavelength intervals generally used in stratospheric photodissociation calculations. A value of  $\sigma_{max} = 3.27 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$  was determined at 223 nm.

- (b) Pulsed laser photolysis of OCS at 222 nm. Doppler profile of  $S(^3P_2)$  was monitored by LIF at 147 nm. CO used to quench  $S(^1D)$ .  $S(^3P_2)$  yield of 0.050 relative to  $S(^1D)$  obtained.  $S(^3P_1)$  and  $S(^3P_0)$  were not monitored but if they were present in statistical amounts then total triplet yield = 0.055.
- (c) Excimer laser flash photolysis of flowing OCS-N<sub>2</sub>-N<sub>2</sub>O and C(O)Cl<sub>2</sub>-N<sub>2</sub>-N<sub>2</sub>O gas mixtures at 248 nm. Concentration of CO was monitored by TDLS.  $\phi$  was measured relative to the quantum yield for production of CO from photolysis of C(O)Cl<sub>2</sub>, which is known to be unity. Measurements were carried out at 297 K and pressures of 5-133 mbar (4 to 100 Torr) N<sub>2</sub> + N<sub>2</sub>O.

### Preferred Values

$\lambda/\text{nm}$	$10^{21} \sigma/\text{cm}^2$ (295 K)	$10^3 \text{B}/\text{K}^{-1}$	$\phi$
300	0.0009		
295	0.0023	8.15	
290	0.0077	11.3	
285	0.0218	13.6	
280	0.0543	13.85	
275	0.1504	12.96	
270	0.376	12.57	
265	0.960	1.17	

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$\lambda/\text{nm}$	$10^{21} \sigma/\text{cm}^2$ (295 K)	$10^3 B/\text{K}^{-1}$	$\phi$
260	2.52	1.11	1.0
255	6.64	9.31	1.0
250	16.5	7.46	1.0
245	38.2	6.00	1.0
240	81.3	4.51	1.0
235	153.6	3.09	1.0
230	243.8	2.01	1.0
225	310.4	1.32	1.0
220	304.8	0.835	1.0
215	241.6	0.323	1.0
210	150.8	-0.0756	
205	82.0	-0.0868	
200	39.3	0	
195	20.2	0.950	
190	39.7	5.61	
185	190.3	4.83	

*Comments on Preferred Values*

There is good agreement among all cross-section measurements for  $\lambda < 280$  nm obtained since 1970.<sup>1,4–9</sup> The data of Molina et al.<sup>1</sup> is the only data set that extends beyond 280 nm, and provides the basis of the recommendation. The temperature dependence of the cross-sections of Molina et al.<sup>1</sup> are described by  $\sigma(\lambda, T) = \sigma(\lambda, 295) \exp[B(\lambda)(T-295)]$  where T is in K and wavelength dependent values of B are taken from the Table above. This simple parameterisation perfectly reproduces the data of Molina et al.<sup>1</sup> at 225 K and accurately reproduces the temperature dependence of the Wu et al.<sup>9</sup> data at 170 to 370 K at  $\lambda > 230$  nm.

The preferred overall quantum yield of 1.0 is based on results reported recently by

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Zhao et al.<sup>3</sup> Results of all studies indicate that S atoms are produced predominately in the S(<sup>1</sup>D) electronically excited state. Sidhu et al.<sup>10</sup> reported  $\phi_2/\phi \geq 0.74$  and Breckenridge and Taube<sup>4</sup> reported  $\phi_2/\phi = 0.74 \pm 0.04$ . Nan et al.<sup>2</sup> reported  $\phi_1/\phi_2 = 0.055$  which, when combined with the preferred value of  $\phi = \phi_1 + \phi_2 = 1.0$ , yields  $\phi_2/\phi = 0.95$ .

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<sup>7</sup> R. N. Rudolf and E. C. Y. Inn, J. Geophys. Res., 86, 9891, 1981.

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<sup>9</sup> C. Y. R. Wu, F. Z. Chen, D. L. Judge, J. Quant. Spectrosc. Radiat. Trans., 61, 265, 1999.

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## CS<sub>2</sub> + hν → products

### Primary photochemical processes

Reaction		$\Delta H_{298}^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CS <sub>2</sub> + hν → CS <sub>2</sub> <sup>*</sup>	(1)		>277
→ CS + S( <sup>3</sup> P)	(2)	432	281
→ CS + S( <sup>1</sup> D)	(3)	543	223

### Absorption cross-section data

Wavelength range/nm	Reference	Comments
180-230	Chen and Wu, 1995 <sup>1</sup>	(a)
187-230	Xu and Joens, 1993 <sup>2</sup>	(b)
185-220	Molina et al., 1981 <sup>3</sup>	(c)
188-213, 287.5-339.5	Ahmed and Kumar, 1992 <sup>4</sup>	(d)
271-374	Hearn and Joens, 1991 <sup>5</sup>	(e)
318-350	Wu and Judge, 1981 <sup>6</sup>	(f)
280-360	Wine et al., 1981 <sup>7</sup>	(g)
315-330	Leroy et al., 1983 <sup>8</sup>	(h)

### Comments

(a) Spectral resolution 0.08 nm. Synchrotron radiation was used as a continuum light source. Measurements were made at 203, 295, and 385 K. Significant tempera-

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ture effects and hot bands were observed. Results were presented in graphical form in the paper but the authors can provide data points at 0.005 nm intervals on request.

- (b) Spectral resolution of 0.2 nm. Deuterium lamp as continuum light source.
- 5 (c) As part of their study of the OCS spectrum. Spectral resolution of 0.2 nm. Results in graphical form.
- (d) Spectral resolution of 0.2 nm. Ar-arc lamp as continuum light source.
- (e) Spectral resolution 0.06 nm. Deuterium lamp as continuum light source. Results presented in graphical form in the paper but the authors can provide data points at 0.02 nm intervals on request.
- 10 (f) Spectral resolution 0.06 nm. Synchrotron radiation was used as a continuum light source.
- (g) Spectral resolution 0.4 nm.
- (h) Spectral resolution 0.2 nm.

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## Preferred Values

$\lambda/\text{nm}$	$10^{20}\sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20}\sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20}\sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20}\sigma/\text{cm}^2$
275	0.017	299	2.017	323	5.180	347	0.328
276	0.020	300	1.879	324	3.517	348	0.109
277	0.027	301	3.269	325	8.628	349	0.368
278	0.043	302	3.166	326	5.023	350	0.239
279	0.050	303	3.131	327	3.481	351	0.127
280	0.053	304	4.438	328	2.849	352	0.255
281	0.062	305	4.461	329	2.848	353	0.066
282	0.080	306	3.658	330	3.802	354	0.172
283	0.103	307	5.122	331	1.301	355	0.247
284	0.122	308	7.101	332	3.057	356	0.052
285	0.158	309	4.930	333	1.552	357	0.133
286	0.209	310	8.838	334	1.506	358	0.055
287	0.254	311	5.611	335	1.375	359	0.059
288	0.309	312	6.692	336	0.861	360	0.119
289	0.445	313	8.148	337	1.377	361	0.042
290	0.438	314	7.842	338	0.591	362	0.048
291	0.635	315	9.440	339	1.121	363	0.021
292	0.640	316	7.039	340	0.489	364	0.037
293	0.878	317	9.462	341	0.386	365	0.012
294	0.801	318	7.159	342	0.573	366	0.036
295	1.137	319	9.803	343	0.387	367	0.023
296	1.134	320	4.518	344	0.556	368	0.020
297	1.861	321	6.122	345	0.353	369	0.011
298	2.287	322	4.221	346	0.350	370	0.018

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$\phi_{OCS} < 1.2 \times 10^{-2}$  for 290-360 nm region in 1 bar air.

### 5 *Comments on Preferred Values*

The UV absorption spectrum of CS<sub>2</sub> shows two absorption bands at  $\approx$  180-210 nm and  $\approx$  290-340 nm, both have fine structure superimposed on a continuum. The cross-sections in both bands display some temperature dependence<sup>1,7</sup> and dependence on instrumental resolution. The measurements of Hearn and Joens<sup>5</sup> on the absorption spectrum were carried out using similar conditions of temperature, resolution, path-length, and gas pressure to those used by Wu and Judge.<sup>6</sup> In both cases the resolution used (0.06 nm) is higher than in the other studies. The values of the cross-section obtained by Hearn and Joens<sup>5</sup> are some 10-15% higher than those obtained by Wu and Judge<sup>6</sup> and there are minor differences in the band structures observed. The preferred values in the long-wavelength band are those of Hearn and Joens<sup>5</sup> whose data set covers the largest spectral region. The data listed are averaged over 1 nm intervals.

The recommended quantum yield for OCS production from the photoinitiated oxidation of CS<sub>2</sub> in air is that reported by Jones et al.,<sup>9</sup> which is in good agreement with the value estimated by Wine et al.<sup>7</sup> from the earlier data of Wood and Heicklen<sup>10</sup> (i.e.  $\phi_{OCS} = 0.01 - 0.015$ ). The recommended value might best be considered an upper limit since the observed slow oxidation of the CS<sub>2</sub> could have been due, at least in part, to other mechanisms, possibly involving excited CS<sub>2</sub>.<sup>11</sup>

### References

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<sup>2</sup> H. Xu and J. A. Joens, Geophys. Res. Lett., 20, 1035, 1993.

<sup>3</sup> L. T. Molina, J. J. Lamb and M. J. Molina, Geophys. Res. Lett., 8, 1008, 1981.

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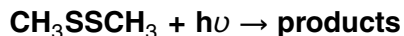
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### Primary photochemical processes

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{SSCH}_3 \rightarrow \text{CH}_3\text{SS} + \text{CH}_3$	(1)	238	502
$\rightarrow 2\text{CH}_3\text{S}$	(2)	274	437

### 5 Absorption cross-section data

Wavelength/nm	Reference	Comments
201-360	Hearn et al., 1990 <sup>1</sup>	(a)

### Quantum yield data

Wavelength/nm	Reference	Comments
193-248	Barone et al., 1994 <sup>2</sup>	(b)

### Comments

- 10 (a) Cary 2300 double beam UV spectrophotometer used with a resolution of 0.10 nm. Photolysis of  $(\text{CH}_3)_2\text{S}_2\text{-N}_2$  mixtures at a constant pressure of 133 mbar (100 Torr). Temperature =  $300 \pm 2$  K.

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- (b) Primary quantum yields for formation of  $\text{H}(^2\text{S})$  and  $\text{CH}_3\text{S}(^2\text{E})$  from photodissociation at excimer wavelengths 193, 222, and 248 nm were measured, with H atom detection by RF and  $\text{CH}_3\text{S}$  detection by pulsed LIF.

### Preferred Values

$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{20} \sigma/\text{cm}^2$
201	1053.0	280	49.8
205	850.0	285	36.0
210	630.0	290	25.15
215	312.0	295	17.06
220	138.7	300	11.27
225	85.6	305	7.24
228 (min)	82.3	310	4.57
230	84.2	315	2.85
235	96.0	320	1.79
240	110.0	325	1.09
245	120.7	330	0.67
250	125.4	335	0.38
251 (max)	125.6	340	0.22
255	123.3	345	0.14
260	113.9	350	0.07
265	99.3	355	0.04
270	82.7	360	<0.01
275	65.4		

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The preferred values for  $\sigma$  are those of Hearn et al.,<sup>1</sup> which agree well with the earlier values cited in Calvert and Pitts.<sup>3</sup> Sheraton and Murray's spectrum<sup>4</sup> agrees qualitatively with the other studies, but the reported absorption coefficients are significantly lower.

Barone et al.<sup>2</sup> report the primary quantum yield for CH<sub>3</sub>S production to be  $1.65 \pm 0.38$  at 248 nm and  $1.20 \pm 0.14$  at 193 nm. These authors report that no H atoms were observed at 248 nm, and that at 193 and 222 nm H atom production was only a minor process and could be due to sample impurities. These results and those of Balla and Hecklen<sup>5</sup> indicate that at wavelengths of importance to atmospheric photochemistry dissociation occurs primarily by S-S bond scission to give 2 CH<sub>3</sub>S. The significantly lower value of  $\phi(\text{CH}_3\text{S})$  at 193 nm implies the existence of an additional channel at these short wavelengths.

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## CH<sub>3</sub>SNO + hν → products

### Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH <sub>3</sub> SNO → CH <sub>3</sub> S + NO (1)		
→ CH <sub>3</sub> + SNO (2)		

### 5 Absorption cross-section data

Wavelength/nm	Reference	Comments
190-430	Niki et al., 1983 <sup>1</sup>	(a)

### Quantum yield data

**No data available**

### Comments

- 10 (a) Cary 14 double beam spectrophotometer used; the spectral resolution was not reported. Measurements of  $\sigma$  were made over the range 190-600 nm, but only the results in the range 190-430 nm were given in graphical form. Values of  $\sigma = 2.4 \times 10^{-20}$  and  $5.8 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$  were quoted for 510 and 545 nm, respectively. Values given in the table were taken from the graph. Temperature =  
15 298 K.

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## Preferred Values

$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$
190	5	310	14.9
195	104	320	18.5
200 (max)	162	330	21.3
205	91	335 (max)	21.6
210 (min)	81	340	21.5
215	98	350	19.6
218 (max)	104	360	16.5
220	96	370	12.7
225	73	380	9.6
230	40	390	6.7
240	16	400	4.5
250	3.5	410	2.9
260	1.7	420	2.0
264 (min)	1.5	430	1.3
270	1.8		
280	2.7	510	0.24
290	5.2	545	0.58
300	9.3		

### Comments on Preferred Values

- 5 The spectrum of  $\text{CH}_3\text{SNO}$  consists of a weak transition in the 500-600 nm region showing some vibrational fine structure and stronger continuous bands at shorter wavelengths.<sup>2</sup> The  $\text{CH}_3\text{S-NO}$  dissociation energy has been estimated<sup>3</sup> to be approximately 110  $\text{kJ mol}^{-1}$  but because more reliable data are not available we do not give wavelength limits for the dissociation channels tabulated.

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The only available data for  $\sigma$  values in the gas phase appear to be those of Niki et al.<sup>1</sup> who have published their results mainly in the form of graphs covering the range 190–430 nm. Their published spectrum shows no fine structure but appears to consist of overlapping continua with three maxima at approximately 200, 218 and 335 nm. The preferred values of  $\sigma$  in the range 190–430 nm are taken from the graphs of Niki et al.<sup>1</sup> and cannot be considered to be very precise. The two values at 510 and 545 nm are numerical values quoted in the same study.<sup>1</sup>

There have been no quantum yield measurements. By analogy with CH<sub>3</sub>ONO photolysis the primary products are expected to be CH<sub>3</sub>S and NO. This is supported by the work of McCoustra and Pfab<sup>2</sup> who studied the photodissociation of CH<sub>3</sub>SNO in a molecular beam and by the study of Niki et al.<sup>1</sup> who found CH<sub>3</sub>SSCH<sub>3</sub> and NO to be the only major products from CH<sub>3</sub>SNO photolysis at 300–400 nm.

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<sup>1</sup> H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, J. Phys. Chem., 87, 7, 1983.

<sup>2</sup> M. R. S. McCoustra and J. Pfab, Chem. Phys. Lett. 137, 355, 1987.

<sup>3</sup> S. W. Benson, Chem. Rev, 78, 23, 1978.

## Appendix 5: Enthalpy Data

Most of the thermochemical data have been taken from evaluations or reviews. In some cases, we have selected more recent experimental data, which appear to be reliable. The error limits are those given by the original author or reviewer.

Species	$\Delta_f H_{298}^\circ / \text{kJ mol}^{-1}$	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}$	Reference
H	217.998 ± 0.006	216.03 ± 0.006	1
H <sub>2</sub>	0	0	1
O( <sup>3</sup> P)	249.18 ± 0.10	246.79 ± 0.10	1
O( <sup>1</sup> D)	438.9	436.6	2
O <sub>2</sub>	0	0	1
O <sub>2</sub> ( <sup>1</sup> Δ)	94.3	94.3	2
O <sub>2</sub> ( <sup>1</sup> Σ)	156.9	156.9	2
O <sub>3</sub>	142.7	145.4	3
HO	37.20 ± 0.38	36.91 ± 0.38	65
HO <sub>2</sub>	14.6		4
H <sub>2</sub> O	-241.826 ± 0.04	-238.92 ± 0.04	1
H <sub>2</sub> O <sub>2</sub>	-136.31	-130.04	3
N	472.68 ± 0.40		1
N <sub>2</sub>	0	0	1
NH	352 ± 10		5
NH <sub>2</sub>	188.7 ± 1.3		4
NH <sub>3</sub>	-45.94 ± 0.35		1
NO	90.25	89.75	3
NO <sub>2</sub>	33.18	35.98	3
NO <sub>3</sub>	73.72 ± 1.4	78.95 ± 1.4	6
N <sub>2</sub> O	82.05	85.500	3

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Species	$\Delta_f H_{298}^\circ / \text{kJ mol}^{-1}$	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}$	Reference
N <sub>2</sub> O <sub>4</sub>	9.1 ± 1.7	18.7 ± 1.7	7
N <sub>2</sub> O <sub>5</sub>	11.3		6,7
HNO	112.95 ± 0.25	110.02 ± 0.25	8
HNO <sub>2</sub>	-79.5		3
HNO <sub>3</sub>	-135.06	-125.27	3
HO <sub>2</sub> NO <sub>2</sub>	-52.7 ± 8		9
CH	596.4 ± 1.2		4
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	390.4 ± 4		4
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	428.3 ± 4		4
CH <sub>3</sub>	146.4 ± 0.4		4
CH <sub>4</sub>	-74.81	-66.818	3
CN	441.4 ± 4.6		4
HCN	135 ± 8		7
HCO	43.1		10,11
CH <sub>2</sub> O	-108.6	-104.7	2
CH <sub>3</sub> O	17.2 ± 3.8		4
CH <sub>2</sub> OH	-17.8 ± 1.3	-11.5 ± 1.3	12
CH <sub>3</sub> OH	-201.6 ± 0.2		13
CO	-110.53 ± 0.17		1
NCO	127.0		4
HOCO	-217 ± 10	-205 ± 10	4,14
HCOOH	-378.8 ± 0.5	-371.6	13
CH <sub>2</sub> OOH	46		67
CH <sub>3</sub> O <sub>2</sub>	9.0 ± 5.1		4
CH <sub>3</sub> OOH	-131		7
HOCH <sub>2</sub> O <sub>2</sub>	-162.1 ± 2.1		15

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Species	$\Delta_f H_{298}^\circ / \text{kJ mol}^{-1}$	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}$	Reference
CH <sub>3</sub> ONO	-65.3		16
CH <sub>3</sub> ONO <sub>2</sub>	-119.7		16
CH <sub>3</sub> O <sub>2</sub> NO <sub>2</sub>	-44		17
CO <sub>2</sub>	-393.51 ± 0.13		1
C <sub>2</sub> H	566.1 ± 2.9		4
C <sub>2</sub> H <sub>2</sub>	228.0 ± 1.0		13
C <sub>2</sub> H <sub>3</sub>	300.0 ± 3.4		4
C <sub>2</sub> H <sub>4</sub>	52.2 ± 1.2		13
C <sub>2</sub> H <sub>5</sub>	120.9 ± 1.6		4
C <sub>2</sub> H <sub>6</sub>	-84.0 ± 0.2		13
CH <sub>2</sub> CN	243.1 ± 11.3		4
CH <sub>3</sub> CN	74.0		18
CH <sub>2</sub> CO	-47.7 ± 1.6		19
CH <sub>3</sub> CO	-10.0 ± 1.2		4
CH <sub>2</sub> CHO	10.5 ± 9.2		4
CH=CHOH		120 ± 10	20
CH <sub>3</sub> CHO	-165.8 ± 0.4		13,21
C <sub>2</sub> H <sub>5</sub> O	-15.5 ± 3.4		4
C <sub>2</sub> H <sub>4</sub> OH		-23 ± 6	20
CH <sub>3</sub> CHOH	-51.6		4
C <sub>2</sub> H <sub>5</sub> OH	-234.8 ± 0.2		13,21
(CHO) <sub>2</sub>	-211.9 ± 0.8		13,21
CH <sub>3</sub> CO <sub>2</sub>	-207.5 ± 4		4
CH <sub>3</sub> CO <sub>2</sub> H	-432.14 ± 0.4		13,21
CH <sub>3</sub> CHOOH	2.0		67
C <sub>2</sub> H <sub>5</sub> O <sub>2</sub>	-27.4 ± 9.9		4

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Species	$\Delta_f H_{298}^\circ / \text{kJ mol}^{-1}$	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}$	Reference
C <sub>2</sub> H <sub>5</sub> OOH	-172.0		67
CH <sub>3</sub> OOCH <sub>3</sub>	-125.7 ± 1.3		13,21
CH <sub>3</sub> C(O)O <sub>2</sub>	-172 ± 20		4
CH <sub>3</sub> C(O)OOH	-337		67
C <sub>2</sub> H <sub>5</sub> ONO	-103.8		13,21
C <sub>2</sub> H <sub>5</sub> ONO <sub>2</sub>	-154.1 ± 1.0		13,21
C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> NO <sub>2</sub>	-63.2		22
CH <sub>3</sub> C(O)O <sub>2</sub> NO <sub>2</sub>	-258 ± 22		23
CH <sub>2</sub> =CHCH <sub>2</sub>	170.7 ± 8.8		4
C <sub>3</sub> H <sub>6</sub>	20.2 ± 0.4		13,21
n-C <sub>3</sub> H <sub>7</sub>	100.8 + 2.1		4
i-C <sub>3</sub> H <sub>7</sub>	86.6 ± 2.0		4
C <sub>3</sub> H <sub>8</sub>	-104.5 ± 0.3		13,21
C <sub>2</sub> H <sub>5</sub> CO	-32.3 ± 4.2		24,25
CH <sub>3</sub> C(O)CH <sub>2</sub> OO	-162.0		67
CH <sub>3</sub> COCH <sub>2</sub>	-23.9 ± 10.9		4
C <sub>2</sub> H <sub>5</sub> CHO	-187.4 ± 1.5		13,21
CH <sub>3</sub> COCH <sub>3</sub>	-217.2 ± 0.4		13,21
CH <sub>3</sub> C(O)CH <sub>2</sub> OH	-367		67
CH <sub>3</sub> C(O)CH <sub>2</sub> OOH	-308		67
CH <sub>3</sub> C(O)CHO	-271		67
CH <sub>3</sub> C(O)COOH	-531		67
C <sub>3</sub> H <sub>6</sub> OH	-74		16
n-C <sub>3</sub> H <sub>7</sub> O	-41.4		4
i-C <sub>3</sub> H <sub>7</sub> O	-52.3		4

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Species	$\Delta_f H_{298}^\circ / \text{kJ mol}^{-1}$	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}$	Reference
i-C <sub>3</sub> H <sub>7</sub> OH	-272.5 ± 0.4		13,21
CH <sub>3</sub> COCHO	-271.1 ± 4.7		13,21
C <sub>3</sub> H <sub>5</sub> O <sub>2</sub>	87.9 ± 5.5		4
i-C <sub>3</sub> H <sub>7</sub> O <sub>2</sub>	-68.8 ± 11.3		4
n-C <sub>3</sub> H <sub>7</sub> ONO <sub>2</sub>	-174.1 ± 1.3		13,21
i-C <sub>3</sub> H <sub>7</sub> ONO <sub>2</sub>	-190.8 ± 1.7		13,21
n-C <sub>4</sub> H <sub>9</sub>	80.9 ± 2.2		4
s-C <sub>4</sub> H <sub>9</sub>	66.7 ± 2.1		4
n-C <sub>4</sub> H <sub>10</sub>	-125.7 ± 0.4		13
n-C <sub>3</sub> H <sub>7</sub> CHO	-211.8 ± 0.9		68
CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub>	-238.5 ± 0.5		13
n-C <sub>4</sub> H <sub>9</sub> O	-62.8		4
s-C <sub>4</sub> H <sub>9</sub> O	-69.5 ± 3.3		4
S	277.17 ± 0.15		1
HS	143.01 ± 2.85	142.55 ± 3.01	26
H <sub>2</sub> S	-20.6 ± 0.5		1
HSO	-4		4
SO	5.0 ± 1.3	5.0 ± 1.3	7
HSO <sub>2</sub>	-222		4
SO <sub>2</sub>	-296.81 ± 0.20		1
HOSO <sub>2</sub>	-385		4
SO <sub>3</sub>	-395.72	-389.99	3
HSNO	94		27
CH <sub>3</sub> S	124.60 ± 1.84		26
CH <sub>3</sub> SH	-22.9 ± 0.6		28
CH <sub>3</sub> SCH <sub>2</sub>	136.8 ± 5.9		4

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Species	$\Delta_f H_{298}^\circ / \text{kJ mol}^{-1}$	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}$	Reference
CH <sub>3</sub> SCH <sub>3</sub>	-37.24	-21.058	3
CS	278.5 ± 3.8		4
CH <sub>3</sub> SO	-67 ± 10		29
CH <sub>3</sub> SOO	75.7 ± 4.2	87.9 ± 4.6	30
OCS	-142.09	-142.218	3
S <sub>2</sub>	128.60		1
CH <sub>3</sub> SS	68.6 ± 8		4
CH <sub>3</sub> SSCH <sub>3</sub>	-24.3		31
CS <sub>2</sub>	117.36	116.57	3
HOCS <sub>2</sub>	110.5 ± 4.6		32
F	79.38 ± 0.30		1
HF	-273.30 ± 0.70		1
HOF	-98.3 ± 4.2	-95.4 ± 4.2	7
FO	109 ± 10	108 ± 10	7
FO <sub>2</sub>	25.4 ± 2	27.2 ± 2	7
FONO	67		33
FNO <sub>2</sub>	-108.8		17
FONO <sub>2</sub>	10	18	7
CH <sub>2</sub> F	-31.8 ± 8.4		4
CH <sub>3</sub> F	-232.6		34
CH <sub>3</sub> CH <sub>2</sub> F	-263 ± 2		35
HCOF		-392.5 ± 6.3	36
FCO	-152.1 ± 12	-172 ± 63	4
F <sub>2</sub>	0	0	1
CHF <sub>2</sub>	-238.9 ± 4		4
CH <sub>2</sub> F <sub>2</sub>	-453 ± 8		35

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Species	$\Delta_f H_{298}^\circ / \text{kJ mol}^{-1}$	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}$	Reference
CH <sub>3</sub> CHF <sub>2</sub>	-501 ± 6		35
CF <sub>2</sub>	-184.1 ± 8.4		4
COF <sub>2</sub>	-634.7	-631.57	3
CHF <sub>3</sub>	-697.6		35
CF <sub>3</sub>	-466.1 ± 3.8		4
CH <sub>2</sub> CF <sub>3</sub>	-517.1 ± 5.0		4
CH <sub>3</sub> CF <sub>3</sub>	-748.7 ± 3.2		37
CH <sub>2</sub> FCHF <sub>2</sub>	-691 ± 10		37
CF <sub>3</sub> O	-655.6 ± 6.3		38
CF <sub>3</sub> OH	-923.4 ± 13.4		39
CF <sub>3</sub> OF	-785		35
CF <sub>3</sub> O <sub>2</sub>	-614.0 ± 15.4		15
CF <sub>3</sub> CO <sub>2</sub> H	-1031		28
CF <sub>3</sub> O <sub>2</sub> NO <sub>2</sub>	-686		22
CF <sub>4</sub>	-933	-927	40
Cl	121.301 ± 0.008		1
HCl	-92.31 ± 0.10		1
HOCl	-78	-75	2,41
ClO	101.63 ± 0.1		7
ClOO	97.457	99.128	42
OCIO	94.6 ± 1.3		43
sym-ClO <sub>3</sub>	217.2 ± 21		44
ClNO	51.7	53.6	7
ClNO <sub>2</sub>	12.5	17.95	3
ClONO	56		17
ClONO <sub>2</sub>	22.9 ± 2.2		45

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Species	$\Delta_f H_{298}^\circ / \text{kJ mol}^{-1}$	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}$	Reference
CH <sub>2</sub> Cl	117.3 ± 3.1		4
CH <sub>2</sub> ClO <sub>2</sub>	-5.1 ± 13.6		4
CH <sub>3</sub> Cl	-81.96 ± 0.67	-74.04 ± 0.67	40
CH <sub>3</sub> OCi	-64.4 ± 6.2		69
CHF <sub>2</sub> Cl	-483.7 ± 5.9		46
CH <sub>3</sub> CHFCi	-313.4 ± 2.6		37
CH <sub>3</sub> CF <sub>2</sub> Cl	-536.2 ± 5.2		37
CiCO	-21.8 ± 2.5	-23.4 ± 2.9	47
COFCi	-427	-423	7
CFCi	31.0 ± 13.4		4
CF <sub>2</sub> Cl	-279.1 ± 8.3		4
CF <sub>2</sub> ClO <sub>2</sub>	-406.5 ± 14.6		15
CF <sub>2</sub> ClO <sub>2</sub> NO <sub>2</sub>	-480		48
CF <sub>3</sub> Cl	-707.9 ± 3.8	-702.8 ± 3.8	46
Cl <sub>2</sub>	0	0	1
Cl <sub>2</sub> O	77.2 ± 3.4		49
Cl <sub>2</sub> O <sub>2</sub>	127.6 ± 2.9		43
Cl <sub>2</sub> O <sub>3</sub>	153		50
CCl <sub>2</sub>	230.1 ± 8.4		4
CHCl <sub>2</sub>	89.0 ± 3.0		4
CHCl <sub>2</sub> O <sub>2</sub>	-19.2 ± 11.2		4
CH <sub>2</sub> Cl <sub>2</sub>	-95.4 ± 0.8	-88.5 ± 0.8	40
CHFCi <sub>2</sub>	-284.9 ± 8.8		46
COCl <sub>2</sub>	-220.1	-218.4	7
CFCl <sub>2</sub>	-89.1 ± 10.0		4
CFCl <sub>2</sub> O <sub>2</sub>	-213.7		4

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Species	$\Delta_f H_{298}^\circ / \text{kJ mol}^{-1}$	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}$	Reference
$\text{CFCl}_2\text{O}_2\text{NO}_2$	-287.4		48
$\text{CF}_2\text{Cl}_2$	$-493.3 \pm 2.5$	$-489.1 \pm 2.5$	46
$\text{CH}_2\text{ClCF}_2\text{Cl}$	$-543 \pm 10$		35
$\text{CF}_3\text{CHCl}_2$	$-740 \pm 10$		35
$\text{CF}_2\text{ClCHFCI}$	$-724 \pm 10$		35
$\text{CF}_2\text{ClCF}_2\text{Cl}$	$-925.5 \pm 4.3$		37
$\text{CCl}_3$	$71.1 \pm 2.5$	$69.9 \pm 2.5$	51
$\text{CCl}_3\text{O}_2$	$-20.9 \pm 8.9$		4
$\text{CCl}_3\text{O}_2\text{NO}_2$	-83.7		48
$\text{CHCl}_3$	$-103.3 \pm 1.3$		7
$\text{C}_2\text{HCl}_3$	-7.78	-4.318	3
$\text{CH}_3\text{CCl}_3$	$-144.6 \pm 0.8$		37
$\text{CFCl}_3$	$-284.9 \pm 1.7$	-281.1	46
$\text{CF}_2\text{ClCFCl}_2$	$-726.8 \pm 2.8$		37
$\text{CCl}_4$	$-95.8 \pm 0.6$	$-93.6 \pm 0.6$	40
$\text{C}_2\text{Cl}_4$	-12.4	-11.9	7
$\text{C}_2\text{Cl}_5$	$33.5 \pm 5.4$	$33.9 \pm 6.3$	52
Br	$111.87 \pm 0.12$		1
HBr	$-36.29 \pm 0.16$		1
HOBr	$\geq -56$		53
BrO	$119.7 \pm 5.9$		54
OBrO	$163.9 \pm 4.4$	$172.9 \pm 4.4$	66
BrOO	$108 \pm 40$	$116 \pm 40$	7
BrNO	82.17	91.46	3
BrONO <sub>2</sub>	$42.3 \pm 8$		55
CH <sub>2</sub> Br	$169.0 \pm 4.2$		4

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Species	$\Delta_f H_{298}^\circ / \text{kJ mol}^{-1}$	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}$	Reference
CH <sub>3</sub> Br	-38.1 ± 1.3		13
CH <sub>2</sub> ClBr	-20 ± 7		56
CF <sub>3</sub> Br	-650		35
CF <sub>2</sub> ClBr	-438 ± 8		35
BrCl	14.6 ± 1.3	22.1 ± 1.3	7
Br <sub>2</sub> (g)	30.91		1
Br <sub>2</sub> O	107.1 ± 3.5		57
Br <sub>2</sub> O <sub>2</sub>	181 ± 12		58
CHBr <sub>2</sub>	188.3 ± 9.2		4
CH <sub>2</sub> Br <sub>2</sub>	-11.1 ± 5.0		59
CF <sub>2</sub> Br <sub>2</sub>	-379 ± 8		35
CF <sub>2</sub> BrCF <sub>2</sub> Br	-789.9		37
CHBr <sub>3</sub>	23.8 ± 4.5		59
I	106.76 ± 0.04		1
HI	26.50		1
HOI	-69.6 ± 5.4	-64.9	60,61
IO	115.9 ± 5.0		62
OIO	76.7 ± 15		61
INO	121.3 ± 4.2	124.3 ± 4.2	63
INO <sub>2</sub>	60.2 ± 4.2	66.5 ± 4.2	63
IONO <sub>2</sub>	70 ± 16		70
CH <sub>2</sub> I	230.1 ± 6.7		4
CH <sub>3</sub> I	14.2 ± 0.9		13
CF <sub>3</sub> I	-589.1 ± 3.3		7
CH <sub>2</sub> ClI	~7.1		34

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CH <sub>2</sub> BrI	~61.9		34
ICl	17.5 ± 0.1	19.1 ± 0.1	7
IBr	40.9 ± 0.1	49.8 ± 0.1	7
I <sub>2</sub> (g)	62.42 ± 0.08		1
CH <sub>2</sub> I <sub>2</sub>	118 ± 4		64

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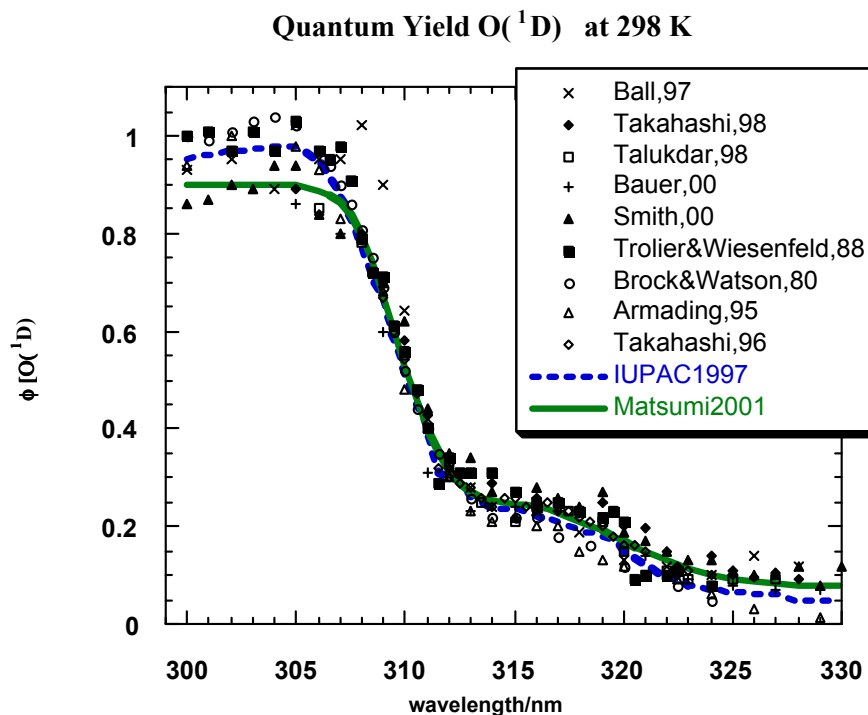
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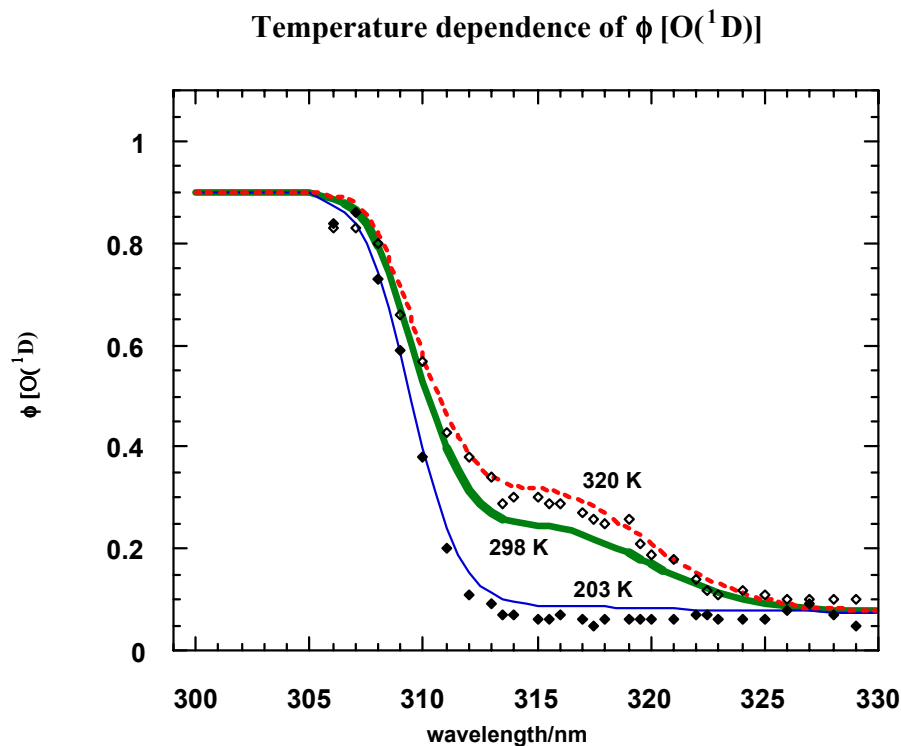


**Fig. 1.** Quantum Yields for O(<sup>1</sup>D) production from O<sub>3</sub> photolysis at 298 K. The data are taken from the cited references without normalisation. The IUPAC recommendation is a mean of the values reported by Brock and Watson,<sup>10</sup> Trolier and Wiesenfeld,<sup>14</sup> Armerding et al.,<sup>20</sup> Takahashi et al.,<sup>22</sup> and Silvente et al.<sup>32</sup> (for  $\lambda > 325$  nm only). The recommendation of Matsumi et al.,<sup>39</sup> which is adopted for this IUPAC evaluation, is derived by averaging the renormalised data from Brock and Watson,<sup>10</sup> Trolier and Wiesenfeld,<sup>14</sup> Armerding et al.,<sup>20</sup> Takahashi et al.,<sup>22</sup> Ball et al.,<sup>23</sup> Talukdar et al.,<sup>24,26</sup> Bauer et al.,<sup>27</sup> Smith et al.,<sup>28</sup> and Taniguchi et al.<sup>29</sup>

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**Fig. 2.** Temperature dependence of Quantum Yields for  $O(^1D)$  production from  $O_3$  photolysis. The curves show values at 202, 298 and 320 K calculated using the expression derived by Matsumi et al.,<sup>39</sup> using three Gaussian terms and a constant term representing the spin-forbidden channel(4). This expression is given in the preferred values. Selected experimental data from Talukdar et al.<sup>26</sup> at 203 and 320 K are also shown.

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