Chemical Kinetic Model for Monomethylhydrazine/Nitrogen Tetroxide Gas-Phase Combustion and Hypergolic Ignition

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A detailed kinetic model devoted to the gas phase hypergolic ignition of MMH/NTO mixtures below 298 K and their combustion above 1000 K is presented in this study. It consists of 403 equilibrated reactions among 82 species. This mechanism has been confronted with theoretical data available in the literature. The agreement between theory and predictions is found to be good. Important reactions for ignition at low initial temperature and pressure have been identified through sensitivity analyses. Two competing pathways can explain hypergolic ignition at low temperature. The formation of molecular preignition products is shown to promote the ignition. This conclusion was unexpected, as the formation of these products was generally considered to inhibit the ignition, by reactant consumption. Important reactions for combustion above 1000 K have been preliminarily identified. Some reactions are important both for low-temperature ignition and combustion, whereas some others are important either for ignition only or combustion only. The study is focused on the need for three reduced kinetic models.

Introduction

BIPROPELLANT systems of monomethylhydrazine (MMH) and nitrogen tetroxide (NTO), in fact the NO_2–N_2O_4 equilibrium, are widely used in space propulsion. This combination is known to be hypergolic at room temperature and below and has been extensively studied experimentally. A hypergolic combination is composed of a fuel and oxidizer that ignite spontaneously (autoignite) when they come into contact with each other, even at temperatures below the ambient. No spark, shock wave, or other ignition device is needed to ignite such a chemical system. This property makes the storable MMH/NTO propellant the best solution for many applications. The ignition reactions for the MMH/NTO system, when injected as liquids, have been found to be gas-phase reactions.[1−3] Experiments also show that the presence of a liquid phase is not necessary to achieve hypergolic ignition.[4] Some studies have been performed on the reactivity between MMH and NO_2–N_2O_4, and although it is rather easy to characterize this system qualitatively, it is very difficult to do the same quantitatively because it is impossible to realize premixed mixtures at room temperature. The gases MMH and NTO react, or ignite, upon contact even if both reactants are highly diluted (at least up to 97 mol% helium[4]). Therefore, the determination of the chemical ignition delay within the global ignition delay (physical ignition delay or mixing + chemical ignition delay) in the case of hypergolic ignition is difficult, especially when ignition takes place locally before mixing is completed. In that case the reactant concentrations of the igniting mixture are not known. Although a new method to isolate the chemical ignition delay has been proposed recently,[5] very little chemical kinetic information is available on the hypergolic systems in general and in particular on the MMH/NTO combination. The details of the chemical kinetic mechanism remain mostly unknown.

However, studies performed with hybrid (solid–liquid) hypergols lead to the conclusion that the main cause of the hypergolicity lies in the rapid generation of heat as a result of the exothermic chemical reactions occurring between the fuel and the oxidizer at the preignition stage.[6,7] To the best of our knowledge, no detailed kinetic model devoted to the hypergolic ignition of MMH/NTO combinations at low temperature has been proposed in the literature, although several physical combustion models for this system have existed for decades.

The present paper describes a detailed kinetic model designed to simulate the hypergolic ignition of MMH/NTO gaseous mixtures in wide temperature (from about 253 K up to several thousand Kelvins) and pressure ranges (from a few millibar up to several tens of bar). That is, it is designed to encompass both the transient regime (ignition) and the permanent regime (combustion) encountered in spacecraft and rockets. For ignition in space ambient conditions, the low temperatures and low pressures are of great interest; therefore, we focus here on the low temperature and simultaneously low pressure ignition as encountered during the transient regime. This model is validated with some data found in the open literature on the estimation of ignition delays at room temperature of such gaseous mixtures. More fundamentally, the aim of this paper is to get, through the kinetic model presented in this study, a comprehensive understanding of what hypergolic ignition is and to allow the development of environmentally friendly hypergolic systems. This last topic is currently of great interest.[8−10]

Reaction Mechanism

From an elementary kinetics point of view, very little has been done specifically on the MMH/NO_2 system. According to Stone,[11] for the reaction MMH + NO_2 → Products at room temperature the mechanism involves a direct H-atom abstraction from MMH by NO_2 with the formation of nitrous acid (HONO) and a methylhydrazyl radical (CH_3NHNH or CH_3NNH_2 or CH_2NHNH_2). The same process was observed by Bedford and Thomas[12] during the reaction between NH_3 and NO_2 in the 615–660 K range. This is the process generally observed for all reactions of molecule + NO_2 to give products. No rate constant for the reaction MMH + NO_2 → HONO + methylhydrazyl radical is available, at least in the open literature. Therefore, this rate constant has been estimated by analogy with the reaction NH_3 + NO_2 → HONO + NH_2 studied by Thaxton et al.[13] For this estimate the preexponential factor was left unchanged, but the activation energy for the H-abstraction reaction was reduced by 19 kcal mol^{-1} to account for the weaker N—H (88 kcal mol^{-1}) bonds in MMH relative to the N—H

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(107 kcal mol^{-1}) bonds in ammonia. As Thaxton et al.[13] report an activation energy of 24.9 kcal mol^{-1} for the direct H abstraction from NH$_3$ by NO$_2$, this leads to an activation energy of 5.9 kcal mol^{-1} for the H abstraction reaction from MMH by NO$_2$. This value, although very low, is consistent with an experimental study on low-temperature gas-phase MMH/NTO ignition performed by Seamans et al.,[2] who deduced a global activation energy of 5.2 kcal mol^{-1} for the MMH/NO$_2$ system. Although this value is, strictly speaking, not the activation energy of MMH + NO$_2$ $\rightarrow$ HONO + methylhydrazyl radical, it should be representative of this reaction, if this reaction is the initiation step in the MMH/NO$_2$ system at room temperature. Tuazon et al.[14] also deduced from kinetic experiments that the activation energy for the reaction UDMH + NO$_2$ $\rightarrow$ dimethylhydrazyl radical + HONO is approximatively 5 kcal mol^{-1}. Unsymmetrical dimethylhydrazine (UDMH) is a methylated derivative of hydrazine similar to MMH. Such low activation energies are observed experimentally for reaction between NO$_2$ and closed shell species because of the unpaired electron of NO$_2$. This is definitely expected to be the case here as a result of the relative instability of the endothermic compound MMH. The reactions between the methylhydrazyl radicals and NO$_2$ have also never been studied. The reaction is assumed to proceed through direct H-atom abstraction by NO$_2$ from the methylhydrazyl radical because the formation of methyldiazene (CH$_3$N=NH) has been experimentally observed. The rate constant for this reaction is assumed to be equal to the CH$_3$NNH$_2$ + OH $\rightarrow$ CH$_3$N=NH + H$_2$O reaction. The rate constant of the reaction CH$_3$N=NH + NO$_2$ $\rightarrow$ CH$_3$N=N + HONO, also never studied, is assumed to be equal with the one of the initiation reaction. The N$_2$O$_4$–NO$_2$ and HONO kinetics at low temperature has been introduced as reported in the literature.[15] The subset describing MMH, CH$_3$NNH$_2$, CH$_3$N=NH, and CH$_3$N=N kinetics is taken from the mechanism of Catoire et al.[16–18]
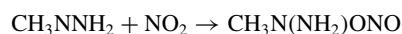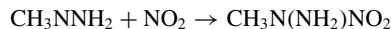
The chemical kinetic model just described is probably sufficient to describe the MMH/NTO combustion for the permanent regime above 1000 K. However, the chemical process at low temperature (below 100°C) is more complicated than that just described because condensed preignition products, described as a fog, are observed in experiments to form from the gaseous reactants.[2,4,19] This formation has been observed when the reactants ignite and also when they do not ignite.[4] Moreover, these formations are not marginal because, at subignition pressures, the condensate represents about 20% by weight of the total reactants, according to Seamans et al.[2] The formation of these compounds can affect the ignition, and it is generally believed that this can prevent or delay the ignition by consuming the reactants. The chemical nature of these preignition products remains uncertain. These products are generally considered to be monomethylhydrazine nitrate (or monomethylhydrazine dinitrate) and often abbreviated as MMH · HNO$_3$ and also MMH$_2$ · NO$_3$. This monomethylhydrazine nitrate forms at or below 0°C from the reaction at 0°C between liquid MMH/nitric acid or MMH/NTO (Refs. 20–22). However, in the gas phase it is probably not chemically the so-called MMH nitrate that is formed. This was demonstrated experimentally by Seamans et al.,[2] who carried out elemental analysis of the condensate formed from gas-phase MMH/NTO during preignition and found C: 14.6; H: 8.1; N: 46.4 and O (by difference): 30.9. These results are quite different from the elemental analysis reported by Breisacher et al.[20] of the product obtained from liquid MMH and liquid HNO$_3$ at about 0°C: C: 11.52; H: 6.6; N: 38.57 and O: 43.31. The calculated element percentages for MMH · HNO$_3$ are C: 11.01; H: 6.46; N: 38.52 and O: 44.01. Recently, new gas-phase bimolecular reactions pathways have been proposed for reactions between NH$_3$ and HNO$_3$ (Ref. 23). This theoretical study, based on ab initio molecular theory calculations, suggests two reaction paths leading to the formation of highly reactive molecules, namely, H$_2$NNO$_2$ and H$_2$NONO. By analogy with ammonia/HNO$_3$, the following nonionic reaction pathways in the gas phase can be proposed for MMH/HNO$_3$:

$$\text{MMH} + \text{HNO}_3 \rightarrow \text{CH}_3\text{NHNHNO}_2 + \text{H}_2\text{O}$$

and/or

$$\text{MMH} + \text{HNO}_3 \rightarrow \text{CH}_3\text{NHNHONO} + \text{H}_2\text{O}$$

The calculated element percentages for these two isomers are C: 13.2; H: 5.5; N: 46.1 and O: 35.1. This is consistent with the elemental analysis of Seamans et al.,[2] the discrepancies being probably caused by the fact that all of the experimental uncertainties are lumped into the O-atom fraction. These species are probably good representatives of the preignition products. However, the actual chemical pathways for the formation of these species cannot be explained by the two preceding chemical reactions because the formation of HNO$_3$ in the gas phase, also introduced in the model, from HONO formed during the course of the MMH/NTO reaction is not quantitatively sufficient to explain the formation of important quantities of these preignition products. Therefore, some other reactions have to be considered between the methylhydrazyl radicals and NO$_2$, such as

$$\text{CH}_3\text{NNH}_2 + \text{NO}_2 \rightarrow \text{CH}_3\text{N(NH}_2)\text{NO}_2$$

$$\text{CH}_3\text{NNH}_2 + \text{NO}_2 \rightarrow \text{CH}_3\text{N(NH}_2)\text{ONO}$$

and others. These reactions are highly probable because the methylhydrazyl radicals formed during the initiation reaction are produced in a medium quite highly concentrated in N$_2$O$_4$–NO$_2$. As the two preceding reactions are recombination ones, they are expected to proceed quite rapidly, with a zero or, at least, low activation energy. No kinetic data have been found in the literature for these recombination reactions. According to Gardiner and Troe,[24] typical values for the high-pressure rate coefficients k_∞ for recombination reactions are of the order of 10^{13} cm^3 mol^{-1} s^{-1}, nearly independent of temperature over a wide temperature range (200–2000 K). For the low-pressure rate coefficients k_0 a value of 10^{17} cm^6 mol^{-2} s^{-1} appears to be reasonable at 298 K. The temperature dependance of k_0 for recombination reactions is often found to be $k_0 = AT^{-\alpha}$ with $\alpha > 0$, that is, k_0 increases when the temperature decreases. This is also probably the case for the preceding recombination reactions but, as the ignition delays given by Seamans et al.[2] are in the 286–298 K temperature range, k_0 can be considered here to be a constant for such a small temperature range. Because the recombination reactions are highly exothermic, their role in the hypergolic ignition is potentially of high importance, and the general statement that the formation of these species can prevent or delay the ignition, because of reactants secondary "useless" consumption, probably has to be revised. However, this statement can only be assessed more than empirically with the knowledge of the enthalpy of reaction, which implies the knowledge of the enthalpy of formation for the CH$_3$N(NH$_2$)ONO and CH$_3$N(NH$_2$)NO$_2$ species. Therefore, with the aim to take into account some features typically observed at low temperatures, the formations of the nitro and nitrito compounds have been introduced into the model as gaseous species. The nucleation of these compounds to form droplets has not been considered. The full mechanism consists of 403 equilibrated elementary reactions and 82 species.

Thermochemistry

Considerable thermodynamic and kinetic data are required as inputs for the modeling of the low-temperature and high-temperature chemistries just described. Some of the thermodynamic data are not available in the literature especially for the modeling of the low-temperature ignition chemistry. Ab initio molecular orbital calculations have been performed for the gaseous species CH$_3$NHNHONO, CH$_3$NHNHNO$_2$, CH$_3$N(NH$_2$)NO$_2$, and CH$_3$N(NH$_2$)ONO, likely to be formed from the methylhydrazyl radicals (CH$_3$NHN · H and CH$_3$N · NH$_2$) reactions with NO$_2$. The enthalpy of formation presented here was calculated based on the enthalpies of atomization computed from the ab initio calculations and the experimental heats of formation of gas-phase atoms at 298.15 K and 1 bar (52.10 kcal mol^{-1} for H, 171.21 kcal mol^{-1} for C, 112.94 kcal mol^{-1} for N, 59.43 kcal mol^{-1} for O). The ab initio energies of the carbon atom and of the oxygen atom were corrected to account for spin-orbit coupling using the experimental spin-orbit interaction energy. Table 1 gives the computed enthalpies of formation at 298.15 K and 1 bar. The results are obtained using the B3LYP method. The geometry optimization and frequency calculations for this method used

Table 1   B3LYP/6-31G(d) enthalpies of formation computed at 298.15 K and 1 bar for the gaseous species presumably formed from the MMH/NTO system during preignition

Species	ΔH_f° (298.15 K), kcal mol^{-1}
$CH_3NHNHNO_2$	-102.33
$CH_3N(NH_2)NO_2$	-103.23
$CH_3NHNHONO$	-84.05
$CH_3N(NH_2)ONO$	-82.99

the 6-31G(d) basis set. The energy at that geometry was then calculated using the 6-311 + G(3df, 2p) basis set. Petersson et al.[25] have presented an assessment of the accuracy of the method used here. For this collection of around 150 molecules with well-known experimental heats of formation, the B3LYP method used here had mean absolute deviation of 3.43 kcal mol^{-1}. Therefore, the results presented here are expected to be accurate to within ± 4 kcal mol^{-1}. The bond additivity corrections (BAC) method established by Petersson et al.[25] cannot be applied for the species considered here because of the lack of BAC parameters for the N—N, N—O, and N=O bonds.

Table 1 shows that the enthalpy of formation of gaseous $CH_3NHNHNO_2$ and $CH_3N(NH_2)NO_2$ are about the same. $CH_3NHNHONO$ and $CH_3N(NH_2)ONO$ also have about the same enthalpy of formation. As the existing MMH/O$_2$ kinetic mechanism includes the formation of the radical CH_3NNH_2, the formation of $CH_3N(NH_2)NO_2$ (nitromethylhydrazine) and of $CH_3N(NH_2)ONO$ (nitritomethylhydrazine) are considered in the present study.

Computational Procedure

The CHEMKIN-II and SENKIN codes were used for computing the full model. For the kinetic computations the reactants are considered to be premixed, and it is assumed that they remain at a constant volume over the reaction time. These assumptions are not the ones encountered in real applications but are consistent with the assumptions made by Seamans et al.[2] for their calculations of theoretical MMH/NTO chemical ignition delays (see next section). The reverse rate constant is computed from the forward rate and the corresponding equilibrium constant. For each mixture under consideration, the amounts of N$_2$O$_4$ and NO$_2$ are the ones at equilibrium at the corresponding initial temperature and initial NTO partial pressure. The ignition delay is defined here as the time at which the rate of temperature (or pressure) rise reaches its maximum. The consideration of other criteria (OH radical concentration profile against time or pressure against time) leads to the same ignition delay values.

Validation of the Chemical Kinetic Model

Because premixed MMH/NTO mixtures are not feasible, chemical ignition delay experiments, such as those performed in static reactors or in shock tubes, or free propagating flames experiments cannot be performed. Therefore, the experimental data available to validate the chemical kinetic model are very scarce. Seamans et al.[2] calculated theoretical MMH/NTO chemical ignition delays for various stoichiometries, temperatures, and pressures by using the theory of thermal explosions. Although the ignition delays calculated by Seamans et al.[2] are quite indirectly derived, no other data are available for MMH/NTO in the open literature. Although it would have been quite easy to adjust the kinetic model to the ignition delays of Seamans et al.,[2] this has not been done here. This procedure, commonly used for the determination of rate coefficient for elementary reactions, is not applicable here, because of the uncertainties in the present kinetic model and in the physical model used by Seamans et al.[2] The predictions for the unadjusted model are shown in Fig. 1. The importance of the formation of the preignition products is also shown in the same figure because if these formations are not introduced the ignition is delayed (dashed line). However, the formation of the preignition products alone is able to lead to ignition (see Fig. 1). The agreement between the calculations of Seamans et al.[2] and the computations presented here is always found to be better than a factor of 2, as shown in Fig. 2.
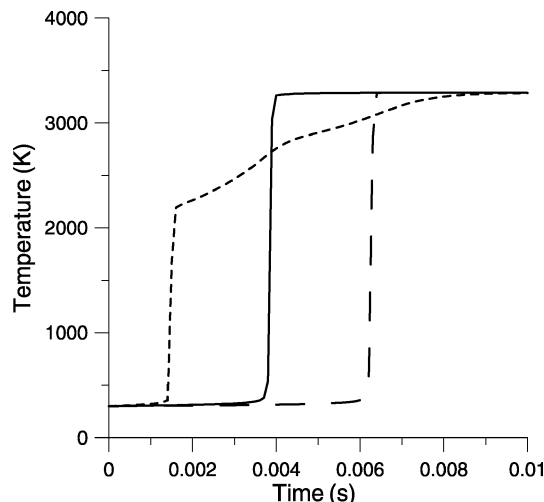
Fig. 1   Typical computed temperature profile during the ignition of MMH/NTO mixtures. Initial $T = 298$ K, initial $P = 0.242$ bar, mixture MMH + 2.5 NTO (1.0275 N$_2$O$_4$ + 1.4725 NO$_2$). Calculated ignition delay by Seamans et al.[2]: 3.62 ms; ——, computed ignition delay with the full kinetic model: 3.81 ms; – – –, computed ignition delay without the formation of the preignition products: 6.25 ms; - - - -, computed ignition only caused by the formation of the preignition products (ignition delay = 1.49 ms).
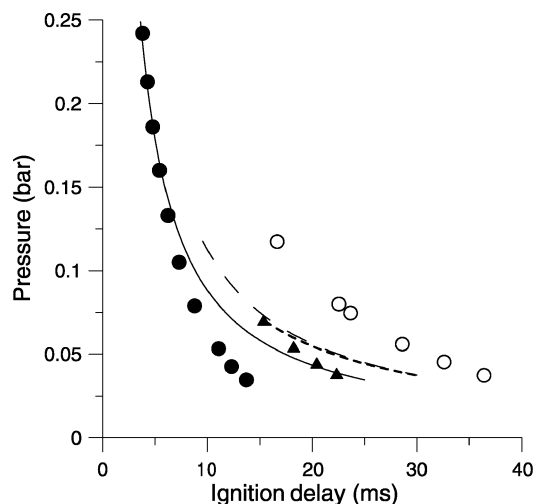
Fig. 2   Comparison between the calculations of Seamans et al.[2] and the predictions of the full kinetic model. The agreement is always better than a factor of 2: ——, calculations of Seamans et al.[2] for MMH + 2.5 NTO, $T = 298$ K; ●, corresponding predictions by using the full chemical kinetic model; – – –, calculations of Seamans et al.[2] for MMH + 2.5 NTO, $T = 286$ K; ○, corresponding predictions by using the full chemical kinetic model; - - - -, calculations of seamans et al.[2] for MMH + NTO, $T = 286$ K; ▲, corresponding predictions by using the full chemical kinetic model.

The chemical kinetic model has been tested against ignition for the MMH/NTO system at temperature below 273.15 K (0°C). At -14.7°C (258.45 K), NTO is a solid with an equilibrium vapor pressure of 0.133 bar. At this temperature MMH is a liquid with an equilibrium vapor pressure of 0.0048 bar. For the mixture MMH + NTO at 258.45 K and 0.0096 bar, the model predicts an ignition delay of about 0.7 s, as shown in Fig. 3. If the mixture consists of the saturated vapor pressure of both reactants, no ignition is predicted by the kinetic model, but the preignition products form.

Important Reactions for the Low-Temperature and Low-Pressure Hypergolic MMH/NTO Ignition

Sensitivity analyses have been performed in order to identify the important reactions for the hypergolic ignition. Figure 4 gives the sensitivity spectrum obtained, for the gas-phase MMH/NTO

Table 2   Rate constants for the seven most important reactions for the low-temperature gas-phase
MMH/NTO hypergolic ignition at room temperature (298 K) at low pressure

Reaction number	Reaction stoichiometry	Rate constants[a]
1	$CH_3NNH_2 + NO_2(+M) \rightarrow CH_3N(NH_2)NO_2(+M)$	$k_\infty = 10^{13}$ $k_0 = 10^{17}$
2	$CH_3NNH_2 + NO_2(+M) \rightarrow CH_3N(NH_2)ONO(+M)$	$k_\infty = 10^{13}$ $k_0 = 10^{17}$
3	$MMH + NO_2 \rightarrow CH_3NNH_2 + HONO$	$k = 2.2 \times 10^{11} \exp(-5900/RT)$
4	$CH_3N{=}NH + NO_2 \rightarrow CH_3N{=}N + HONO$	$k = k_3$
5	$CH_3NNH_2 + NO_2 \rightarrow CH_3N{=}NH + HONO$	$k = 10^8 \times T^2$
6	$CH_3N{=}N \rightarrow CH_3 + N_2$	$k = 3 \times 10^6$
7	$N_2O_4(+M) \rightarrow NO_2 + NO_2(+M)$	$k_\infty = 4.05 \times 10^{18} \, T^{-1.1} \exp(-12840/RT)$ $k_0 = 1.96 \times 10^{28} T^{-3.8} \exp(-12800/RT)$

[a]Units are mol, cm^3, cal, K, s.
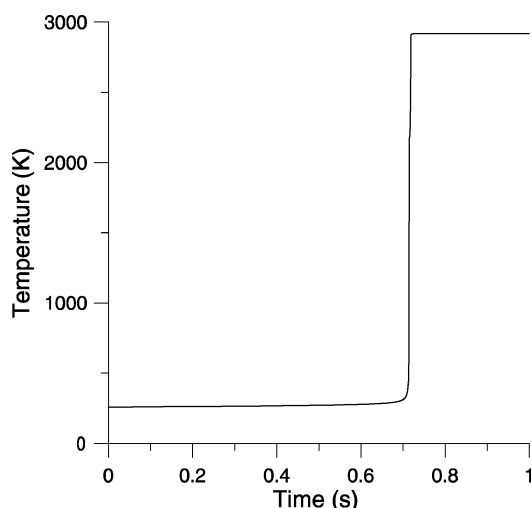
Fig. 3   Computed MMH/NTO hypergolic ignition below 0°C. Mixture MMH + NTO ($0.401 N_2O_4 + 0.599 NO_2$). Initial temperature = 258.45 K (−14.7°C), initial pressure = 0.0096 bar (or 960 Pa), initial partial pressure of MMH is 0.0048 bar, temperature is 2919 K, and the pressure is 0.33 bar at equilibrium.
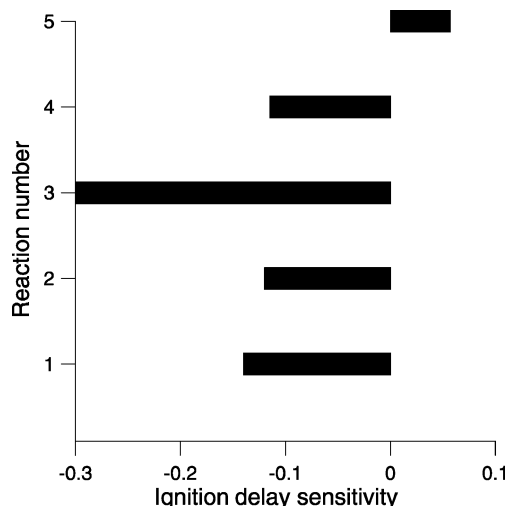
Fig. 4   Sensitivity spectrum for the gas-phase hypergolic ignition of MMH/NTO. Mixture MMH + 2.5 NTO ($1.0275 N_2O_4 + 1.4725 NO_2$) at initial temperature $T = 298$ K and at initial pressure $P = 0.242$ bar. The ignition delay sensitivity is defined as $(\tau - \tau_0)/\tau_0$, where τ_0 is the ignition delay computed with the full non-modified model. Reaction #1: $CH_3NNH_2 + NO_2 \rightarrow CH_3N(NH_2)NO_2$ (preignition product formation). Reaction #2: $CH_3NNH_2 + NO_2 \rightarrow CH_3N(NH_2)ONO$ (alternative preignition product formation). Reaction #3: $MMH + NO_2 \rightarrow CH_3NNH_2 + HONO$ (initiation reaction). Reaction #4: $CH_3N{=}NH + NO_2 \rightarrow CH_3N{=}N + HONO$. Reaction #5: $CH_3NNH_2 + NO_2 \rightarrow CH_3N{=}NH + HONO$.

hypergolic ignition, by multiplying alternatively each rate constant by a factor of 2.

This sensitivity analysis shows that the computed ignition delays are mainly sensitive to five reactions. These reactions are given in Table 2. As expected, the initiation reaction (reaction #3) is the most influential but, as shown in Fig. 1, the formation of the preignition products also plays an important role in the ignition. This can be explained by the fact that the formations of the two preignition products are exothermic: $CH_3NNH_2 + NO_2 \rightarrow CH_3N(NH_2)NO_2$ by 170.57 kcal mol^{-1} and $CH_3NNH_2 + NO_2 \rightarrow CH_3N(NH_2)ONO$ by 150.33 kcal mol^{-1}. The ignition delay does not show significant sensitivity to the rates of the decomposition reactions of $CH_3N{=}N$, HONO and N_2O_4.

To check the degree to which specific reactions are required, a sensitivity analysis was carried out in which each of the reactions was successively eliminated from the kinetic model. Reactions number 1 to number 5 (see Table 2) are found to be individually important for the ignition, the initiation reaction number 3 being the only one absolutely required to get ignition. Deleting reaction number 4 or reaction $CH_3N{=}N \rightarrow CH_3 + N_2$ (reaction #6) leads to a two-step ignition. Deleting of reaction number 5 leads to ignition, but the approach to equilibrium is considerably delayed (see also Fig. 1). The deletion of the nitrous acid decomposition $HONO \rightarrow OH + NO$ does not change anything significantly. On the contrary, the suppression of the N_2O_4 decomposition (reaction #7 in Table 2) leads to a shorter ignition delay (1 ms, instead of 3.81 ms). This can be explained by the fact that the decomposition of N_2O_4 is endothermic, and therefore the global exothermicity, when the reaction is in the model, is reduced, and consequently the ignition is more delayed than when the reaction is deleted. The rate constants of the seven important reactions for hypergolic ignition are given in Table 2. It is not stated here that these seven reactions are the only ones needed to build a reduced chemical kinetic model, but that it is essential to include these seven reactions. The two sensitivity methods just used, although preliminary, are generally sufficient to identify the most important reactions for ignition.[26] They are not sufficient to reduce a detailed kinetic model, but this is beyond the scope of the present paper. First-order sensitivity analyses are needed, or more comprehensive technics such as the Principal Component Analysis of Matrix F (Ref. 27) and others[28,29] among numerous available, to provide more kinetics informations. For completeness, first-order local sensitivity analysis for temperature is presented Fig. 5 for the conditions of Fig. 1 during the preignition period. No other reactions than the preceding ones are identified here. The first-oder sensitivity coefficients are calculated following the methods implemented in the code SENKIN.[30] (The SENKIN program is part of the CHEMKIN collection.)

Important Reactions for the High-Temperature MMH/NTO Combustion

The combustion of MMH/NTO is generally believed to consist of the simultaneous thermal decompositions of both reactants MMH and NO_2. As reported in the Reaction Mechanism section, the high-temperature thermal decomposition of MMH is included in the full
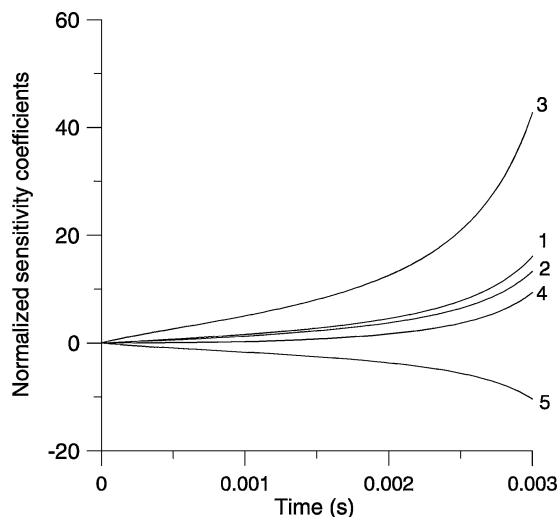
Fig. 5   First-order sensitivity analysis for temperature during the preignition period with respect to the important reactions: Initial $T = 298$ K, initial $P = 0.242$ bar, mixtures MMH + 2.5 NTO (1.0275 $N_2O_4 + 1.4725$ NO_2). Calculated ignition delay by Seamans et al.[2]: 3.62 ms, Numerals 1, 2, 3, 4, and 5 in the figure indicate the reaction number.

Fig. 7   High-temperature MMH/NTO combustion. MMH + 2.5 NO2 initially at 1500 K and 1 bar: ——, temperature profile computed by using the full kinetic model; – – – –, temperature profile computed with the model once reaction #3 deleted.
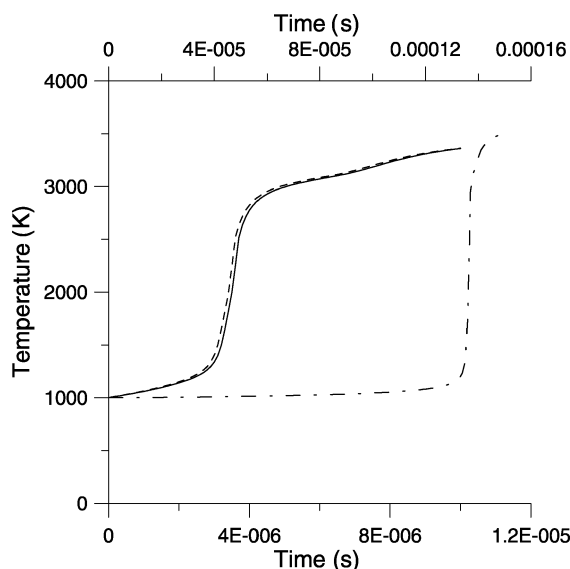

Fig. 6   High-temperature MMH/NTO combustion. MMH + 2.5 NO2 initially at 1000 K and 1 bar: ——, temperature profile computed by using the full kinetic model (curve to be read with the bottom time axis); - - - -, temperature profile computed without the formation of the preignition products (reactions #1 and reactions #2 deleted from the full model, curve to be read with the bottom time axis); – – – –, temperature profile computed with the model once reaction #3 deleted (curve to be read with the top time axis).

detailed model. This submechanism has been validated experimentally for temperatures above 900 K. Further, all of the decomposition steps of NO_2 are introduced in the kinetic model. Therefore the model can be used to simulate the MMH/NTO combustion as encountered in the permanent regime to see whether or not the same reactions are relevant at high and low temperature. The importance of the formation of the preignition products (reaction #1 and reaction #2) and the importance of the reaction #3 are adressed here.

Figure 6 shows unambiguously that the formation of the preignition products does not play a role for the combustion of the mixture MMH + 2.5 NO_2 at initial temperature 1000 K and initial pressure 1 bar as the temperature profile is the same for either reaction #1 and reaction #2 in the model or both removed from it. However, the formation of these preignition products at such high temperature is
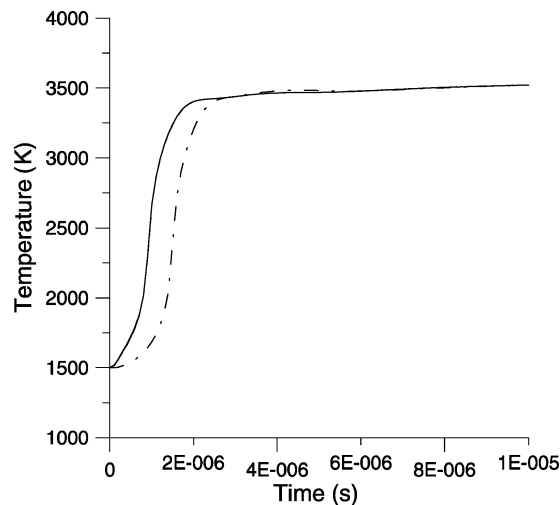
not likely, as the fog described in the Reaction Mechanism section is not experimentally observed above 400 K. Reaction #3 remains necessary to get "instantaneous" ignition (in fact, a very short ignition delay of 3 μs here), but this reaction is no longer absolutely needed to get ignition caused by the thermal decomposition of MMH and subsequent reactions between the species formed during the thermal decomposition of MMH and NO_2 (see Fig. 6). This means that at much higher temperature reaction #3 will probably play a much less important role. This can be seen in Fig. 7, where it is shown that the temperature profiles are about the same with or without reaction #3 at 1500 K, whereas at 2000 K the temperature profiles (not given here) with or without reaction #3 are exactly the same.

Conclusions

A kinetic model devoted to the low-temperature and simultaneously low-pressure gas-phase MMH/NTO hypergolic ignition has been built. The proposed mechanism is not claimed to be unique as several other reaction pathways are possible. This paper demonstrates that hypergolic ignition can be simulated with finite rate chemistry. This can allow or stimulate the more rigorous calculations of the rate constants of all of the possible reactions by using modern quantum chemistry tools.

This model consists of 403 balanced reactions and 82 species and focuses exclusively on the chemical ignition delay, a parameter still difficult to measure. In the model the formation of preignition products has been introduced, although in a simplified way. This model has been validated with theoretical ignition delays available in the literature, which where calculated with the help of a thermal explosion theory. The model is shown to predict ignition delays in good agreement with the theoretical ignition delays reported in the literature. Sensitivity analyses show that the formation of the preignition products promotes the ignition as these formation reactions are exothermic. For the MMH/NTO system it appears that two competing reaction pathways are leading to ignition: the first one, as already specified, is the preignition products formation (reactions #3, then reactions #1 and 2), and the second one is based on H abstraction by NO_2 from intermediates following the initiation reaction (reactions #3 then reactions 4 and 5). More importantly, both channels are able to ensure ignition independently (with different ignition delays), and the computed ignition delay results from the competition between the two channels. From this work it appears that the chemical key to get hypergolic mixtures from two non-hypergolic reactants is to introduce, either in the fuel or in the oxidizer, a third species able to react exothemically, either with the fuel or with the oxidizer, to produce preignition products. Some other concepts derived from this study can be developed to make more environmentally friendly

combinations hypergolic. For instance, the MMH/NTO system can be added to the environmentally friendly non-hypergolic bipropellant combination in the smallest amounts able to ensure hypergolic ignition. The model can also be used to predict the inhibiting or promoting effects of additives on the MMH/NTO ignition delays.

The details presented here for the low-temperature and low-pressure MMH/NTO hypergolic ignition should also be helpful for the simulations of the hydrazine/NTO and UDMH/NTO hypergolic ignitions, which exhibit about the same features as MMH/NTO.

This model can also be used to predict, in the permanent regime, the combustion of the MMH/NTO combination at much higher temperatures and pressures. Above 1000 K the low-temperature preignition products do not play a role. In the 1000–1500 K temperature range the H abstraction reaction from MMH by NO_2 cannot be neglected to simulate the ignition/combustion sequence. Above 2000 K combustion consists of the simultaneous thermal decomposition of both MMH and NO_2. As is, the full kinetic model is too large for implementation in codes dealing with all of the physics of combustion. Therefore a reduced kinetic model has to be written. However, as some of the reactions needed to simulate ignition at low temperature and combustion are different, a unique reduced model also should be too cumbersome, and there is probably a need for several reduced models: one for low-temperature ignition (below roughly 400 K), one for combustion in the 1000–1500 K temperature range, and one for combustion above 2000 K.

Acknowledgments

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