The reaction of $\bullet\text{OH}$ with O_2 , the decay of $\text{O}_3\bullet^-$ and the pKa of $\text{HO}_3\bullet$ – interrelated questions in aqueous free-radical chemistry

Journal:	<i>Journal of Physical Organic Chemistry</i>
Manuscript ID:	POC-10-0183.R2
Wiley - Manuscript type:	Research Article
Date Submitted by the Author:	22-Sep-2010
Complete List of Authors:	von Sonntag, Clemens; MPI für Bioanorganische Chemie Naumov, Sergej; IOM-Leipzig
Keywords:	Ozone, Hydroxyl radical, Ozonide radical anion, Oxygen, Thermodynamic cycle

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The reaction of $\cdot\text{OH}$ with O_2 , the decay of O_3^- and the pK_a of $\text{HO}_3\cdot$ – interrelated questions in aqueous free-radical chemistry

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The reactions $\text{O}^- + \text{O}_2 \rightleftharpoons \text{O}_3^-$ (1), $\text{H}^+ + \text{O}^- \rightleftharpoons \cdot\text{OH}$ (8), $\cdot\text{OH} + \text{O}_2 \rightleftharpoons \text{HO}_3\cdot$ (6) and $\text{H}^+ + \text{O}_3^- \rightleftharpoons \text{HO}_3\cdot$ (5) are interconnected by a thermodynamic cycle. For equilibria (1) and (8) reliable equilibrium constants, and hence Gibbs energies are available ($\Delta G^0(1) = -32 \text{ kJ mol}^{-1}$, $\Delta G^0(8) = 67 \text{ kJ mol}^{-1}$). For reaction (6), a Gibbs energy of $\Delta G^0(6) = 47 \text{ kJ mol}^{-1}$ ($K_6 = 10^{-8.2} \text{ M}$) has now been calculated by G1. From the thermodynamic cycle one hence arrives at $\Delta G^0(5) = -12 \text{ kJ mol}^{-1}$. This relates to $\text{pK}_a(\text{HO}_3\cdot) = -2.1$. Thus, the $\text{HO}_3\cdot$ radical is a very strong acid. This value agrees with a value of -2.0 obtained from the Bielski and Schwarz relationship for pK_a values of O_xH_y compounds. Reaction (6) must be very slow, $0.1 < k_6 < 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

INTRODUCTION

Three aspects of free-radical chemistry in aqueous solution has been troubling free-radical chemist for a long time. Why reacts the anion of the $\cdot\text{OH}$ radical, $\text{O}^{\cdot-}$, fast with O_2 [reaction (1), $k_1 = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$]^[1] while $\cdot\text{OH}$ does not, how decays $\text{O}_3^{\cdot-}$ into $\cdot\text{OH}$, and what is the pK_a value of the $\text{HO}_3^{\cdot}$ radical?

In ozone reactions, $\text{O}_3^{\cdot-}$ is a common intermediate.^[2-4] It may be generated in a direct electron transfer reaction [reaction (2)],^[5] but more often an adduct is an intermediate [reactions (3) and (4)].^[6-8]

The formation of $\text{O}_3^{\cdot-}$ in ozone reactions is of considerable importance in water treatment. There is a general agreement that $\text{O}_3^{\cdot-}$ must be the precursor of $\cdot\text{OH}$ that is made responsible for the degradation of ozone-refractory micropollutants in the treatment of drinking water and wastewater with ozone. In this context it may be noted that upon reacting with ozone, the organic matter contained in wastewater produces as much as 13% $\cdot\text{OH}$ with respect to ozone consumed.^[9] Beyond this general statement that $\text{O}_3^{\cdot-}$ must be the precursor of $\cdot\text{OH}$, there is, however, a continuing discussion as to how $\text{O}_3^{\cdot-}$ is converted into $\cdot\text{OH}$.

According to a pulse radiolysis study, $\text{O}_3^{\cdot-}$ is protonated [reaction (–5)], and $\text{HO}_3^{\cdot}$ thus generated loses O_2 [reaction (–6)].^[10]

A $\text{pK}_a(\text{HO}_3^{\cdot}) = 6.15$ (revised to 8.2, Bühler, private communication) has been estimated from these experiments,^[10] and this mechanism is also found in the most recent review on the chemistry of ozone in aqueous solution.^[4]

A pK_a as high as this is doubtful as $HO_3^{\cdot}$ should be more acidic than $HO_2^{\cdot}$ whose $pK_a = 4.8$ is well established.^[11] In fact, Bielski and Schwarz^[12] developed an experimental relationship for the pK_a values of O_xH_y acids [equation (7)], wherefrom one arrives at $pK_a(HO_3^{\cdot}) = -2.0$.

$$pK_a(O_xH_y) = 19 - 7 \times (O/H) \tag{7}$$

We have, therefore, suggested that $O_3^{\cdot-}$ decays according to equilibria (1) and (8) [$pK_a(^{\cdot}OH) = 11.8$].^[7;13]

From the above, it can be seen that the reaction of $^{\cdot}OH$ with O_2 and the pK_a of $HO_3^{\cdot}$ radical are interconnected by a thermodynamic cycle (Fig.1).

Figure 1. Thermodynamic cycle involving O_2 , $^{\cdot}OH/O^{\cdot-}$ and $HO_3^{\cdot}/O_3^{\cdot-}$

From this, one can arrive at $pK_a(HO_3^{\cdot})$ upon calculating the Gibbs energy for the reaction of O_2 with $^{\cdot}OH$, reaction (6), as the two other Gibbs energies are well known. Such calculations have been carried out in the present study.

RESULTS AND DISCUSSION

The Gibbs energy of reaction (6) has been calculated by various approaches (Table 1).

Table 1. Compilation of experimental und calculated Gibbs energies (kJ mol^{-1})

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Among the above methods, the most reliable one proved to be G1 (for a discussion see Ref.^[8]) followed by B3LYP/6-311+G(d,p)/PBF. Calculations of charged species as required for the Gibbs energy of equilibrium (1) are inherently poorer. G1 does not allow calculating charged species. Here B3LYP/6-311+G(d,p)/PBF has been tested to be the best. Indeed, the calculated value using this method for comes closest to the experimental value. For equilibrium (1), a reliable experimental value is available, and for further discussions one can neglect the calculated ones.

The Gibbs energy of reaction (6) relates to the equilibrium constant of reaction (6) according to equation (9).

$$\ln K = -\Delta G^0 / RT \quad (9)$$

From the above value of +47 kJ mol⁻¹ for the Gibbs energy of equilibrium (6), an equilibrium constant of $K_6 = 10^{-8.2}$ is calculated. The anion of the hydroxyl radical, O⁻, reacts fast with O₂ ($k_1 = 3.5 \times 10^9$ M⁻¹ s⁻¹) giving rise to O₃⁻, and details of equilibrium (1) are well established ($K_1 = 10^{5.7}$ M, $k_{-1} = 1.94 \times 10^3$ s⁻¹).^[1] Thus, the Gibbs energy for reaction (1) is $\Delta G^0 = -32$ kJ mol⁻¹. A Gibbs energy of $\Delta G^0 = +67$ kJ mol⁻¹ for reaction (8) is calculated from $pK_a(\cdot\text{OH}) = 11.8$.

Based on the thermodynamic cycle (Fig. 1), a Gibbs energy of $\Delta G^0 = -12$ kJ mol⁻¹ is arrived at for reaction (5). This relates to a pK_a value of the HO₃[•] radical of -2.1 in good agreement with Bielski and Schwarz relationship^[12] that yields $pK_a(\text{HO}_3^{\cdot}) = -2.0$.

This good agreement supports our earlier statement^[7] that the reported^[10] $pK_a(\text{HO}_3^\bullet) = 6.15$ [revised to 8.2 (Bühler, private communication)] must have been an experimental artifact (so-called “reactivity pK ”).

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In other reactions of ozone with free radicals; such adducts are often only transition states (Naumov and von Sonntag, submitted). This points to a lifetime of $\text{HO}_3^\bullet$ beyond several vibrations, that is, $k_{-6} < 10^{12} \text{ s}^{-1}$. With K_6 in the order of 10^{-8} , k_6 must be $< 10^4 \text{ M}^{-1} \text{ s}^{-1}$. From the pulse radiolysis study of the reaction of $\text{H}^\bullet$ with O_3 , carried out at pH 2,^[15] there was no indication that $\text{O}_3^{\bullet-}$ is present at about 1 μs . Thus the lifetime of $\text{HO}_3^\bullet$ must be $< 10^7 \text{ s}$. This narrows the range to $0.1 > k_6 < 10^4 \text{ M}^{-1} \text{ s}^{-1}$. In any case, the reaction of $^\bullet\text{OH}$ with O_2 must be very slow, as generally assumed, and can thus be neglected for most purposes.

CONCLUSION

The equilibrium constants for the reactions of O_2 with $^\bullet\text{OH}$ and its anion, $\text{O}^{\bullet-}$, differ by as much as fourteen orders of magnitude. The generally accepted statement that the $^\bullet\text{OH}$ radical does not react with O_2 is substantiated here by bracketing the rate constant: $0.1 > k_6 < 10^4 \text{ M}^{-1} \text{ s}^{-1}$. It is now established that $\text{HO}_3^\bullet$ is a very strong acid with a pK_a near –2. With this revised pK_a value at hand, modeling of ozone reactions in aqueous solution can now be carried out with much higher accuracy.

EXPERIMENTAL

The Gibbs energy of reaction (6) was calculated using a number of approaches. Density Functional Theory (DFT) calculations were carried out using B3LYP correlation functional^[16;17] (Jaguar 7.6 program)^[18]. The molecular geometries of all calculated molecules were optimized in water at the B3LYP/6-311+G(d,p)/PBF level of theory. The interactions between the molecule and the solvent were evaluated by Jaguar's Poisson-Boltzmann solver (PBF).^[19] Gibbs free energies (G^0) were calculated at the same level of theory at a standard temperature of 298.15 K and a pressure of 1 atm using unscaled frequencies. Reaction parameters were calculated as the difference of the Gibbs free energies ΔG^0 between reactants and products. Calculations were also made in water (self-consistent reaction field SCRF=COSMO models)^[20;21] at Gaussian-1 (G1)^[22;23], Gaussian-3 (G3MP2B3)^[24], and DFT B3LYP/6-311+G(3df,3pd) levels (as implemented in Gaussian 03)^[25].

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The reaction of $\cdot\text{OH}$ with O_2 , the decay of $\text{O}_3^{\cdot-}$ and the $\text{p}K_{\text{a}}$ of $\text{HO}_3^{\cdot}$ – interrelated questions in aqueous free-radical chemistry

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In the reactions of ozone with organic compounds in aqueous solution, $\text{O}_3^{\cdot-}$ is an abundant intermediate. A basic aspect of its conversion into $\cdot\text{OH}$ is addressed here. The reactions $\text{O}^{\cdot-} + \text{O}_2 \rightleftharpoons \text{O}_3^{\cdot-}$ (1), $\text{H}^+ + \text{O}^{\cdot-} \rightleftharpoons \cdot\text{OH}$ (8), $\cdot\text{OH} + \text{O}_2 \rightleftharpoons \text{HO}_3^{\cdot}$ (6) and $\text{H}^+ + \text{O}_3^{\cdot-} \rightleftharpoons \text{HO}_3^{\cdot}$ (5) are interconnected by a thermodynamic cycle. For equilibria (1) and (8) reliable equilibrium constants, and hence Gibbs energies are available ($\Delta G^0(1) = -32 \text{ kJ mol}^{-1}$, $\Delta G^0(8) = 67 \text{ kJ mol}^{-1}$). For reaction (6), a Gibbs energy of $\Delta G^0(6) = 47 \text{ kJ mol}^{-1}$ ($K_6 = 10^{-8.2} \text{ M}$) has now been calculated by G1. From the thermodynamic cycle one hence arrives at $\Delta G^0(5) = -12 \text{ kJ mol}^{-1}$. This relates to $\text{p}K_{\text{a}}(\text{HO}_3^{\cdot}) = -2.1$. Thus, the $\text{HO}_3^{\cdot}$ radical is a very strong acid. This value agrees with a value of -2.0 obtained from the Bielski and Schwarz relationship for $\text{p}K_{\text{a}}$ values of O_xH_y compounds. Reaction (6) must be very slow, $0.1 < k_6 < 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

INTRODUCTION

Three aspects of free-radical chemistry in aqueous solution have been troubling free-radical chemist for a long time: (i) why reacts the anion of the $\cdot\text{OH}$ radical, $\text{O}^{\cdot-}$, fast with O_2 [reaction (1), $k_1 = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$]^[1] while $\cdot\text{OH}$ does not, (ii) how decays $\text{O}_3^{\cdot-}$ into $\cdot\text{OH}$, and (iii) what is the pK_a value of the $\text{HO}_3^{\cdot}$ radical?

In reactions of ozone with organic compounds in aqueous solution, $\text{O}_3^{\cdot-}$ is a common intermediate.^[2-4] It may be generated in a direct electron transfer reaction [reaction (2)],^[5] but more often an adduct is an intermediate [reactions (3) and (4)].^[6-8]

This is depicted for the reaction of ozone with 1,3,5-trimethoxybenzene in Fig. 1, where electron transfer competes with the formation of an adduct [reaction (b)].

From this zwitterionic adduct, three competing reactions are evident from the products that are formed. Release of singlet dioxygen [reaction (c)] gives rise to the phenol [reaction (d)]. Closure of the zwitterion leads to an ozonide which is the precursor of the muconic product

[reactions (e) and (f)]. The quinone is thought to arise from the hydrotrioxide formed upon proton transfer [reactions (g) and (h)]. Details are discussed elsewhere^[5].

The formation of $O_3^{\cdot-}$ in ozone reactions is of considerable importance in water treatment. There is a general agreement that $O_3^{\cdot-}$ must be the precursor of $\cdot OH$ that is made responsible for the degradation of ozone-refractory micropollutants in the treatment of drinking water and wastewater with ozone. In this context it may be noted that upon reacting with ozone, the organic matter contained in wastewater produces as much as 13% $\cdot OH$ with respect to ozone consumed.^[9] Beyond this general statement that $O_3^{\cdot-}$ must be the precursor of $\cdot OH$, there is, however, a continuing discussion as to how $O_3^{\cdot-}$ is converted into $\cdot OH$. Without having solved this question, it is not possible to simulate such ozone reactions with some confidence.

According to a pulse radiolysis study, $O_3^{\cdot-}$ is protonated [reaction (–5)], and $HO_3^{\cdot}$ thus generated loses O_2 [reaction (–6)].^[10]

A $pK_a(HO_3^{\cdot}) = 6.15$ (revised to 8.2, Bühler, private communication) has been estimated from these experiments,^[10] and this mechanism is also found in the most recent review on the chemistry of ozone in aqueous solution.^[4]

A pK_a as high as this is doubtful as $HO_3^{\cdot}$ should be more acidic than $HO_2^{\cdot}$ whose $pK_a = 4.8$ is well established.^[11] In fact, Bielski and Schwarz^[12] developed an experimental relationship for the pK_a values of O_xH_y acids [equation (7)], wherefrom one arrives at $pK_a(HO_3^{\cdot}) = -2.0$.

$$pK_a(O_xH_y) = 19 - 7 \times (O/H) \quad (7)$$

We have, therefore, suggested that $O_3^{\cdot-}$ decays according to equilibria (1) and (8) [$pK_a(\cdot OH) = 11.8$].^[7;13]

From the above, it can be seen that the reaction of $\cdot\text{OH}$ with O_2 and the $\text{p}K_{\text{a}}$ of $\text{HO}_3\cdot$ radical are interconnected by a thermodynamic cycle (Fig.2).

Figure 2. Thermodynamic cycle involving O_2 , $\cdot\text{OH}/\text{O}^{\cdot-}$ and $\text{HO}_3\cdot/\text{O}_3^{\cdot-}$

From this, one can arrive at $\text{p}K_{\text{a}}(\text{HO}_3\cdot)$ upon calculating the Gibbs energy for the reaction of O_2 with $\cdot\text{OH}$, reaction (6), as the two other Gibbs energies are well known. Such calculations have been carried out in the present study.

RESULTS AND DISCUSSION

The Gibbs energy of reaction (6) has been calculated by various approaches (Table 1).

Table 1. Compilation of experimental und calculated Gibbs energies (kJ mol^{-1})

Method	Equilibrium (1)	Equilibrium (6)
Experimental	−32	Not available
G1	Not possible	+47
B3LYP/6-311+G(d,p)/PBF	−51	+38
G3MP2B3/COSMO	−69	+34
B3LYP/6-311+G(3df,3pd)/COSMO	−65	+33

Among the above methods, the most reliable one proved to be G1 (for a discussion see Ref.^[8]) followed by B3LYP/6-311+G(d,p)/PBF. Calculations of charged species as required for the Gibbs energy of equilibrium (1) are inherently poorer. G1 does not allow calculating charged species. Here B3LYP/6-311+G(d,p)/PBF has been tested to be the best. Indeed, the calculated value using this method for comes closest to the experimental value. For equilibrium (1), a reliable experimental value is available, and for further discussions one can neglect the calculated ones.

The Gibbs energy of reaction (6) relates to the equilibrium constant of reaction (6) according to equation (9).

$$\ln K = -\Delta G^0 / RT \quad (9)$$

From the above value of +47 kJ mol⁻¹ for the Gibbs energy of equilibrium (6), an equilibrium constant of $K_6 = 10^{-8.2}$ is calculated. The anion of the hydroxyl radical, O⁻, reacts fast with O₂ ($k_1 = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) giving rise to O₃⁻, and details of equilibrium (1) are well established ($K_1 = 10^{5.7} \text{ M}$, $k_{-1} = 1.94 \times 10^3 \text{ s}^{-1}$).^[1] Thus, the Gibbs energy for reaction (1) is $\Delta G^0 = -32 \text{ kJ mol}^{-1}$. A Gibbs energy of $\Delta G^0 = +67 \text{ kJ mol}^{-1}$ for reaction (8) is calculated from $\text{p}K_{\text{a}}(\text{'OH}) = 11.8$.

Based on the thermodynamic cycle (Fig. 1), a Gibbs energy of $\Delta G^0 = -12 \text{ kJ mol}^{-1}$ is arrived at for reaction (5). This relates to a $\text{p}K_{\text{a}}$ value of the HO₃[•] radical of -2.1 in good agreement with Bielski and Schwarz relationship^[12] that yields $\text{p}K_{\text{a}}(\text{HO}_3^{\bullet}) = -2.0$.

This good agreement supports our earlier statement^[7] that the reported^[10] $\text{p}K_{\text{a}}(\text{HO}_3^{\bullet}) = 6.15$ [revised to 8.2 (Bühler, private communication)] must have been an experimental artifact (so-called "reactivity $\text{p}K^{\bullet}$ ").

As the rate constant for reaction (-5) must be in the order of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$,^[14] the rate of deprotonation of HO₃[•], reaction (5), must be in the order of 10^{12} s^{-1} . This reaction is in competition with its decay into 'OH and O₂ [reaction (-6)]. Upon calculating the Gibbs energy

of the reaction of $\text{H}^\bullet$ with O_3 , the adduct $\text{HO}_3^\bullet$ proved to be sufficiently stable to qualify as an intermediate [reactions (10) and (–6); $\Delta G^0_{\text{overall}} = -411 \text{ kJ mol}^{-1}$].

In other reactions of ozone with free radicals; such adducts are often only transition states (Naumov and von Sonntag, submitted). This points to a lifetime of $\text{HO}_3^\bullet$ beyond several vibrations, that is, $k_{-6} < 10^{12} \text{ s}^{-1}$. With K_6 in the order of 10^{-8} , k_6 must be $< 10^4 \text{ M}^{-1} \text{ s}^{-1}$. From the pulse radiolysis study of the reaction of $\text{H}^\bullet$ with O_3 , carried out at pH 2,^[15] there was no indication that O_3^- is present at about 1 μs . Thus the lifetime of $\text{HO}_3^\bullet$ must be $< 10^7 \text{ s}$. This narrows the range to $0.1 < k_6 < 10^4 \text{ M}^{-1} \text{ s}^{-1}$. In any case, the reaction of $^\bullet\text{OH}$ with O_2 must be very slow, as generally assumed, and can thus be neglected for most purposes.

CONCLUSION

The equilibrium constants for the reactions of O_2 with $^\bullet\text{OH}$ and its anion, O^- , differ by as much as fourteen orders of magnitude. The generally accepted statement that the $^\bullet\text{OH}$ radical does not react with O_2 is substantiated here by bracketing the rate constant: $0.1 > k_6 < 10^4 \text{ M}^{-1} \text{ s}^{-1}$. It is now established that $\text{HO}_3^\bullet$ is a very strong acid with a $\text{p}K_a$ near -2 . With this revised $\text{p}K_a$ value at hand, modeling of ozone reactions in aqueous solution can now be carried out with much higher accuracy.

EXPERIMENTAL

The Gibbs energy of reaction (6) was calculated using a number of approaches. Density Functional Theory (DFT) calculations were carried out using B3LYP correlation functional^[16;17] (Jaguar 7.6 program)^[18]. The molecular geometries of all calculated molecules were optimized in water at the B3LYP/6-311+G(d,p)/PBF level of theory. The interactions between the molecule and the solvent were evaluated by Jaguar's Poisson-Boltzmann solver (PBF).^[19] Gibbs free energies (G^0) were calculated at the same level of theory at a standard

134 temperature of 298.15 K and a pressure of 1 atm using unscaled frequencies. Reaction
 135 parameters were calculated as the difference of the Gibbs free energies ΔG^0 between reactants
 136 and products. Calculations were also made in water (self-consistent reaction field
 137 SCRF=COSMO models)^[20;21] at Gaussian-1 (G1)^[22;23], Gaussian-3 (G3MP2B3)^[24], and DFT
 138 B3LYP/6-311+G(3df,3pd) levels (as implemented in Gaussian 03)^[25].

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