

## Full Paper

# Thermochemistry of Species Potentially Formed During NTO/MMH Hypergolic Ignition

**Antoine Osmont**

ICARE-CNRS, 1C, Avenue de la Recherche Scientifique, 45071 Orleans Cedex 2 (France)

**Laurent Catoire\***

ICARE-CNRS, 1C, Avenue de la Recherche Scientifique, 45071 Orleans Cedex 2 and Department of Chemistry, University of Orleans, Orleans (France)

**Thomas M. Klapötke**

Department of Chemistry and Biochemistry, Ludwig-Maximilians University of Munich, Butenandtstr. 5-13 (Haus D), D-81377 Munich (Germany)

**Ghanshyam L. Vaghjiani**

Propellant Branch, Space and Missile Propulsion Division, Propulsion Directorate, Air Force Research Laboratory, AFRL/PRSP, 10 E. Saturn Boulevard, Edwards AFB, CA 93524 (USA)

**Mark T. Swihart**

Department of Chemical and Biological Engineering, 303 Furnas Hall, State University of New York at Buffalo, Buffalo, NY 14260-4200 (USA).

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## Abstract

This paper deals with the gas-phase thermodynamic properties of endothermic compounds potentially formed during monomethylhydrazine (MMH)/nitrogen tetroxide (NTO) hypergolic reactivity. The standard enthalpies of formation at 298.15 K are determined by means of quantum chemistry calculations along with protocols developed for these compounds. The resultant data, currently previously unavailable for almost all of these compounds, are potentially critical to the modeling of combustion chemistry of this bipropellant combination.

**Keywords:** Standard Enthalpies of Formation, Monomethylhydrazine, Nitrogen Tetroxide, Unsymmetrical Dimethyl Hydrazine

## 1 Introduction

Nitrogen tetroxide (NTO)/monomethylhydrazine (MMH), NTO/unsymmetrical dimethyl hydrazine (UDMH) and NTO/Aerozine 50 (MMH/UDMH mixture)

are chemical systems used for in-space liquid propulsion. These systems are very interesting because they are able to autoignite at low temperature (room temperature and below), i.e. they ignite without any external ignition device. This phenomenon is called hypergolicity. From a fundamental research point of view, much more work is needed to understand all the features of hypergolic ignition. Fuels are stored in the liquid state but, as usual for liquids, ignition (hypergolic or not) occurs in the gas-phase above the liquids. This has been recently shown for a hypergolic system by Alfano et al. [1]. Gas-phase species and condensed-phase species form during the reaction between NTO and MMH or UDMH. Experimental observations show that condensed species form when the reaction does not lead to ignition and that condensed species form when hypergolic ignition occurs, i.e. during the ignition delay [2]. The chemical nature of these compounds is not clearly established, despite numerous studies. In fact, the NTO/MMH chemistry depends on the experimental conditions: equivalence ratios, temperature, and pressure. Liquid-liquid reactions at low temperature lead to condensed methylhy-

\* Corresponding author; e-mail: catoire@cnrs-orleans.fr

drazinium nitrate. It can also be the case that methylhydrazinium azide forms. However, even if these species can play a role in other related topics, such as hard starts, their role in hypergolic ignition is not completely clear. A detailed chemical kinetic model was proposed to interpret the gas-phase NTO/MMH reactivity [3]. This mechanism includes a sub-mechanism devoted to MMH thermal decomposition, validated with MMH profiles observed in shock tube experiments [4] and a sub-mechanism devoted to the oxidation of MMH validated with MMH/O<sub>2</sub> [5] and MMH/O<sub>2</sub>/H<sub>2</sub> [6] ignition delays. The formation of methyl-diazene CH<sub>3</sub>N=NH and its subsequent thermal decomposition together with the exothermic formation of nitrite and nitro compounds resulting from termolecular recombinations between methylhydrazyl radicals and NO<sub>2</sub> explain gas-phase hypergolic ignition and gas-phase non-ignition. It remains uncertain whether this model is sufficiently detailed, but it allows the simulation of gas-phase MMH/NTO self-ignition at low temperature (ambient and below), for any pressure, and this is certainly a major achievement. It is commonly the case that only about 10% of the reactions given in a detailed chemical kinetic model play a role on the ignition/combustion process and therefore the writing of all the likely reactions is not always appropriate. Sun and Law [7] recently proposed rate constants for some elementary reactions needed to simulate the thermal decomposition of MMH. These reactions are not expected to play a role in MMH/NTO hypergolic ignition, but this remains to be demonstrated. Nonnenberg et al. [8], and Frank et al. [9] used molecular dynamics to simulate NTO/MMH reactivity and found that methyl-diazene can be assumed to be the main product during NTO/MMH hypergolic ignition. According to this paper, the recombination of methylhydrazyl radicals can lead to dimethyltetrazanes. Indeed these termolecular recombination reactions are exothermic and must be considered in the NTO/MMH detailed chemical kinetic model. Thermodynamic data needed for the writing of MMH-based detailed kinetic models are presented in Ref. [10] and [11]. The thermochemistry presented by Sun and Law [7] for methylhydrazyl radicals CH<sub>3</sub>N•NH<sub>2</sub>, CH<sub>3</sub>NHNH• and CH<sub>2</sub>•NHNH<sub>2</sub> is consistent with the data presented by Catoire and Swihart [10]. However, the thermochemistry of the dimethyltetrazanes is not available and remains to be studied. McQuaid et al. [12, 13] also present considerations for MMH/IRFNA hypergolic ignition, which partially validate the NTO/MMH detailed chemical kinetic model proposed. Finally, the formation of a number of nitroso, nitrite, nitro, and nitrate compounds, not previously taken into account, must be considered for completeness. Nitroso, nitro, nitrite, and nitrate compounds considered here have an –NO group, –NO<sub>2</sub> group, –ONO group, or –ONO<sub>2</sub> group attached to nitrogen atom, respectively. Experimental data for such derivatives of MMH and UDMH are scarce. The thermochemistry of these compounds is needed to allow the construction of more detailed chemical kinetic models able to simulate hypergolic ignition. The aim of this work is to present gas-phase standard enthalpy of formation of nitroso, nitro, nitrite, and nitrate

derivatives of MMH and UDMH, not considered previously, and gas-phase standard enthalpy of formation of dimethyltetrazane compounds. These data are obtained by using two ab initio methods, specifically derived and validated for this purpose, one for compounds containing NO<sub>2</sub>, ONO, ONO<sub>2</sub> groups and one for general organic compounds.

## 2 Computational Details

The gas-phase standard enthalpy of formation of molecule *j* at 298.15 K can be determined from the following equation:

$$\Delta_f H_{298.15\text{K(g)}}^0 = 2625.5 \times \left( E_j + \text{ZPE}_j + \text{thermal corrections} + \sum_i \alpha_i c_i^* \right)$$

where  $\alpha_i$  is the number of atoms *i* in molecule *j* and  $c_i^*$  the atomic correction for atom *i*.  $E_j$  and  $\text{ZPE}_j$  denote, respectively, the absolute electronic energy and zero-point energy, calculated using the Gaussian 98W [14] and Gaussian 03 [15] softwares. The units are Hartree molecule<sup>−1</sup> for  $E_j$ ,  $\text{ZPE}_j$  and thermal corrections, and Hartree atom<sup>−1</sup> for  $c_i^*$ , whereas  $\Delta_f H_{298.15\text{K(g)}}^0$  is in kJ mol<sup>−1</sup>. Two classes of compounds are considered in this study: C/H/N/O compounds and C/H/N compounds. The method established and validated for nitroso, nitro, nitrite, and nitrate compounds, i.e. C/H/N/O compounds, is described in Osmont et al. [16]. The method established and validated for tetrazanes, i.e. C/H/N compounds, is described in Osmont et al. [17, 18].

## 3 Results

Experimental difficulties in isolating these compounds for calorimetric studies are substantial, and therefore estimation methods have to be used. Such methods can be more or less sophisticated. In this study, we used two ab initio methods with empirical atomic corrections. The details of these methods are beyond the scope of this paper. One of these methods was specifically established and validated with experimental data known on nitro, nitrite, and nitrate compounds. This method was derived with data from 28 compounds and validated with 16 compounds. The average absolute deviation between experiments and calculations is 7.1 kJ mol<sup>−1</sup> for the derivation set and 10.0 kJ mol<sup>−1</sup> for the validation set. Table 1 gives the comparison between calculated and experimental gas-phase standard enthalpies of formation at 298.15 K for some compounds included in the derivation and validation datasets. The agreement between experiments and calculations is good. The average absolute deviation for this method, in general, is expected to be ±13 kJ mol<sup>−1</sup>. In Table 1, the average absolute deviation is 5.4 kJ mol<sup>−1</sup> for the nitrite compounds, 8.8 kJ mol<sup>−1</sup> for the nitro compounds and 11.3 kJ mol<sup>−1</sup> for the nitrate com-

**Table 1.** Comparison between experimental and calculated (within parenthesis) gas-phase standard enthalpy of formation at 298.15 K for nitrite, nitro, and nitrate compounds from the validation database. Units are kJ mol<sup>-1</sup>.

-X	-ONO	-NO <sub>2</sub>	-ONO <sub>2</sub>
CH <sub>3</sub> X	-65.3 (-65.3)	-80.7 (-82.0)	-122.2 (-129.3)
C <sub>2</sub> H <sub>5</sub> X	-108.4 (-102.9)	-102.5 (-117.1)	-154.8 (-166.5)
C <sub>3</sub> H <sub>7</sub> X	-118.8 (-128.9)	-124.7 (-138.5)	-174.0 (-187.9)
CH <sub>3</sub> -CHX-CH <sub>3</sub>	-133.5 (-141.0)	-140.2 (-150.2)	-190.8 (-202.5)
(CH <sub>3</sub> ) <sub>3</sub> C-X	-171.5 (-167.4)	-177.0 (-180.7)	No experimental data

**Table 2.** Calculated gas-phase standard enthalpies at 298.15 K for nitroso, nitrite, nitro, and nitrate derivatives of MMH and UDMH. Units are kJ mol<sup>-1</sup>.

-X	-NO	-ONO	-NO <sub>2</sub>	-ONO <sub>2</sub>
CH <sub>3</sub> -NH-NH-X	197.9	173.6	102.1	142.3
CH <sub>3</sub> -NX-NH <sub>2</sub>	158.2	173.6	95.8	113.8
CH <sub>3</sub> -NH-NX <sub>2</sub>	342.7	292.0	183.8	172.4
CH <sub>3</sub> -NX-NH-X	278.7	284.9	143.9	167.4
CH <sub>3</sub> -NX-NX <sub>2</sub>	427.6	387.0	247.7	232.6
(CH <sub>3</sub> ) <sub>2</sub> -N-NH-X	174.9	187.9	103.8	123.8
(CH <sub>3</sub> ) <sub>2</sub> -N-NX <sub>2</sub>	319.2	288.3	182.0	177.0

**Table 3.** Gas-phase standard enthalpy of formation at 298 K of nitro and nitrite derivatives of MMH calculated by McQuaid et al. [12, 13]. Units are kJ mol<sup>-1</sup>.

-X	-ONO	-NO <sub>2</sub>
CH <sub>3</sub> -NX-NH <sub>2</sub>	161.1	101.3

pounds. It is to be noted that experimental determination is often unique and therefore experimental uncertainties are often underestimated. The same method, once applied to nitroso, nitro, nitrite, and nitrate compounds derived from MMH and UDMH, leads to data given in Table 2. McQuaid et al. [12, 13] used another ab initio method to compute the gas-phase standard enthalpy of formation of some of the CH<sub>3</sub>-NX-NH<sub>2</sub> species given in Table 2. Comparisons of methods are always interesting especially when no experimental data are available. Their results are given in Table 3 for two of the 28 compounds presented in Table 2. Results given in Tables 2 and 3 are consistent for the nitro and nitrite compounds considered. Therefore, the data presented for 26 remaining compounds presented in Table 2 can be considered to be reliable. These results, and the reappraisal of some thermodynamic data, may help to explain hypergolic ignition. All the compounds in Table 2 are endothermic compounds, i.e. their enthalpies of formation are positive. Such compounds are able to decompose exothermically under thermal stress and this may be of interest to explain ignition or reactivity characteristics and to interpret hard start phenomenon observed occasionally in engines using NTO/MMH.

Another theoretical method specifically devoted to general organic compounds not containing NO, NO<sub>2</sub>, ONO, and/or ONO<sub>2</sub> groups was then used to compute the thermochemistry of dimethyltetrazanes. These compounds

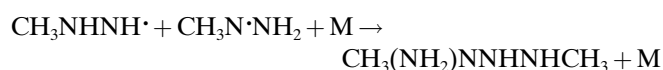
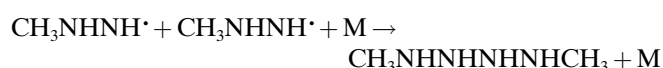
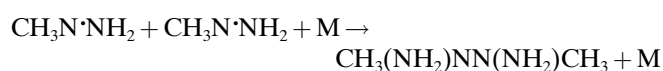
**Table 4.** Gas-phase standard enthalpy of formation at 298 K of hydrazine, MMH, and UDMH calculated by using a ab initio method developed for this study. Units are kJ mol<sup>-1</sup>.

Compound	Method used here	Experimental data
Hydrazine	95.4	95.4
MMH	93.3	94.1

**Table 5.** Gas-phase standard enthalpy of formation at 298 K of three dimethyltetrazanes by using a ab initio method developed for this study. Units are kJ mol<sup>-1</sup>.

Compound	Method used here	Experimental data
CH <sub>3</sub> (NH <sub>2</sub> )NN(NH <sub>2</sub> )CH <sub>3</sub>	269.4	-
CH <sub>3</sub> NHNHNHNHCH <sub>3</sub>	258.6	-
CH <sub>3</sub> (NH <sub>2</sub> )NNHNHCH <sub>3</sub>	262.3	-

are formed through the termolecular recombination of two methylhydrazyl radicals, namely CH<sub>3</sub>N<sup>•</sup>NH<sub>2</sub> and CH<sub>3</sub>NHNH<sup>•</sup>. Their termolecular recombination reactions lead to three different dimethyltetrazanes according to:



The agreement between experiments and calculations is shown in Table 4 for hydrazine and MMH. Table 5 gives the calculated data for the three dimethyltetrazanes given above. The formation of these tetrazanes is exothermic and these compounds are endothermic, i.e. they can decompose exothermically. These species can play a role in ignition and this role needs to be further studied.

## 4 Conclusion

Protocols have been derived and validated for predicting the thermodynamic data needed for thermochemical calcu-

lations and for building detailed chemical kinetic models to simulate hypergolic ignition and combustion. The level of theory, hybrid density functional theory with a modest basis set, plus empirical corrections, is found appropriate for the current state of knowledge (quite minimal) of their thermochemistry. This paper provides thermochemical data for 31 molecules potentially formed during the MMH/NTO reactivity. No experimental data are available for these compounds. The model previously proposed to explain hypergolic NTO/MMH ignition can be improved, as can almost all kinetic models. Detailed kinetic models developed for mixtures easier to study, and therefore intensively studied, such as premixed methane/air or hydrogen/air, have been continuously improved over the past 50 years, and new models have been proposed in recent years to explain ignition characteristics of these mixtures. Therefore, complementary studies need to be performed for the complex MMH/NTO combustion chemistry. The impact of the thermochemistry proposed in this study on the predictions of the MMH/NTO detailed kinetic model must be examined. Alternative reaction paths also need to be considered. The development of visualization techniques and of new analytical techniques, along with the development and application of methods for calculating the thermochemistry of reactants, products, and intermediate species should lead in the near future to a better understanding of the features of hypergolic ignition and to new tools for the design and screening of new hypergolic fuels.

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