Thermochemistry and Reaction Mechanisms of Nitromethane Ignition

C. Melius

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Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551-0969, U.S.A.

Abstract: The thermochemistry and reaction mechanisms of nitromethane initiation are modeled using detailed chemical kinetics. Initial conditions correspond to gaseous nitromethane at atmospheric and liquid-like densities and initial temperatures between 1100 and 2000 K. Global reactions as well as elementary reactions are identified for each of the two stages of ignition. The chemical steps to convert the nitro group to N_2 involve a complex set of elementary reactions. The time-dependence of the ignition steps (ignition delay times) as a function of temperature and pressure is used to determine effective activation energies and pressure dependencies to ignition. The ignition delay times range from several nanoseconds to tens of microseconds. At atmospheric conditions, the delay times for both ignition stages are in excellent agreement with observed experimental data. At the high densities, the ignition times at these elevated temperatures appear to be dominated by the same reaction mechanism that occurs for atmospheric gaseous nitromethane initiation. This is to be contrasted with lower temperature, condensed-phase ignition studies where it appears that solvent-assisted reactions dominate.

1. INTRODUCTION

The ability to identify the chemical reactions involved in the initiation of energetic materials is challenging due to the extremely short time scales involved as well as the high temperatures and pressures that are generated. Furthermore, the chemical intermediates of ignition are highly reactive. The chemistry of nitro compounds, such as nitramines and nitroaromatics, is further complicated by the fact that they may undergo two-stage ignition. We therefore have investigated the initiation of nitromethane as a prototype of an energetic material containing the nitro moiety. The ignition of nitromethane has been studied both experimentally [1-9] and computationally [1,10-15]. In particular, the ignition delay time of gas-phase ignition of nitromethane has been studied by Guirguis *et al.* [1] in which they were able to observe two stages of ignition. Several groups have modeled the ignition process using detailed chemical kinetics [1,9], including previous work by us [13,14]. The modeling was able to treat the first-stage ignition reasonably well, but the second-stage ignition delay times were off by several orders of magnitude. Recent work by Lin and coworkers [16-18] have improved our understanding of the elementary reactions involving the NO, HNO, NO_2, and HCN species. This has enabled us to generate an improved detailed reaction mechanism for nitromethane. We use this improved mechanism to study the initiation of gaseous nitromethane at atmospheric conditions as well as at densities corresponding to that of

liquid nitromethane. We present the thermodynamics and reaction pathways of the ignition steps. We then use the ignition delay times to determine effective activation energies and pressure dependencies.

2. METHOD

The study of ignition in a uniformly heated system, such as in a shock tube, allows us to study the combustion chemistry of energetic materials in a environment that can provide the initial decomposition and initiation reaction mechanisms. The energetic material can be treated as a homogeneous gas mixture in a closed system, in which we follow the time-dependent evolution of the chemical species. For instance, we can treat an adiabatic system with constant pressure or volume, or we can follow the chemistry under shock detonation conditions. We use the SENKIN program [19], which includes sensitivity analysis, for the integration of the energy and mass conservation equations.

In this section, we study the chemistry of gaseous nitromethane initiation. The ignition of nitromethane is treated as being under constant volume. The governing equations are [14,19]

$$\frac{dY_k}{dt} = v \, \dot{\omega}_k \, W_k \quad (k = 1, ..., K). \tag{1}$$

and

$$c_v \frac{dT}{dt} = - v \sum_{k=1}^{K} e_k \, \dot{\omega}_k \, W_k, \tag{2}$$

In the above equations, T is the temperature, Y_k the mass fraction of the kth species, W_k is the molecular weight of the kth species, t is time, $v = V/m$ is the specific volume, e_k is the internal energy of the kth species, c_v is the constant volume heat capacity of the mixture, and $\dot{\omega}_k$ is the molar rate of production of the kth species. The chemical reaction mechanism included 48 species and 312 elementary reactions. The thermochemical dynamic properties and chemical production rates are evaluated using the Chemkin package [19]. The 48 species and their heats of formation are presented in Table I.

Table I. The chemical species used in the detailed chemical kinetic modeling of nitromethane. Also given are the heats of formation at 298 K (ΔH^o_{f298}), where energies are given in kcal-mol^{-1}.

1	CH_3NO_2	-16.84	2	CH_3ONO	-15.25
3	NO	21.58	4	NO_2	7.91
5	HNO	23.80	6	HONO	-18.34
7	N_2O	19.61	8	H	52.10
9	H_2	0.0	10	O	59.56
11	O_2	0.0	12	OH	9.32
13	H_2O	-57.8	14	HO_2	2.50
15	N	112.96	16	N_2	0.0
16	NH	85.2	18	NH_2	45.50
19	NH_3	-11.97	20	NNH	58.57
21	HNNO	55.20	22	HNOH	21.06
23	H_2NO	15.82	24	N_2H_2	50.90
25	CO	-26.42	26	CO_2	-94.06
27	HCO	10.40	28	CH_2O	-27.70
29	CH_3O	3.90	30	CH_2OH	-4.10

Table I. (Cont.)

31	CH_3OH	-48.06	32	CH_3	34.82
33	CH_4	-17.90	34	CN	104.01
35	HCN	31.89	36	H_2CN	59.11
37	CH_3NH	44.94	38	HCNO	38.43
39	HOCN	-3.53	40	HNCO	-28.22
41	NCO	31.51	42	NCN	107.60
43	CH_3NO	18.95	44	H_2CNO_2	36.47
45	H_2CNO	41.43	46	CH_3NHO	13.32
47	H_2CNOH	5.15	48	CH_2NO_2H	-2.86

3. RESULTS

In Figs. 1 and 2, we present the temperature and species profiles as a function of time for the initiation of 100 per cent gaseous CH_3NO_2 at 7.25 atmospheres and 1131 K. These conditions are representative of the experimental conditions of Guirguis et al. [1]. The initiation undergoes two ignition stages, at 13.3 μsec and 25.8 μsec, respectively. The final temperature is 3598 K.

The chemistry can be subdivided by time into several stages: (I) a preliminary stage of slow decomposition followed by (II) a first-stage ignition that undergoes a rapid temperature rise followed by (III) an intermediate stage in which the temperature remains on a plateau followed by (IV) a second-stage ignition where the temperature again rises rapidly to form the final products. The reaction mechanism flow diagrams for the first-stage ignition (II), the intermediate stage (III), and the second-stage ignition (IV) are shown in Figs. 3-5. These reaction pathways show the dominating elementary reactions occurring in each of these stages, with thick arrows being the major pathways while thin arrows are the minor pathways. We have separately shown the reaction chemistry for the carbon atom and the nitrogen atom of nitromethane. The carbon atom must be oxidized, to form CO and, to a lesser extent, CO_2 (note that there is not enough oxygen in nitromethane to oxidize the carbon to CO_2 and the hydrogen to H_2O). Meanwhile, the nitrogen, which is in an oxidized state as part of the nitro group moiety, must be reduced to N_2. The reaction flow diagram for the preliminary decomposition stage (I) is similar to that of the first-stage ignition (II) and thus is not shown. The major difference is that the preliminary stage (I) occurs at the low end of the temperature range, giving rise to slower rates and resulting in a greater variety of minor intermediate species being formed.

In Figs. 6-8, we show the enthalpies and free energies of possible species corresponding to the composition $C_1H_3N_1O_2$. This represents the composition of nitromethane and includes tautomers of nitromethane as well as various product species. Besides the ΔH at 300K (see Table I for individual species heats of formation), we present the ΔG's at 300K and 2000K.

Fig. 1 showed the time profile for nitromethane initiation at 7.25 atmospheres and 1131 K, indicating two rapid temperature rises at 13.6 μsec and 26.1 μsec, designated τ_1 and τ_2 respectively. In Table II, we present these ignition delay times, τ_1 and τ_2, for various initial temperatures and pressures. These results are used to determine activation energies of ignition, defined by the relation $ln\ (\tau_a/\tau_b) \propto (\Delta E/R)\ (1/T_a - 1/T_b)$. The resulting ΔE's for the first-stage and second-stage ignitions are presented in Table III. In a similar manner, we can define pressure dependencies to the ignition delay time by the relation $ln\ (\tau_a/\tau_b) \propto n\ ln\ (P_a/P_b)$, which corresponds to τ being proportional to P^n. The resulting pressure exponents are given in Table IV.
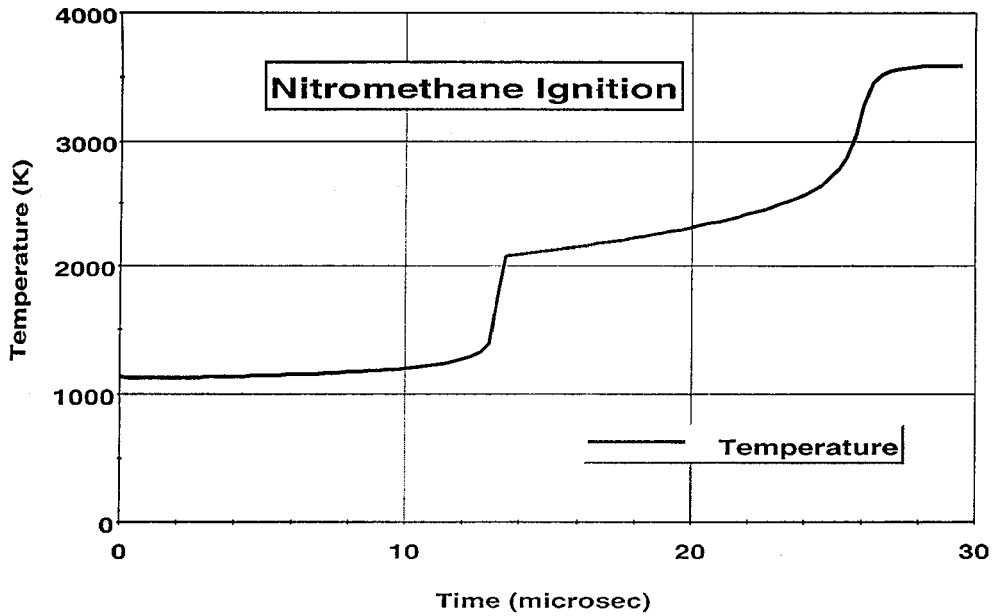
Fig. 1. Temperature vs. time profile for ignition of nitromethane. Initial conditions are 1131 K and 7.25 atm.
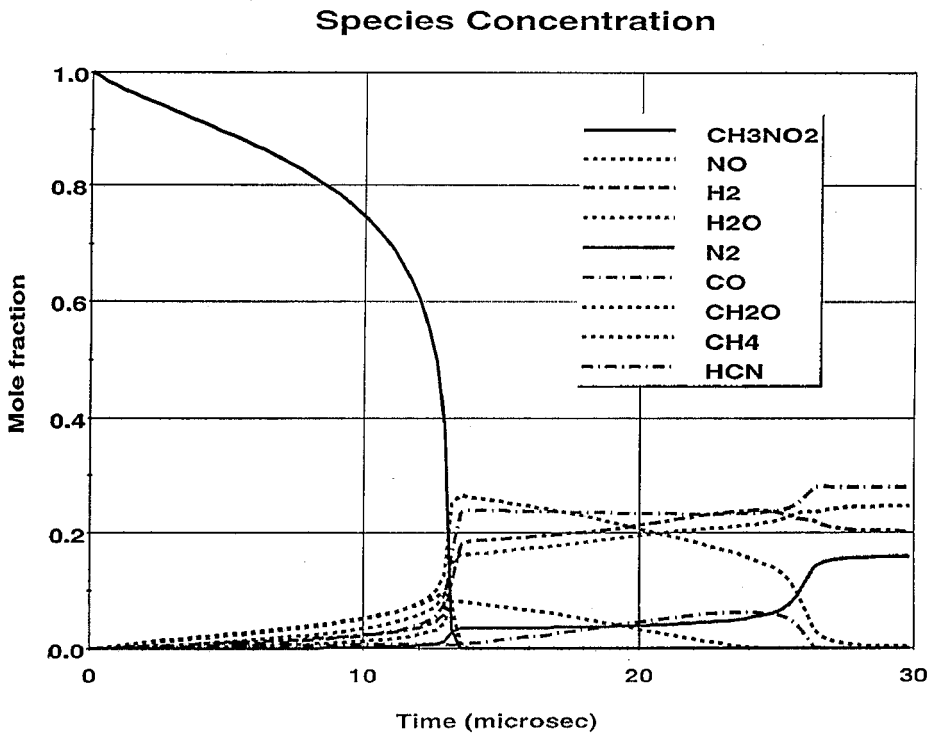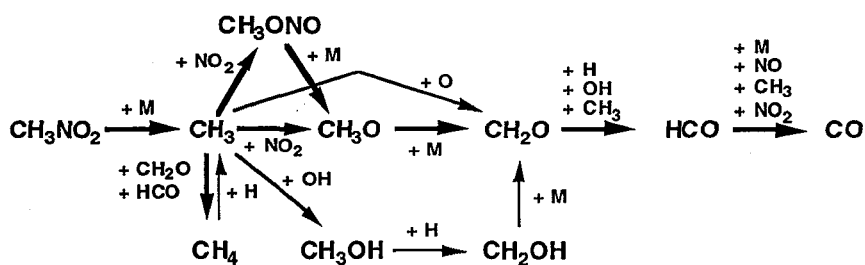

Fig. 2. Species vs. time profile for ignition of nitromethane. Intial conditions are 1131 K and 7.25 atm.

Nitromethane First Stage Ignition Chemistry

Carbon Mechanism

Nitrogen Mechanism
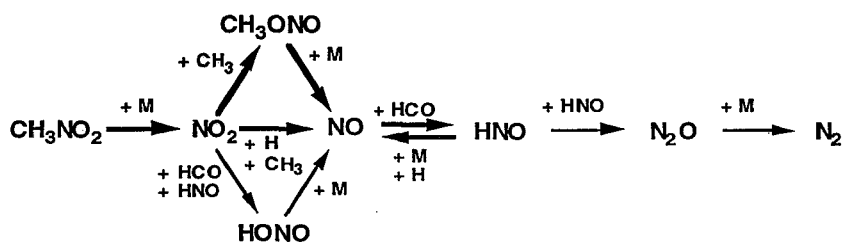
Fig. 3. Reaction mechanism flow diagrams for the first stage-ignition of nitromethane. Thick arrows indicate major pathways. Dominant collision partners for bimolecular reactions are indicated next to arrows. Unimolecular decomposition reactions are indicated by the third-body notation +M. The chemistry of carbon- and nitrogen-containing species are presented separately.

Nitromethane Intermediate Stage Chemistry

Carbon Mechanism
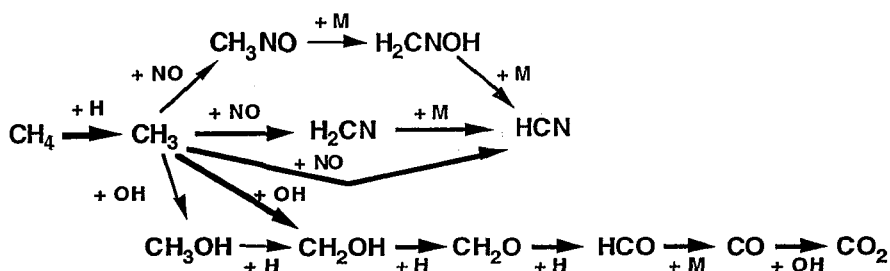
Nitrogen Mechanism
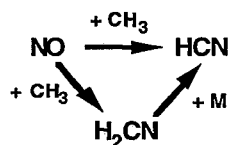
Fig. 4. Reaction mechanism flow diagrams for the intermediate stage (between first- and second-stage) ignition of nitromethane. See Fig. 3 for further caption descriptions.

Nitromethane Second Stage Ignition Chemistry
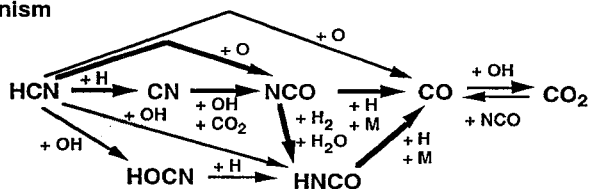
Carbon Mechanism

Nitrogen Mechanism from HCN   **Nitrogen Mechanism from NO**
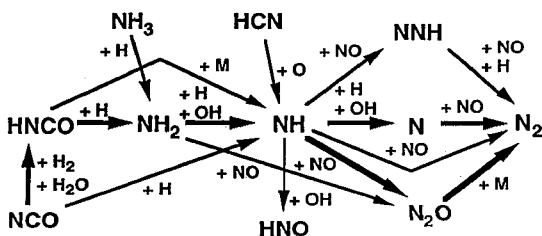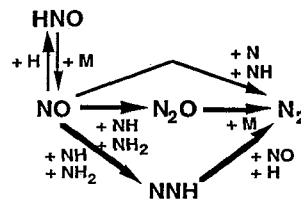
Fig. 5. Reaction mechanism flow diagrams for the second-stage ignition of nitromethane. See Fig. 3 for further caption descriptions.

Heats of Formation for Nitromethane and Its Tautomers at 300K
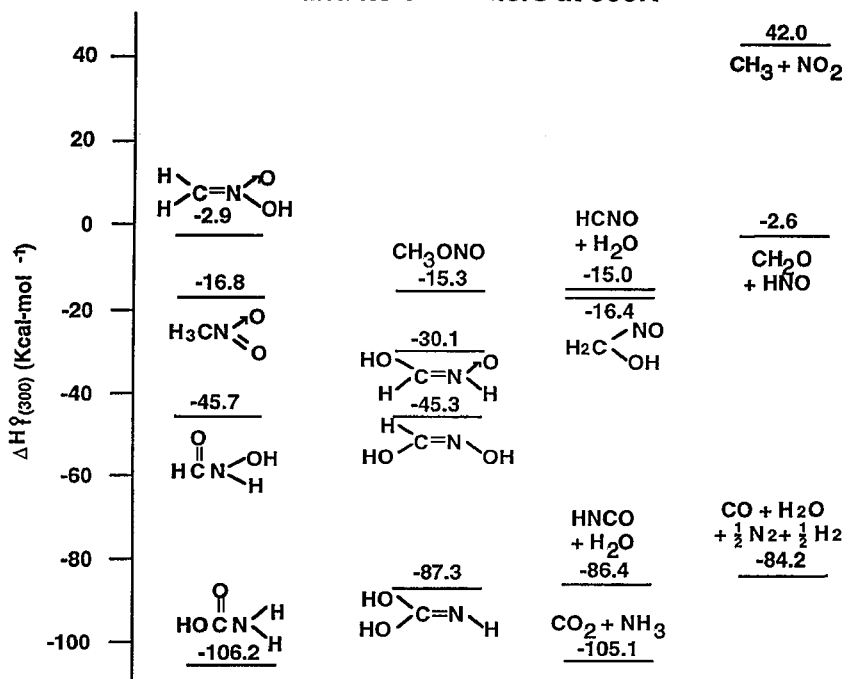
Fig. 6. Heats of formation, ΔH's, at 300 K for nitromethane and its tautomers and other stoichiometric products. Enthalpies are in kcal-mol^{-1}.
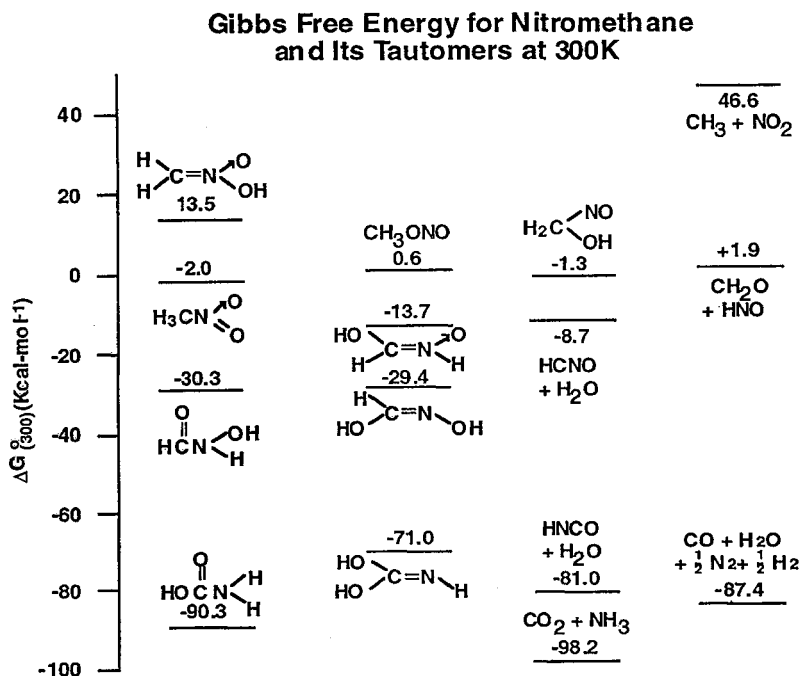
Gibbs Free Energy for Nitromethane and Its Tautomers at 300K

Fig. 7. Free energies, ΔG's, at 300 K for nitromethane and its tautomers and other stoichiometric products. Free energies are in kcal-mol^{-1}.

Gibbs Free Energy for Nitromethane and Its Tautomers at 2000K
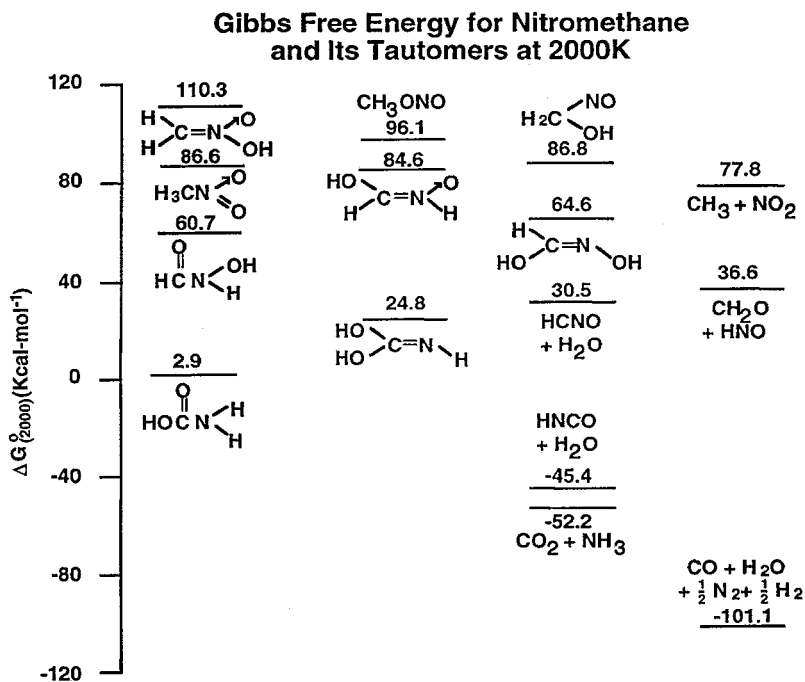
Fig. 8. Free energies, ΔG's, at 2000 K for nitromethane and its tautomers and other stoichiometric products. Free energies are in kcal-mol^{-1}.

Table II. Ignition delay times for gaseous nitromethane for different initial temperatures and pressures.

T (K)	P (Atm)	τ_1	τ_2	$\tau_2 - \tau_1$
1131	5.25	14.9 µs	35.5 µs	20.6 µs
1131	7.25	13.3 µs	25.8 µs	12.5 µs
1331	5.25	1.6 µs	25.3 µs	23.7 µs
1331	7.25	1.2 µs	15.5 µs	14.3 µs
1331	8.53	1.2 µs	12.3 µs	11.1 µs
1131	1574.4	4.352 µs	4.403 µs	.051 µs
1131	1852.8	4.288 µs	4.298 µs	.010 µs
1331	1574.4	0.208 µs	0.219 µs	.010 µs
1331	1852.8	0.202 µs	0.208 µs	.006 µs
1900	2644.8	2.52 ns	4.76 ns	2.24 ns
2000	2784.	1.59 ns	3.59 ns	2.00 ns

Table III. Activation energies of ignition (defined by $ln\,(\,\tau_a\,/\,\tau_b\,)\;\propto\;\Delta E\,/\,R\,(\,1/T_a - 1/T_b))$. Ignition delay times are taken from Table II. Energies in kcal-mol^{-1}.

Constant Pressure	T(K)	P (Atm)	ΔE_1	ΔE_2
	1230	5.25	33.2	7.6
	1230	7.25	35.6	5.1
	1230	1574.4	45.4	44.9
	1230	1852.8	45.7	45.3

Constant Volume	T(K)	P (Atm)	ΔE_1	ΔE_2
	1230	5.25	35.7	11.0
	1230	1574.4	45.9	45.6
	1950	2644.8	34.8	21.3

Table IV. Pressure dependence of ignition delay times for gaseous nitromethane. Pressure dependence is defined by $\tau \propto P^n$ or $ln\,(\,\tau_a\,/\,\tau_b\,) \propto n\,ln\,(\,P_a\,/\,P_b\,)$. Ignition delay times are taken from Table II.

Low Pressure	T (K)	n_1	n_2
	1131	-0.36	-0.99
	1331	-0.85	-1.52
Low to High	T (K)	n_1	n_2
	1131	-0.22	-0.37
	1331	-0.35	-0.82
High Pressure	T (K)	n_1	n_2
	1131	-0.09	-0.15
	1331	-0.19	-0.32

4. DICUSSION

4.1 Chemical Reactions

Several points regarding the nitromethane thermochemistry can be observed from Figs. 6-8. First, from the ΔH's presented in Fig. 6, it is seen that indeed nitromethane is an unstable tautomer of $C_1H_3N_1O_2$, lying ~90 kcal-mol^{-1} above the most stable form, $C(O)OHNH_2$. In fact, $C(O)OHNH_2$ is more stable than the major products of detonation, CO, H_2O, N_2, and H_2 (see Fig. 2). Furthermore, as can be seen in Fig. 6, the lowest bond-breaking moiety for CH_3NO_2 is the breaking of the C-N bond to form $CH_3 + NO_2$. which is endothermic by nearly 59 kcal-mol.$^{-1}$ Thus, from an enthalpy view point, CH_3NO_2 would appear to be a reasonable energetic material.

However, while one tends to think of the thermochemistry of the reactions in terms of enthalpies (e.g., heats of reaction), it is the free energy of the system that drives the reaction. Dividing the $C_1H_3N_1O_2$ molecular species into two or more species lowers the free energy, particularly at higher temperatures. As one can see from Fig. 8, at 2000K, the ΔG of $CH_3 + NO_2$ is more stable than that of CH_3NO_2 itself. And the breakup of CH_3NO_2 into its small product molecules, CO, H_2O, N_2, and H_2, forming three molecules from one reactant molecule is extremely exothermic. Thus, it is necessary to have more than the thermostability to bond breaking to make an insensitive energetic material. As we shall see, it is necessary to have a reaction pathway which prevents direct conversion of the energetic material to products.

The overall reaction chemistry converting nitromethane to products is

$$CH_3NO_2 \rightarrow CO + \tfrac{1}{2}\,N_2 + H_2O + \tfrac{1}{2}\,H_2 \qquad\qquad \Delta H_{Rxn} = -67 \qquad (R1)$$

with minor contributions of the following reactions

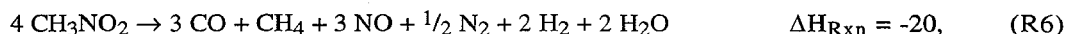|			
$CO + H_2O \rightarrow CO_2 + H_2$	$(^1/_{10})$	$\Delta H_{Rxn} = -10$	(R2)
$H_2O \rightarrow H + OH$	$(^1/_{15})$	$\Delta H_{Rxn} = +119$	(R3)
$H_2 \rightarrow H + H$	$(^1/_{30})$	$\Delta H_{Rxn} = +104$	(R4)

Contributions of R2-R4 relative to reaction R1 are given in parentheses. The heats of reaction ΔH_{Rxn} are given in kcal-mol^{-1}.

As stated above, the chemistry can be subdivided by time into several stages: (I) a preliminary stage of slow decomposition followed by (II) a first-stage ignition that undergoes a rapid temperature rise followed by (III) an intermediate stage in which the temperature remains on a plateau followed by (IV) a second-stage ignition where the temperature again rises rapidly forming the final products. This temporal division of chemical reactions, as indicated in Fig. 2, is consistent with the temporal division of the temperature into a preliminary, first-stage ignition, intermediate region, and second-stage ignition, as indicated in Fig. 1. The reaction chemistry during the preliminary stage (I) is
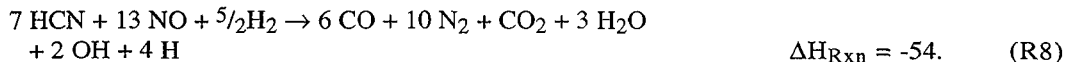
$$9\ CH_3NO_2 \rightarrow 5\ CH_2O + {}^5\!/_8\ HNO + {}^7\!/_4\ CO + {}^{35}\!/_8\ NO + {}^5\!/_2\ H_2 + 3\ H_2O + {}^3\!/_4\ N_2O$$
$$+\ HCN + CH_4 + {}^5\!/_8\ NO_2 + {}^1\!/_4\ CO_2 + {}^1\!/_4\ N_2 + {}^3\!/_8\ HONO \qquad \Delta H_{Rxn} = -10, \qquad (R5)$$
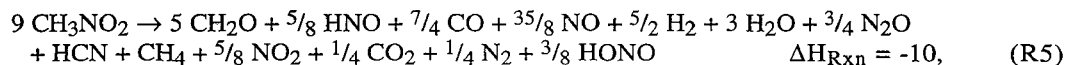
the reaction during the first-stage ignition (II) is

$$4\ CH_3NO_2 \rightarrow 3\ CO + CH_4 + 3\ NO + {}^1\!/_2\ N_2 + 2\ H_2 + 2\ H_2O \qquad \Delta H_{Rxn} = -20, \qquad (R6)$$

the reaction during the intermediate-stage ignition (III) between the first- and second-stage ignitions is

$$4\ CH_4 + 6\ NO + CO \rightarrow 4\ HCN + 5\ H_2O + H_2 + N_2 + CO_2 \qquad \Delta H_{Rxn} = -48, \qquad (R7)$$
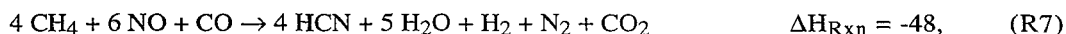
while the reaction during the second-stage ignition (IV) is

$$7\ HCN + 13\ NO + {}^5\!/_2 H_2 \rightarrow 6\ CO + 10\ N_2 + CO_2 + 3\ H_2O$$
$$+\ 2\ OH + 4\ H \qquad \Delta H_{Rxn} = -54. \qquad (R8)$$

In order to relate the heats of reaction, ΔH_{Rxn}, of the individual reactions to each other, we have normalized the ΔH_{Rxn} for each of the reactions to the CH_3NO_2 molecule. Thus, the ΔH_{Rxn}'s are normalized per CH_3NO_2 (R5 and R6) or NO (R7 and R8) molecule.

The global reactions for each stage in the nitromethane initiation can be further subdivided into subglobal reactions which begin to indicate the reaction mechanism of each stage. While this reaction subdivision is not unique, we have attempted to define those subglobal reactions which represent simple combinations of elementary reactions, as indicated in Figs. 3-5. In addition to the subglobal reaction, we also indicate the relative contribution of each reaction to the net reactions presented above. We also give the absolute heat of reaction, ΔH_{Rxn}, for each of the subglobal reactions.

The preliminary stage (I) global reaction R5 is composed of the subglobal reactions

$CH_3NO_2 \rightarrow CH_2O + HNO$	(4)	$\Delta H_{Rxn} = +13$	(R5a)
$CH_3NO_2 \rightarrow CO + NO + {}^3\!/_2\ H_2$	(1)	$\Delta H_{Rxn} = +12$	(R5b)
$2\ CH_3NO_2 \rightarrow CH_4 + CO + H_2 + NO + NO_2$	(1)	$\Delta H_{Rxn} = +19$	(R5c)
$2\ CH_3NO_2 + HNO \rightarrow HCN + CH_2O + 2\ H_2O + 2\ NO$	(1)	$\Delta H_{Rxn} = -58$	(R5d)
$2\ HNO \rightarrow N_2O + H_2O$	$({}^3\!/_4)$	$\Delta H_{Rxn} = -85$	(R5e)
$NO_2 + HNO \rightarrow HONO + NO$	$({}^3\!/_8)$	$\Delta H_{Rxn} = -28$	(R5f)
$CO + 2\ HNO \rightarrow CO_2 + N_2 + H_2O$	$({}^3\!/_8)$	$\Delta H_{Rxn} = -173.$	(R5g)
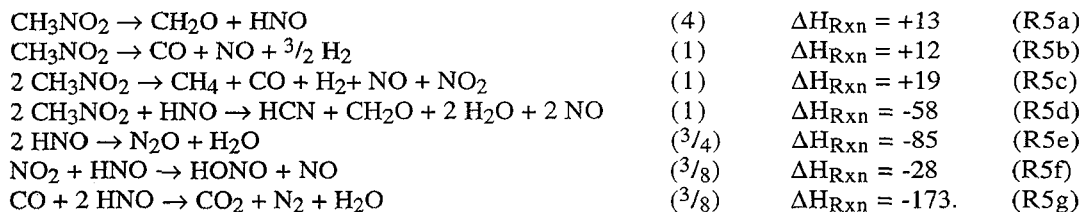
The first-stage global reaction R6 is composed of the subglobal reactions

$CH_3NO_2 \rightarrow CO + NO + {}^3\!/_2\ H_2$	(3)	$\Delta H_{Rxn} = +12$	(R6a)
$CH_3NO_2 + {}^3\!/_2 H_2 \rightarrow CH_4 + NO + H_2O$	(1)	$\Delta H_{Rxn} = -37$	(R6b)

$H_2 + NO \rightarrow H_2O + \frac{1}{2} N_2$ (1) $\Delta H_{Rxn} = -79.$ (R6c)

The intermediate-stage global reaction R7 is composed of the subglobal reactions

$CH_4 + NO \rightarrow HCN + H_2O + \frac{1}{2} H_2$ (4) $\Delta H_{Rxn} = -30$ (R7a)

$H_2 + NO \rightarrow H_2O + \frac{1}{2} N_2$ (2) $\Delta H_{Rxn} = -79$ (R7b)

$CO + H_2O \rightarrow CO_2 + H_2$ (1) $\Delta H_{Rxn} = -10.$ (R7c)

The second-stage global reaction R8 is composed of the subglobal reactions

$HCN + NO \rightarrow CO + N_2 + \frac{1}{2} H_2$ (7) $\Delta H_{Rxn} = -80$ (R8a)

$CO + H_2O \rightarrow CO_2 + H_2$ (1) $\Delta H_{Rxn} = -10$ (R8b)

$H_2 + 2 NO \rightarrow N_2 + 2 OH$ (3) $\Delta H_{Rxn} = -25$ (R8c)

$OH + H_2 \rightarrow H_2O + H$ (4) $\Delta H_{Rxn} = -15.$ (R8d)

The net result of the preliminary (I) and first-stage ignition (II) reactions steps is the conversion of the NO_2 moiety to NO. During the preliminary stage (I), the decomposition of CH_3NO_2 is only slightly exothermic. In fact, the dominant decomposition reaction R5a is endothermic. Subsequent reactions involving the HNO species provide the exothermic heat release. The first-stage ignition (II) chemistry is slightly more exothermic. However, the major exothermic heat release of initiation arises during the second-stage ignition chemistry.

The net result of the intermediate (III) and second-stage ignition (IV) reactions is the conversion of NO to N_2. The NO to N_2 conversion does not occur readily and requires the presence of hydrogen and HCN. The formation of HCN occurs primarily during the intermediate stage (III). This stage (III), which removes the CH_4, is also exothermic but slow. The rapid reaction rates of the second-stage ignition are a result of the high temperatures.

While the net reaction is conversion of CH_3NO_2 to CO, H_2O, N_2, and H_2, the overall chemical process of ignition is complicated. Many steps are required to form the final exothermic products. The chemistry can be divided into two major efforts, (1) conversion of the NO_2 moiety to NO and (2) conversion of the NO moiety to N_2. This process is generic to all nitro-containing energetic materials, including nitrate esters and nitramines [14]. The result is two separated ignition stages, denoted the first or primary stage and the secondary stage.

The primary-stage ignition is conversion of the NO_2 to NO. This can be written stoichiometrically as $CH_3NO_2 \rightarrow CO + NO + \frac{3}{2} H_2$. Note that this reaction is itself endothermic (see reaction R6a). On the other hand, three and a half molecules are formed for each nitromethane molecule, so the entropy of this reaction if favorable, leading to a favorable free energy of reaction as the temperature increases. In order to gain heat release, some of the NO must be reduced. In the preliminary stage (I), N_2O is formed via the HNO intermediate. During the first-stage ignition (II), the temperature rise is sufficient to allow thermal decomposition of the N_2O to form N_2. The relative importance of CH_4 and CH_3OH has changed from our previous investigation [14], with CH_4 now playing the more significant role. The relative importance of CH_4 to CH_3OH is extremely sensitive to the pressure dependence used for various elementary rate constants. In both cases, these species serve to create a temporary heat source (see reaction R6b). The formation of CH_4 occurs earlier in the reaction mechanism (arising from CH_3) than does formation of CH_3OH (arising from CH_3O as indicated in ref. 14).

One can see from Fig. 3 that even the oxidation of the carbon of nitromethane to CO is a multistep process. The major pathway has the CH_3NO_2 breaking the C-N bond to form $CH_3 + NO_2$ which recombines to form CH_3ONO which breaks the O-N bond to form $CH_3O + NO$. The NO then abstracts the H from CH_3O to form $CH_2O + HNO$. Subsequent abstraction of hydrogen atoms

from CH_2O lead to CO. As one can see from Figs. 6-8, this series of reactions is itself endothermic. Thus, the initial set of reactions do not produce significant heat release. This complex set of reactions plays an important role in keeping the nitro compounds from spontaneously decomposing. The heat release from any exothermic reactions is converted into net endothermic reactions. These series of elementary reactions are necessary to move the oxygen atom from the nitrogen atom to the carbon atom, which cannot occur until the C-N bond is first broken.

The secondary stage ignition is the reduction of NO to N_2. This occurs by first reducing one of the nitrogen atoms to a reduced state in HCN. This reduced nitrogen is then oxidized with another oxidized nitrogen of NO to form the formally neutral N_2. The formation of the reduced state of nitrogen, HCN, occurs during the intermediate stage (III). This step is necessary because the NO molecule is very stable, even at the intermediate temperatures.

As noted above, the large free energy release of the reaction is enhanced by the net increase in the entropy of the reaction. The majority of this entropy increase occurs during the preliminary and first-stage ignition, where the decomposition of each nitromethane molecule leads to between two and three new molecules. Thus, while the exothermicity of the preliminary and first stages of the reaction are small compared to that of the intermediate and second stages, the increase in entropy plays an important role in driving the initiation process, allowing the initial reactions to proceed.

4.2 Ignition Delay Times

As discussed in the above section on the reaction mechanism, the nitromethane molecule cannot "spontaneously" decompose to form exothermic products but rather must undergo a series of intermediate steps, many of which are endothermic. These reactions lead to finite ignition delay times, both for the primary and secondary stages. We can analyze these ignition delay times, τ_1 and τ_2, in terms of energies of activation, ΔE_1 and ΔE_2, and pressure dependencies n_1 and n_2, as defined above and in Tables II-IV. The ΔE's and n_i's are define as derivatives of the ignition delay times τ_i's with respect to temperature and pressure, respectively, and thus, have meaning only in the near region of the temperature and pressure specified. We have calculated the ignition delay times for atmospheric pressures as well as a high pressure range corresponding to a nitromethane density of that of liquid nitromethane. The pressure values presented in Tables II-IV are an idealized gas effective pressure with the real gas pressure being much higher. For the constant volume calculations, it is better to view the calculations as constant density calculations.

The atmospheric conditions match the experimental data of Guirguis et al. [1]. The ignition delay times are in quite good agreement with the experimental data. The 7.25 atm, 1131 K conditions, for which the experimental was able to separate the two ignition stages, yielded a τ_1 and a τ_2 of 13.3 and 25.8 μsec, which are in remarkable agreement with the experimental data of ~12 and ~25 μsec respectively. These results give us confidence that the elementary reactions for modeling nitromethane are accurate. This represents an improvement over the reaction mechanism used previously [14], which had a reasonable first-stage ignition but a much delayed second stage ignition. The ignition delay times range from microseconds at the low pressure to hundreds of nanoseconds in the high density regime. At the high temperatures and densities, the τ_1's approach the nanosecond time scale.

The effective activation energies of ignition are presented in Table III. The resulting ΔE's indicate that the first-stage ignition has an activation energy ΔE_1 of ~33-36 kcal-mol^{-1} at atmospheric pressures, consistent with the experimental data [1]. At high densities, the ΔE_1 is larger, ~46 kcal-mol,$^{-1}$ though at elevated temperatures (1950 K), the ΔE_1 is ~35 kcal-mol.$^{-1}$ These large activation energies are dominated by the initial C-N bond breaking process, which has a bond dissociation energy of 59 kcal-mol.$^{-1}$ The second-stage ignition delay times, τ_2's, show a wide variation in activation energies. This occurs because the τ_2's decrease significantly faster than the τ_1's with increasing temperature and pressure. Ultimately, the τ_2's approach the τ_1's and are

dominated by the τ_1 times at high densities. However, the difference between the two stages, $\tau_2 - \tau_1$, is still several nanoseconds (see Table II).

The effective pressure dependencies of ignition (at constant temperature) are presented in Table IV. The resulting n_i's exhibit varied behavior. At low temperature and pressure, the first-stage n_1 pressure dependence is between zeroth order ($n_1 = 0$) and first order ($n_2 = 1$), corresponding to effective unimolecular and bimolecular behavior. The secondary stage n_2 pressure dependence at the low temperature and pressure is first order and greater. At high pressures, both the n_1 and n_2 pressure dependencies approach zeroth order, indicating the dominance of the first-stage ignition delay time and the high effective activation energy representative of C-N bond breaking. It is difficult to relate these pressure dependencies to shock induced experiments where temperature changes occur simultaneously with pressure changes.

The comparison of our high density results with the experimental ignition delay times at kilobar pressures and low temperatures indicate some significant differences. As an example, we use the experimental ignition delay times measured by Lee et al. [3] for 10 and 50 kbar and 400-600 K. Their τ's range from 10 - 100 seconds and have an effective activation energy of $\sim$16 kcal-mol.$^{-1}$ While this activation energy is significantly lower than what we calculate for the higher temperature (1100-1300K) conditions ($\sim$45 kcal-mol^{-1}), our pre-exponential rate constants are much larger. Defining the rate constant k as the inverse of the ignition delay time, the effective high temperature rate constant is $k_g = 1.4\ 10^{14}\ exp(-45.4/RT)$ while the effective low temperature rate constant (at 10 kbar) is $2.7\ 10^4\ exp(-15.7/RT)$. That is, our ignition delay times are between 200 nsec - 4 μsec while their extrapolated τ's are still longer than 100 μsec. On the other hand, our τ's in the 400-600K range would be longer than theirs. This suggests a switch in mechanism in which at the lower temperatures, the reaction mechanism is "condensed phase"-like, involving proton transfer and hydrolysis reactions, while at high temperatures above 1000 K, the reaction mechanism is "gas phase"-like, involving radical species. We have investigated the inclusion of bimolecular as well as solvent-assisted proton transfer and hydrolysis reactions in our mechanism to mimic the condensed phase reaction process. The results are encouraging. The small pre-exponential rate constants for such reactions (possessing severe entropy constraints) make such reactions important in the 400-600 K temperature range while they have essentially no effect in the 1100-1900 K range. Considerable work remains in order to elucidate the actual elementary reactions for the low temperature, condensed-phase regime.

5. CONCLUSIONS

We have calculated the initiation process for nitromethane using detailed chemical kinetics. The starting conditions were gaseous nitromethane at atmospheric pressures as well as elevated pressures corresponding to liquid density and temperature above 1000 K. The results indicate that the chemical reaction mechanism requires multiple steps, in which many of the initial steps are endothermic. This complex chemical mechanism prevents the energetic nitro-compound from releasing its stored chemical energy immediately as a shock wave passes by. Ignition delay times indicate relatively high activation energies and low pressure dependencies, indicative of initial bond-breaking of the C-N bond. The agreement between our ignition delay times and the experimental data of Guirguis et al. [1] is encouraging for the modeling of other nitro-containing energetic material. These systems will have similar NO, HNO, N_2O, and HCN chemistry, particularly for the second-stage ignition. These results indicate that a different mechanism is occurring at elevated temperatures (> 1000 K) compared to lower temperatures.

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