JOURNAL OF PROPULSION AND POWER
Vol. 21, No. 6, November–December 2005

Search for Green Hypergolic Propellants: Gas-Phase Ethanol/Nitrogen Tetroxide Reactivity

Servane Pichon,* Laurent Catoire,† Nabiha Chaumeix,‡ and Claude Paillard§
Centre National de la Recherche Scientifique and University of Orleans, F-45071 Orleans CEDEX 02, France

Monomethylhydrazine (MMH)/nitrogen tetroxide (NTO) is a well-known bipropellant combination system, the main advantage of which is low temperature ignition without ignition device, also called hypergolicity. The use of other chemical systems, less toxic, less hazardous, less corrosive, and more environmentally friendly than MMH/NTO are nowadays desirable. The replacement of the fuel MMH by ethanol (EtOH) is examined here. It is shown that ethanol/NTO mixtures are not hypergolic, but that reactions take place at room temperature and that these reactions form ethyl nitrite. Chemical reasons able to explain this reactivity, which does not lead to ignition, are discussed. In particular, it is shown that the EtOH/NTO initiation reactions going through H abstraction by NO_2, whatever this initiation reaction is, and especially the one leading to ethyl nitrite, are considerably more endothermic than the corresponding MMH/NTO initiation reactions.

Introduction

HYPERGOLIC systems are interesting for space and military propulsion. Several of those systems have been used in the past, and they are still used nowadays. Hydrazine/nitrogen tetroxide (NTO, which is the $2\,NO_2 = N_2O_4$ equilibrium), monomethylhydrazine (MMH)/nitrogen tetroxide, unsymmetrical dimethylhydrazine (UDMH)/nitrogen tetroxide, or mixtures of hydrazine and UDMH (Aerozine 50)/nitrogen tetroxide are among the most widely used bipropellant systems. MMH/NTO is nowadays the reference propellant for manned capsules, landing retrorockets, automatic interplanetary missions, and satellite propulsion. Hydrazine is also used as a monopropellant (catalytic ignition) and both as a bipropellant and monopropellant in dual-mode propulsion engines. Occasionaly, NTO is replaced by either red-fuming nitric acid or white-fuming nitric acid. The major advantage of these propellant combinations is that they are hypergolic. Hypergolicity can be described as a low-temperature (298 K and below) self-ignition, and therefore no ignition devices are needed to generate thrust, and the engines using these liquid fuels are restartable at will. These two characteristics are obviously very interesting for satellites. However, these chemical systems also have drawbacks. Both, fuel and oxidant, are toxic, and moreover hydrazine and its methylated derivatives are carcinogenic. Hydrazine, MMH, and UDMH are also quite hazardous materials because they have low flash point value and also because these fuels are endothermic compounds, which are able to sustain decomposition flames without any oxidant. These fuels have also compatibility problems with a lot of materials. Briefly said, these chemicals are not environmentally friendly compounds. They are moreover quite expensive. These last years many studies have been performed concerning the search for environmentally friendly hypergolic systems. Unfortunately, environmentally friendly systems such as ethanol/O_2, liquid oxygen (LOX)-based combinations (LOX/HC or LOX/LH_2), and N_2O-based combinations (N_2O/HC) are not hypergolic combinations. For all of these systems, an ignition device is requested whatever its nature is: spark, torch (fed with the propellants' vapor pressures), catalytic bed. Practically, it can be interesting to replace only one of the toxic propellants, either the fuel or the oxidant, to go on with the existing engines, slightly modified. It is probably more logical to replace the fuels, hydrazine, MMH, or UDMH, which are toxic, hazardous, and carcinogenic and to keep the oxidant (NTO), which is "only" toxic. For this purpose, an Earth-storable fuel is needed. Among all of the storable fuel used in the past, ethanol (EtOH or C_2H_5OH) is certainly one of the most interesting: it is cheap, and the threshold limit value and time weighted average are equal to 1000 ppm. These values are much higher than the values for MMH (0.2 ppm), hydrazine (0.1 ppm), and UDMH (0.5 ppm). The major drawback of ethanol (EtOH) is that this fuel is highly flammable, as hydrazine fuels are. However, EtOH is not an endothermic fuel, that is, a compound able to decompose exothermically, and it is therefore much less hazardous to store and to handle than hydrazine and its methylated derivatives. The EtOH/NTO combination is not known as to be an hypergolic system. However, it is interesting to study the reasons for which a chemical system is not hypergolic as it can bring information on how to render this system hypergolic. The aims of this study are 1) to study the reactivity of gaseous EtOH with gaseous NTO at room temperature, 2) to interpret from chemical kinetics viewpoint the experimental results, and 3) to discuss the reasons able to explain why EtOH/NTO mixtures are not hypergolic.

Experimental Setup

EtOH is liquid at room temperature and atmospheric pressure, and NTO is either gaseous or liquid but with a high vapor pressure. Liquid ethanol, provided by ACROS ORGANICS, has a purity of 99% and liquid NTO, provided by Air Liquide, has a purity of 99%.

Gaseous EtOH/argon (Ar) and gaseous NTO/Ar mixtures are prepared separately at room temperature according to the partial pressure law by mixing argon with the vapor pressures of the liquids and stored in two 10 liters Pyrex glass vessels. The vaporization system is made of Pyrex and equipped with valves made of glass or Teflon.® The vaporization setup can be pumped down by a primary pump. One pressure gauge, in the range 0–100 kPa, and one mercury manometer have been used to measure the pressures. Then, two types of experiments have been performed with these vapor/inert gaseous mixtures. Although EtOH/NTO mixtures are not considered as hypergolic, the hazards resulting from mixing of EtOH/argon and NTO/argon have been studied in the experimental setup given in Fig. 1. In this setup made of Pyrex, a jet of NTO/argon is introduced in a spherical vessel (made of Pyrex glass with a

---

Received 18 November 2004; revision received 29 March 2005; accepted for publication 21 April 2005.

*Ph.D. Student, Laboratoire de Combustion et Systèmes Réactifs, 1C, av. de la Recherche Scientifique.

†Assistant Professor, Laboratoire de Combustion et Systèmes Réactifs, 1C, av. de la Recherche Scientifique.

‡Senior Researcher, Laboratoire de Combustion et Systèmes Réactifs, 1C, av. de la Recherche Scientifique.

§Professor, Laboratoire de Combustion et Systèmes Réactifs, 1C, av. de la Recherche Scientifique.

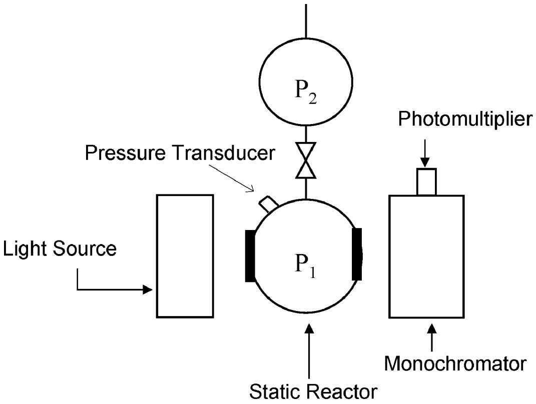

Fig. 1 Sketch of the experimental setup used for the study of the hazards resulting from the mixing of gaseous EtOH/Ar and gaseous NTO/Ar.

surface/volume ratio of 61 m^{-1}), which contains gaseous EtOH/argon. NTO/argon, at a static pressure P_2, is allowed to expand into the vessel containing EtOH/argon at a static pressure P_1. P_1 and P_2 are measured when the gaseous mixtures are at rest. Direct visualization (or visible light emission in the 400–800 nm spectral range) and UV absorption spectrophotometry have been used to follow the reaction, if any, for times up to 100 ms.

EtOH/NTO gaseous premixed mixtures have been realized by mixing EtOH/Ar with NTO/Ar and the reactivity of these gases at room temperature is followed by absorption in the infrared (IR) spectral range for times up to several days.

Results and Discussion

Reactivity of EtOH/Ar and NTO/Ar When Mixed at Room Temperature

Experiments have been perfomed in the experimental setup described in the Experimental Setup section and shown in Fig. 1. The tests were carried out at room temperature in the dark for the experimental conditions described in Fig. 2. For all of the tests performed, no ignition, in fact no light emission in the visible spectral domain, has been observed even once pure EtOH and pure NTO are mixed and one has to conclude that the EtOH/NTO combination is not hypergolic. Unfortunately, it was not possible for safety reasons to study the EtOH/NTO system at pressures above the atmospheric pressure (1 atm = 101,325 Pa = 760 torr = 760 mm Hg). However, these observations that EtOH and NTO are not hypergolic in the pressure range studied do not mean that there is no reactivity between those two compounds. Actually, it appears to the naked eye that products form, the mixture is not reddish-brown colored (the color of NTO because EtOH and Ar do not absorb in the visible spectral domain) but yellow-orange colored, and it appears quite opaque. To assess more unambiguously whether there is a reactivity, the mixing of the two gases was followed by using the UV spectrophotometry as described Fig. 1. Spectra obtained in the 190–800 nm spectral range with the compounds, diluted or not, show that EtOH does not absorb in the visible spectral domain (400–800 nm) and that NTO absorbs in the 250–400 nm spectral domain and also in the visible spectral domain. Moreover, as in NTO the proportion of NO_2 and N_2O_4 is pressure dependent; the NTO absorption is also pressure dependent. It is therefore logical, at first, to work here with a P_2 pressure of EtOH/Ar and a P_1 pressure of NTO/Ar. Figure 3 gives the absorption signal observed when a jet of pure EtOH enters in the vessel filled with a mixture of 50 mol% NTO in argon. As just specified, NTO absorbs at 750 nm. The introduction of EtOH should not modify the absorption level because EtOH does not absorb at 750 nm. In fact, as soon as both gaseous mixtures come into contact, the absorption increases strongly, indicating that a reaction takes place. The increase of absorption can be caused either by the formation of absorbing species or can be caused by the formation of liquid droplets (fog) or both. The naked-eye observation that the mixture EtOH/NTO is opaque is an indication that a fog forms. To assess that a reaction takes place, and that no other phenomenon is responsible for this increase of absorption, a blank test is performed. It consists of the introduction of Ar in a NTO/Ar mixture. The corresponding absorption signals are given in Fig. 4. Argon, as EtOH, does not absorb at 750 nm. Figure 4 shows unambiguously that the absorption level is constant when a nonabsorbing inert is introduced in NTO. For completeness, the introduction of a NTO/Ar jet in EtOH has also been studied. Results are given in Fig. 5 and are consistent with the conclusions of Fig. 4. The first increase in absorption is caused by the time-dependent absorption of NTO at 750 nm (introduction and mixing) followed by a second increase in absorption caused by the reaction between EtOH and NTO. The occurrence of a reaction between EtOH and NTO at room temperature is assessed. This reaction takes place in the gas phase. This point needs some discussion. The question whether the reaction takes place homogeneously in the gas phase or whether it is heterogeneously catalyzed by Pyrex glass surface is questionable for years. Few previous studies have been reported in the literature concerning the reactivity of alcohols (particularly methanol) with NTO (nitrogen dioxide/nitrogen tetroxide equilibrium). Fairlie et al.[1] found that, at room temperature, the initial rates for the reaction alcohol + NO_2 to give products is not proportional to surface/volume ratio for a surface/volume ratio comprised between 0.3 cm^{-1} (30 m^{-1}) and 1 cm^{-1} (100 m^{-1}). This shows that

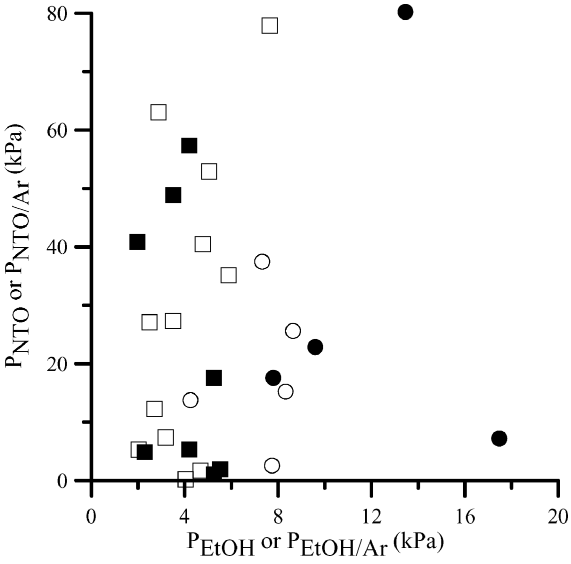

Fig. 2 Experiments performed for the study of the EtOH/NTO/Ar reactivity upon mixing of EtOH/Ar and NTO/Ar. Pressure units are kPa: ●, 3 mol% EtOH in argon and 3 mol% NTO in argon; ○, 50 mol% EtOH in argon and 50 mol% NTO in argon; ■, pure EtOH and 50 mol% NTO in argon; and □, pure EtOH and pure NTO.

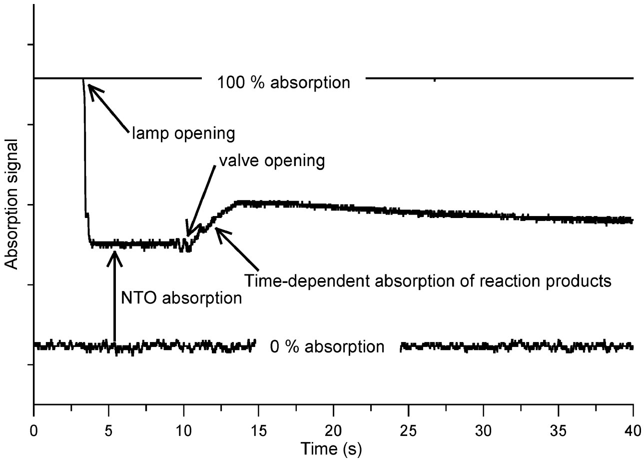

Fig. 3 Absorption signal observed at λ = 750 nm. P_2 (pure ethanol) = 5436 Pa, and P_1 (50 mol% NTO in Ar) = 2258 Pa.

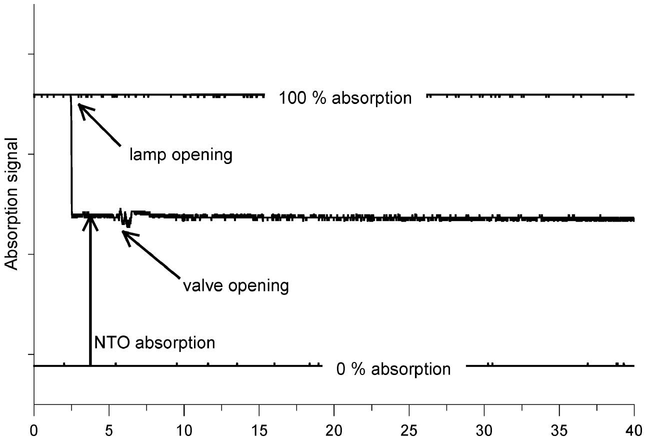

Fig. 4 Absorption signal observed at λ = 750 nm. P_2 is pure argon, and P_1 is NTO/Ar mixture.

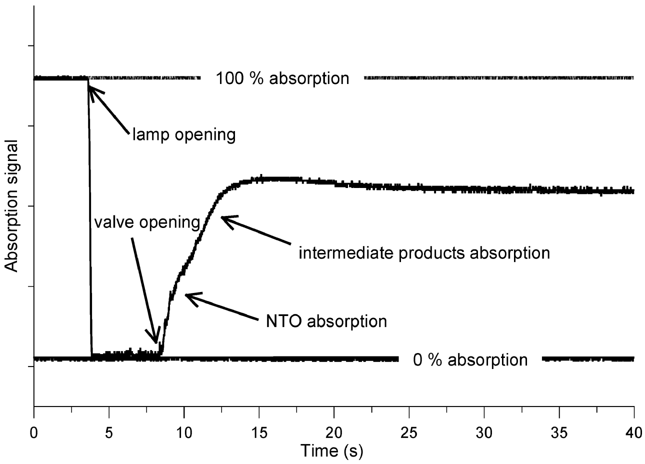

Fig. 5 Absorption signal observed at λ = 750 nm. P_2 (50 mol% NTO in Ar) = 5416 Pa, and P_1 (pure EtOH) = 2298 Pa.

the reaction between EtOH and NTO is not surface catalyzed or at least not surface catalyzed at the beginning of the process. Koda et al.[2] and Niki et al.[3] also found evidence that the reaction takes place homogeneously in the gas phase. All of these data and the experiments performed here show that the observed reaction takes place in the gas phase.

It is however not doubtful that a high surface/volume ratio Pyrex glass surface will play a role in the reaction as shown by Nguyen et al.,[4] among others. Niki et al.[3] show that the gas-phase reaction at room temperature produces ethylnitrite (C_2H_5ONO) and nitric acid (HNO_3) according to the global reaction:

$$2\,NO_2 + EtOH \longrightarrow C_2H_5ONO + HNO_3$$

However, as underlined by Niki et al., these experiments do not establish whether the reaction actually involves two NO_2 or N_2O_4 because N_2O_4 was present in equilibrium with NO_2 under the experimental conditions used in this study. Although not discussed by Niki et al.,[3] this global termolecular reaction can probably be rationalized by the following elementary reactions:

$$N_2O_4 \longrightarrow NO_2 + NO_2$$

$$C_2H_5OH + NO_2 \longrightarrow C_2H_5 + HNO_3(HONO_2 \quad \text{or} \quad HOONO)$$

$$C_2H_5 + NO_2 \longrightarrow C_2H_5ONO$$

This scheme is the most likely to explain the formation of ethyl nitrite if the reaction involves two NO_2. Koda et al.[2] studied the gas-phase reaction between methanol (CH_3OH) and NTO. They consider that the reaction is globally $2\,NO_2 + CH_3OH \longrightarrow CH_3ONO + HNO_3$, but that the reaction proceeds via a molecular reaction, that is, a NO_2 dimer, namely, ONO-NO_2, is formed, and then react with the alcohol to form methyl nitrite and nitric acid. The choice between a molecular pathway (dinitrogen tetroxide dimer + alcohol) and a chain pathway through NO_2 is not simple. In the case of a chain pathway, the formations of other compounds than ethyl nitrite are likely: $C_2H_5NO_2$ (nitroethane), $C_2H_5ONO_2$ (ethyl nitrate), $CH_3CH(NO_2)OH$ (1-nitroethanol), $CH_3CH(ONO)OH$ (1-nitritoethanol), $CH_2(NO_2)CH_2OH$ (2-nitroethanol), and $CH_2(ONO)CH_2OH$ (2-nitritoethanol). This does not seem to be the case because previous study observed almost exclusively the formation of nitrite compounds. Although all previous studies[1–3,5] observed or deduced the formation of methyl nitrite (fuel: methanol) or ethyl nitrite (fuel: ethanol), the formation of ethylnitrite should also be assessed for this study because some of the experimental parameters of interest here are quite different, in particular the pressure, from the previous studies. For this purpose, the fate of gaseous NTO/EtOH premixed mixtures, diluted or not by argon, have been followed by gas-phase IR absorption spectrometry (Nicolet MAGNA-IR infrared spectrometer 550). The gaseous mixtures are stocked in a 10-liter Pyrex spherical glass vessel, which surface/volume ratio is 22 m^{-1} to minimize the role of the surface of the vessel. As for the previous experiments in smaller spherical vessels, a fog forms upon mixing in the whole volume. Although short reactions times are more interesting for this study, the reaction was followed up to several days. Figure 6 gives the infrared spectra obtained with one of the premixed mixtures studied at room temperature. The absorption spectra of EtOH and NTO have been substracted to observe the absorption spectra of the products. The spectrum given Fig. 6 at $t = 12$ min is absolutely the same as the reference spectrum of gas-phase ethyl nitrite (C_2H_5ONO) given by Niki et al.[3] Other compounds in much lower amounts also form: an aldehyde (probably acetaldehyde) and acetic acid. The mixture

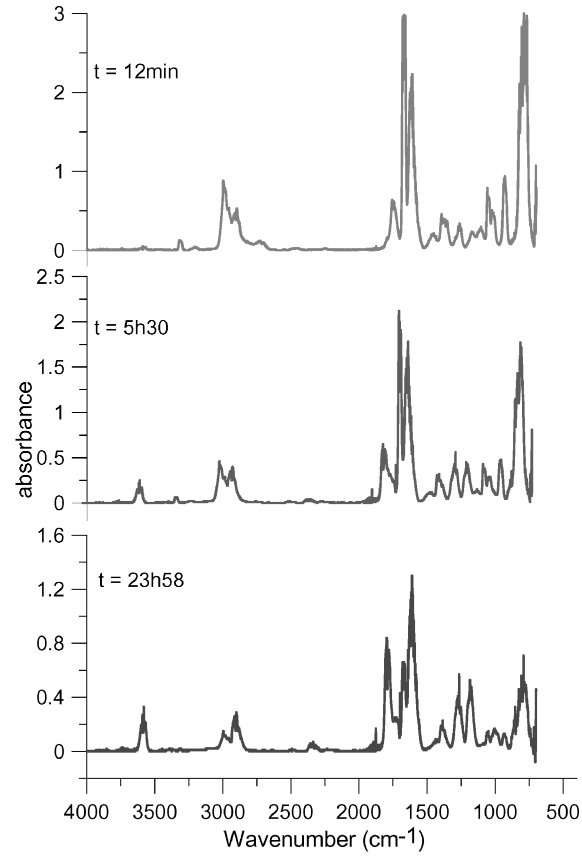

Fig. 6 IR spectra vs time obtained for the EtOH/NTO gas-phase reaction at room temperature (about 298 K) at different times *t* after mixing. Initial pressure: 41.2 kPa. Initial composition: 12 mol% EtOH and 38 mol% NTO in argon.

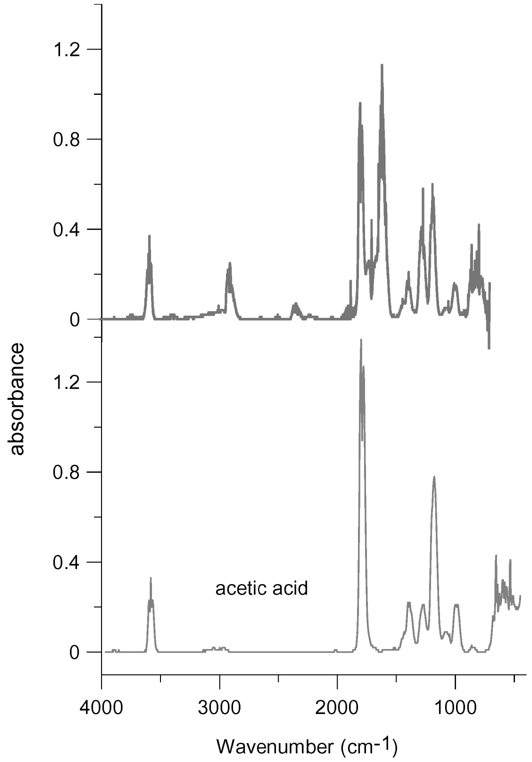

Fig. 7 IR spectrum of the products of the gas-phase EtOH/NTO reaction (top) at *t* = 73 h compared to the reference IR absorption spectrum of gas-phase acetic acid (bottom). Initial composition (pressure, temperature, composition) is given Fig. 6.

continuously evolves, and after three days the major product is a carboxylic acid, presumably acetic acid according to Fig. 7. It is however beyond the scope of this study to give in this paper all of the features of the slow oxidation of ethyl nitrite once formed, and these details will be presented elsewhere. The formation of ethyl nitrite is also observed for nondiluted mixtures and for highly diluted mixtures (up to 97 mol% Ar). The corresponding spectra are not given here but are similar to the spectrum obtained Fig. 7 at $t = 12$ min. Nitric acid appears to absorb weakly, but a liquid phase forms, which contains probably most of the nitric acid formed.

Thermochemistry and Chemical Kinetics

The features of EtOH/NTO reaction are almost the same as the MMH/NTO reaction. Intermediate species form, and this formation was shown to lead to ignition in the case of MMH/NTO (except for highly diluted mixtures).[6,7] The hypergolicity of MMH/NTO can, in the frame of some of our previous works, be explained by the sequence:

$$\text{MMH} + \text{NO}_2 \longrightarrow \text{methylhydrazyl radical} + \text{HNO}_2 \text{ (initiation reaction)}$$

$$\text{Methylhydrazyl radical} + \text{NO}_2 \longrightarrow \text{nitro or nitrite compounds}$$

together with H-abstraction reactions by NO_2 from the methylhydrazyl radical formed during the initiation reaction.

The initiation reaction is endothermic by 16 kJ mol^{-1} or by 8 kJ mol^{-1}, depending on the methylhydrazyl radical formed, $CH_3NHN^{\bullet}H$ or $CH_3N^{\bullet}NH_2$, respectively.[8] Then, if the radical $CH_3N^{\bullet}NH_2$ is considered, the second step is exothermic by 95 kJ mol^{-1} in the case of the formation of a nitrite compound or by 178 kJ mol^{-1} in the case of the formation of a nitro compound. The same about holds for the $CH_3NHN^{\bullet}H$ radical. Therefore the reaction

$$\text{MMH} + 2\,\text{NO}_2 \longrightarrow \text{nitro or nitrite compound} + \text{HNO}_2$$

is exothermic by at least 87 kJ mol^{-1} up to 170 kJ mol^{-1}.

In the contrary, for EtOH/NO_2 the initiation reaction $C_2H_5OH + NO_2 \longrightarrow C_2H_5^{\bullet} + HNO_3$ is highly endothermic by 187 kJ mol^{-1}, and the reaction $C_2H_5^{\bullet} + NO_2 \longrightarrow C_2H_5ONO$ is exothermic by 253 kJ mol^{-1}. The global reaction

$$\text{EtOH} + 2\,\text{NO}_2 \longrightarrow \text{C}_2\text{H}_5\text{ONO} + \text{HNO}_3$$

is therefore exothermic by only 66 kJ mol^{-1}. The exothermicity in the case of EtOH/NTO is therefore, by a factor 1.3 up to 2.6, lower than the exothermicity of the MMH/NTO system. Moreover, the initiation reaction of the EtOH/NTO system is more than 10 times more endothermic than the initiation reaction of the MMH/NTO system. This, under adiabatic conditions, should lead to a dramatic decrease of the temperature of the medium. This important decrease in temperature will slow the chemical kinetics and will hamper ignition. Furthermore, experimental evidence leads to the conclusion that almost only ethyl nitrite (C_2H_5ONO) forms. The formation of nitroethane ($C_2H_5NO_2$) according to

$$\text{C}_2\text{H}_5\text{OH} + \text{NO}_2 \longrightarrow \text{C}_2\text{H}_5^{\bullet} + \text{HNO}_3 \text{(initiation reaction)}$$

$$\text{C}_2\text{H}_5^{\bullet} + \text{NO}_2 \longrightarrow \text{C}_2\text{H}_5\text{NO}_2$$

would not change things too much as ethyl nitrite and nitroethane have almost the same standard enthalpy of formation at 298 K, −101.25 kJ mol^{-1} (Ref. 9), and −102.3 kJ mol^{-1} (Ref. 10), respectively, and because the initiation reaction for the formation of nitroethane is the same than the initiation reaction for the formation of ethyl nitrite. Alternative initiation reactions are

$$\text{CH}_3\text{CH}_2\text{OH} + \text{NO}_2 \longrightarrow \text{CH}_3\text{CH}_2\text{O}^{\bullet} + \text{HNO}_2$$

$$\Delta_r\text{H}^{\circ}298\text{ K} = +108.7\text{ kJ mol}^{-1}$$

or

$$\text{CH}_3\text{CH}_2\text{OH} + \text{NO}_2 \longrightarrow \text{CH}_3\text{C}^{\bullet}\text{HOH} + \text{HNO}_2$$

$$\Delta_r\text{H}^{\circ}298\text{ K} = +104.5\text{ kJ mol}^{-1}$$

or

$$\text{CH}_3\text{CH}_2\text{OH} + \text{NO}_2 \longrightarrow \text{C}^{\bullet}\text{H}_2\text{CH}_2\text{OH} + \text{HNO}_2$$

$$\Delta_r\text{H}^{\circ}298\text{ K} = +104.5\text{ kJ mol}^{-1}$$

but all of these initiation pathways also appear to be highly endothermic. In fact all of the EtOH + NO_2 initiation reactions are from a thermochemical viewpoint unlikely, and moreover the only one supposed to lead to ethyl nitrite, that is, $C_2H_5OH + NO_2 \longrightarrow C_2H_5^{\bullet} + HNO_3$, is the most endothermic of all of the initiation reactions and therefore the least probable. One has to conclude that the reaction between EtOH and NTO goes through a molecular reaction channel. Two molecular reaction pathways are possible according to Koda et al.[2] One goes through a five-center reaction channel between EtOH and the N-N bonded isomer of N_2O_4 (NO_2NO_2) according to

$$\text{EtOH} + \text{NO}_2\text{NO}_2 \longrightarrow \text{adduct}$$

$$\text{Adduct} \longrightarrow \text{C}_2\text{H}_5\text{ONO}_2 + \text{HNO}_2$$

This channel leads to ethyl nitrate and nitrous acid and is therefore not the one followed by the EtOH/NTO reaction.

The other proposed by Koda et al.[2] goes through a six-center molecular reaction channel between EtOH and a N_2O_4 isomer ($ONONO_2$) according to

$$\text{EtOH} + \text{ONONO}_2 \longrightarrow \text{adduct}$$

$$\text{Adduct} \longrightarrow \text{C}_2\text{H}_5\text{ONO} + \text{HNO}_3$$

This channel leads to the formation of ethyl nitrite, which is shown to form experimentally. Such molecule-molecule reactions generally exhibit high activation energies from about 80 kJ mol^{-1} up to about 210 kJ mol^{-1} according to Benson.[11] Therefore quite a low rate constant is expected for this process. $ONONO_2$ exists, and some spectroscopic data are available for the $ONONO_2$ species.[¶] However, the amount of $ONONO_2$ in NTO is unknown because no thermodynamic data are available for $ONONO_2$, especially its enthalpy of formation. Ab initio calculations[12] show that the lowest isomer of N_2O_4 in energy is the well-known N_2O_4 dimer with D2h symmetry (N-N bonded O_2N-NO_2). These calculations also show that two isomers of the asymmetrical N_2O_4 or $ONONO_2$ can exist, namely, trans-$ONONO_2$ and cis-$ONONO_2$ with the trans isomer being lower in energy than the cis isomer. The same study also shows that two other N_2O_4 isomers, namely, cis-perp-trans ONOONO and trans-perp-trans ONOONO, also exist, but these isomers are too high in energy to exist in significant amounts. It is not possible to evaluate quantitatively the amount of $ONONO_2$ in NTO because the thermochemistry of $ONONO_2$ is unknown, but, qualitatively, the amount of $ONONO_2$ (or asymmetric N_2O_4) is likely to be small compared to the amount of symmetric N_2O_4 (NO_2NO_2).

Conclusions

This study brings a chemical kinetic interpretation to explain why the EtOH/NTO system is not hypergolic, although EtOH/NTO reactivity at room temperature exists. It appears that all of the possible initiation reactions (H abstraction by NO_2) are too endothermic to be of importance. This represents a major difference with the MMH/NTO combination. The EtOH/NTO reactivity observed at room temperature during this study, and during other studies, takes place in the gas phase, at least at the beginning of the reaction process. This reactivity can be explained by a molecular reaction between ethanol and an isomer of N_2O_4, which is not the most common one NO_2NO_2, but $ONONO_2$. The existence of this N_2O_4 isomer is assessed, but only a small amount of it should exist in NTO. This small amount of reactant together with a high activation energy for the reaction should lead to a small rate of reaction unable to ensure ignition. More generally, this study and its chemical interpretation lead to the proposal of a criterion to detect likely NTO-based hypergolic systems.

References

[1] Fairlie, A. M., Carberry, J. J., and Treacy, J. C., "A Study of the Kinetics of the Reaction Between Nitrogen Dioxide and Alcohols," *Journal of the American Chemical Society*, Vol. 75, No. 15, 1953, pp. 3786–3789.

[2] Koda, S., Yoshikawa, K., Okada, J., and Akita, K., "Reaction Kinetics of Nitrogen Dioxide with Methanol in the Gas Phase," *Environmental Science and Technology*, Vol. 19, No. 3, 1985, pp. 262–264.

[3] Niki, H., Maker, P. D., Savage, C. M., and Breitenbach, L. P., "An FTIR Study of the Reaction Between Nitrogen Dioxide and Alcohols," *International Journal of Chemical Kinetics*, Vol. 14, No. 11, 1982, pp. 1199–1209.

[4] Nguyen, H. T.-H., Takenaka, N., Bandow, H., and Yasuaki, M., "Flow Analysis Method for Determining the Concentration of Methanol and Ethanol in the Gas Phase Using the Nitrite Formation Reaction," *Analytical Chemistry*, Vol. 72, No. 23, 2000, pp. 5847–5851.

[5] Jonsson, A., and Bertilsson, B. M., "Formation of Methyl Nitrite with Gasoline/Methanol and Methanol/Diesel," *Environmental Science and Technology*, Vol. 16, No. 2, 1982, pp. 106–110.

[6] Catoire, L., Chaumeix, N., and Paillard, C., "Chemical Kinetic Model for Monomethylhydrazine/Nitrogen Tetroxide Gas-Phase Combustion and Hypergolic Ignition," *Journal of Propulsion and Power*, Vol. 20, No. 1, 2004, pp. 87–92.

[7] Catoire, L., Chaumeix, N., Pichon, S., and Paillard, C., "Visualizations of Gas-Phase MMH/NTO Reactivity at Room Temperature," *Journal of Propulsion and Power* (accepted for publication).

[8] Catoire, L., and Swihart, M. T., "Thermochemistry of Species Produced from Monomethylhydrazine in Propulsion and Space-Related Applications," *Journal of Propulsion and Power*, Vol. 18, No. 6, 2002, pp. 1242–1253.

[9] Domalski, E. S., and Hearing, E. D., "Estimation of the Thermodynamic Properties of C-H-N-O-S-Halogen Compounds at 298.15 K," *Journal of Physical and Chemical Reference Data*, Vol. 22, No. 4, 1993, pp. 805–1105.

[10] Holcomb, D. E., and Dorsey, C. L., "Thermodynamic Properties of Nitroparaffins," *Industrial and Engineering Chemistry*, Vol. 41, No. 12, 1949, pp. 2788–2792.

[11] Benson, S. W., *Thermochemical Kinetics*, 2nd ed., Wiley, New York, 1976.

[12] Wang, X., Qin, Q.-Z., and Fan, K., "Ab Initio Study on the Characterization of N_2O_4 Isomers," *Journal of Molecular Structure (Theochem)*, Vol. 432, No. 1, 1998, pp. 55–62.

[¶] Data available online at http://webbook.nist.gov.