JOURNAL OF PROPULSION AND POWER
Vol. 18, No. 6, November–December 2002

Thermochemistry of Species Produced from Monomethylhydrazine in Propulsion and Space-Related Applications

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This paper focuses on the chemistry of the widely used propellant monomethylhydrazine. Several different chemistries of this compound are of interest to study propulsion, environmental, and safety issues in wide ranges of temperature (from below the ambient up to thousands of Kelvins), pressure (from millibars up to several tens of bars), and concentration. Here, we present gas-phase thermochemical properties of more than 50 C/H/N species expected to play a role in the chemistry of monomethylhydrazine. These were obtained from high-level *ab initio* quantum chemistry calculations. Groups of them are discussed in terms of the conditions under which they are expected to be of potential importance.

Introduction

APPLICATION of combustion science, for the building of chemical kinetic models for aerospace propulsion systems, requires a large amount of physico-chemical data. Ab initio quantum chemistry methods allow the reliable computation of important parts of this, including the thermodynamic properties of chemical species that have not been studied experimentally.

Monomethylhydrazine (CH_3NHNH_2), abbreviated as MMH, is used in a wide variety of applications, and the bipropellant hypergolic combination MMH/NTO (nitrogen tetroxide) is particularly important for spacecraft and rockets. Extensively used in the past,[1] it continues to be of great interest as a fuel in propellant formulations. It is currently used for the space shuttles, for numerous satellites, and for the launcher Ariane 5. The bipropellant hypergolic MMH/NTO combination is not, strictly speaking, a high-temperature chemistry, at least at the beginning of the process. Typically, the reactants are initially at about 298 K, and therefore both high-temperature and low-temperature chemistries are of interest in this system. MMH is also a component of some advanced propellant systems including gelled fuels (IRFNA/MMH) and metalized gelled propellants.[2] As the metal suggested for these applications is aluminum, some reactions between Al atoms and MMH or MMH-derived radicals are likely, even if most of the aluminum will react with the MMH/NTO combustion products at the flame temperature of the MMH/NTO system. MMH is also considered in a number of other projects associated with various oxidizers (NTO, O_2) (Ref. 2). Furthermore, some of the data presented here can be of interest for the modeling of the combustion of some advanced high-performance propellants such as the metallized gelled propellants or also for the high-energy-density propellants.

Interest in MMH is not limited to its combustion chemistry applied to propulsion but also to other chemistries directly related to its use for propulsion purposes. The fate of MMH released into the troposphere, from normal handling or during accidents, has been the subject of several studies,[3,4] and the atmospheric chemistry, as well as the combustion chemistry, is of interest for this molecule.[5] The fate of MMH at low Earth orbit is also of interest.[6] Although most of the MMH fuel aboard spacecraft is combusted, appreciable amounts are released in an unburned state as the engine is shut down. Therefore, the reactions of MMH with high-altitude atmospheric species have to be considered to assess the importance of fuel products as potential contaminants in the spacecraft environment. The storage of MMH is also a subject of importance because MMH is subject to surface-catalyzed thermal decomposition reactions[7] that are exothermic and gas-producing. Hazards can result from such heterogeneous decompositions. Therefore, some chemical species and reactions will be considered even if they are not of direct interest for combustion modeling.

MMH is also of interest for non-space-related applications such as material synthesis by chemical vapor deposition (CVD) processes. MMH has been used as a nitrogen precursor to replace NH_3 for the organometallic vapor-phase epitaxy (OMVPE) growth of the group III nitrides.[8] It has also been used as a nitrogen source in the metal organic molecular beam epitaxy (MOMBE) growth of GaN (Ref. 9) and for the vapor-phase epitaxial (VPE) growth of InN (Ref. 10).

Considerable thermodynamic and kinetic data are required as input for the modeling of all of the chemistries briefly described in the preceding paragraphs. Some of the thermodynamic data and most of the chemical kinetic data are not available in the literature. The first aim of this study is to establish the thermochemistry of H/C/N species likely to be present during the MMH thermal decomposition and oxidation through high-level *ab initio* calculations. To avoid the computational expense of *ab initio* calculations, group additivity methods can be used to estimate the enthalpy of formation for species never studied experimentally or theoretically.[11] However, as pointed out by Burcat and Gardiner,[12] group additivity cannot be used for many of the species studied here or can only be used with high uncertainty because of the lack of group data for the groups and molecules considered here. For completeness, the electronic spin state, moments of inertia, and vibrational frequencies for each molecule are given in this paper. The thermodata have been fitted, over a wide temperature range, to the CHEMKIN-NASA format, and the results are presented in that format at the end of this manuscript.

Received 21 January 2002; revision received 24 June 2002; accepted for publication 11 July 2002.

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As the number of species potentially formed in this system is huge, we focus here on the species potentially important for ignition rather than on species likely to be present in small amounts in the combustion products. In this work no attempt has been made to distinguish all the possible conformers for a given molecule, but rather we have taken a single conformer that might reasonably be expected to be the lowest in energy, as representative of each molecule. Errors in thermochemical properties introduced by this simplification are expected to be smaller than uncertainties in the underlying calculations. Of course, different structural isomers have been treated separately. Although the present paper will focus on the chemistries related to spacecraft propulsion applications, much of the information presented here is also of interest for CVD processes.

The present paper focuses exclusively on computing thermochemical properties of molecules in the H/C/N system. These species are methylhydrazine; the methylhydrazyl radicals C•H2NHNH2, CH3NHN•H, and CH3N•NH2; azo compounds [methyldiazene CH3N=NH, dimethyldiazene CH3N=NCH3 also called azomethane, ethylmethyldiazene C2H5N=NCH3, dimethylaminodiazene CH3N(H)N=NN(H)CH3] and related radicals (methyldiazenyl radicals C•H2N=NH and CH3N=N•, dimethyldiazenylradical C•H2N=NCH3, CHN=NH, C•H2N=N•); CH2=NNH2 and related radicals (C•H=NNH2, CH2=NN•H, C•H=NN•H, C=NNH2, CH2=NN); CH3N(H)N=CH2, CH3N=NN=NH, CH3N=NN(H)N=CH2, CH2=NN=NCH3, diaziridine, 3H-diazirine, 1H-diazirine and related radicals; 1,4-dimethylperhydrotetrazine, as well as ions. Future work will address 1) the thermochemistry of the relevant H/C/N/O species and 2) the building of detailed kinetic models for the applications just described briefly.

Thermochemistry of Species in MMH-Based Systems

MMH Homogeneous Gas-Phase Thermal Decomposition (Pyrolysis)

The performance of a fuel/oxidizer propellant is typically characterized by the ignition delay. One detailed kinetic model for the MMH/O_2/Ar gaseous ignition delay has been proposed by Catoire et al.[13,14] and validated by comparison with shock-tube experiments. Of all of the submechanisms included in the just mentioned detailed kinetic model, the thermal decomposition of MMH has to be considered first. It has been observed that one of the MMH oxidation regimes is a two-step one consisting of an oxidative pyrolysis (step 1), that is, a thermal decomposition promoted by O_2, followed by the explosive oxidation (step 2).[15] The thermal decomposition has been studied very little from an elementary kinetics point of view, and therefore many of the reactions, and therefore of the species, potentially of importance in this process are not well known. Golden et al.[16] did not observe the N—N scission in MMH, although they observed it in hydrazine and unsymmetrical dimethylhydrazine (UDMH), but instead saw H_2 and NH_3 elimination. Golden et al.'s experiments have been performed at very low pressure, using the very low pressure pyrolysis (VLPP) technique, and they extrapolated their results using the Rice-Ramsperges-Kassel-Marcus (RRKM) theory to obtain a value for the high-pressure rate constant for the N—N bond scission in MMH. Global experiments of relatively highly concentrated MMH have been interpreted by considering the N—N bond scission in MMH. Catoire et al.[17] proposed a detailed kinetic model for MMH pyrolysis consisting of 99 reversible elementary reactions. The initiation step in this model is the N—N bond scission because this bond is the weakest in the MMH molecule and also because the experiments have been performed at much higher pressures than the ones of Golden et al.[16] This mechanism has been validated with MMH concentration profiles observed during shock-tube experiments performed[17,18] in the 1040–1370 K temperature range, 140–455 kPa pressure range, and in mixtures containing 1 to 3 mol.% MMH in Ar. However, because of the lack of thermodynamic data and also of kinetic data several possible pathways have been neglected, and therefore this kinetic model cannot be claimed to be unique. The two other combustion regimes observed, below about 1000 K, lead to products in one apparent step.[18] Therefore, some direct oxidation channels between molecular MMH and O_2, negligible above 1000 K, become important below 1000 K. Consequently some oxygenated species, such as peroxides, should also be considered.

The species described next are relevant to the homogeneous gas-phase thermal decomposition of MMH. Although relatively good agreement for the MMH half-life is obtained between experiments and predictions of the existing kinetic model for diluted mixtures,[17,18] some experimental facts are not correctly predicted and explained by it.[18] For example, the ignition delay of MMH/diluent mixtures with high MMH concentration is not predicted accurately.

Fourteen initiation reactions can be considered during MMH thermal decomposition:

$$\mathrm{MMH} \rightarrow \mathrm{C^{\bullet}H_2NHNH_2} + \mathrm{H} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = 95.24\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{MMH} \rightarrow \mathrm{CH_3N^{\bullet}NH_2} + \mathrm{H} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = 79.92\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{MMH} \rightarrow \mathrm{CH_3NHN^{\bullet}H} + \mathrm{H} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = 81.92\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{MMH} \rightarrow \mathrm{CH_3N^{\bullet}H} + \mathrm{NH_2} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = 65.18\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{MMH} \rightarrow \mathrm{CH_3} + \mathrm{N^{\bullet}HNH_2} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = 67.26\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{MMH} \rightarrow \mathrm{CH_2{=}NNH_2} + \mathrm{H_2} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = 17.39\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{MMH} \rightarrow \mathrm{CH_3N{=}NH} + \mathrm{H_2} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = 18.88\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{MMH} \rightarrow {}^1\mathrm{CH_2NHNH} + \mathrm{H_2} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = 39.64\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{MMH} \rightarrow {}^3\mathrm{CH_2NHNH} + \mathrm{H_2} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = 81.57\ \mathrm{kcal\ mol^{-1}}$$

(spin forbidden)

$$\mathrm{MMH} \rightarrow {}^3\mathrm{CH_3N} + \mathrm{NH_3} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = 42.74\ \mathrm{kcal\ mol^{-1}}$$

(spin forbidden)

$$\mathrm{MMH} \rightarrow {}^1\mathrm{CH_3N} + \mathrm{NH_3} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = 76.51\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{MMH} \rightarrow \mathrm{CH_4} + {}^3\mathrm{NNH_2} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = 48.63\ \mathrm{kcal\ mol^{-1}}$$

(spin forbidden)

$$\mathrm{MMH} \rightarrow \mathrm{CH_4} + {}^1\mathrm{NNH_2} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = 31.23\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{MMH} \rightarrow \mathrm{CH_2NH} + \mathrm{NH_3} \qquad \Delta H^0_{\mathrm{rxn}}\ (298\ \mathrm{K}) = -10.83\ \mathrm{kcal\ mol^{-1}}$$

For the preceding reactions the following molecules and radicals have to be considered: MMH, $CH_2{=}NNH_2$, $CH_3N{=}NH$, CH_4, NH_3, $CH_2{=}NH$, H_2, $CH_3N^{\bullet}H$, NH_2, CH_3, $N^{\bullet}HNH_2$, $CH_3N^{\bullet}NH_2$, $CH_3NHN^{\bullet}H$, $C^{\bullet}H_2NHNH_2$, CH_3N (both triplet and singlet states), NNH_2 (both triplet and singlet states), and $^{\bullet}CH_2NHN^{\bullet}H$ (both singlet and triplet states). Some of these species are well known (NH_2, CH_3, CH_4, NH_3, H_2, MMH, CH2=NH) but some others (especially the radicals $C^{\bullet}H_2NHNH_2$, $CH_3N^{\bullet}NH_2$ and $CH_3NHN^{\bullet}H$) are less well known, and no experimental data are available. Data for some of these species have been calculated by Melius by using the BAC-MP4 method, and the results of these calculations are available on-line at http://z.ca.sandia.gov/~melius/bac/bac082897.eng0 [cited Aug. 1997] and also, partially, in the thermodynamic tables of Burcat and McBride.[19]

Ab initio molecular orbital calculations have been performed for all of the species, including the well-known NH_2, CH_3, NH_3, and CH_4 that can be used to verify the validity of the calculations performed here. The CBS-Q and G2 methods used here have been shown to be reliable for a wide range of molecules, radicals, and ions by Ochterski et al.,[20] Petersson et al.,[21] and many others. These methods are described well elsewhere.[21] The enthalpies of formation presented here were 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 for H, 171.21 kcal/mol for C, and 112.94 kcal/mol for N). The *ab initio* energy of the carbon atom was corrected to account for spin-orbit coupling using the experimental spin-orbit interaction energy (0.0847 kcal/mol). Table 1 gives the computed enthalpies of formation at 0 K and at 298.15 K and 1 bar for all of the species.

From the collection of Petersson et al.[21] of around 150 molecules with well-established experimental heats of formation, the results

Table 1 Computed enthalpies of formation at 0 and 298.15 K and 1 bar for the species under consideration for the MMH thermal decomposition initiation reaction (Units are kcal mol^{-1})

Species	CBS-Q (0 K)	CBS-Q (298 K)	G2 (0 K)	G2 (298 K)	Exp (298 K)
MMH (singlet)	29.93	24.79	28.00	22.90	
					22.75[a]
					22.20[b]
					22.30[c]
$C^{\bullet}H_2NHNH_2$ (doublet)	70.68	66.52	70.16	66.04	—[d]
$CH_3NHN^{\bullet}H$ (doublet)	56.96	52.79	56.86	52.72	——[e]
$CH_3N^{\bullet}NH_2$ (doublet)	54.95	50.83	54.81	50.72	——
CH_2NHNH (singlet)	67.43	63.89	66.05	62.54	—
CH_2NHNH (triplet)	106.87	103.73	107.56	104.47	—
$CH_3N{=}NH$ (singlet)	47.08	43.66	45.17	41.78	
					37.4 ± 3[f]
					45 ± 2[g]
$CH_2{=}NNH_2$ (singlet)	44.96	41.49	43.74	40.29	—
NNH_2 (triplet)	90.64	88.98	91.07	89.42	—
NNH_2 (singlet)[h]	74.40	72.71	73.62	71.93	—
$N^{\circ}HNH_2$ (doublet)	57.27	54.71	57.52	54.97	
					55.3 ± 0.3[i]
CH_3N (triplet)[h]	78.74	76.87	78.34	76.47	—
$CH_3N^{\bullet}H$ (doublet)	46.50	43.91	45.68	43.11	44
NH_2 (doublet)	46.12	45.43	45.66	44.97	45.48
CH_3 (doublet)	35.94	35.35	35.81	35.19	35.13
NH_3	−8.34	−10.03	−9.14	−10.83	−10.97
CH_4	−15.72	−17.62	−16.62	−18.52	−17.80

[a] Ref. 22.
[b] Ref. 23.
[c] Ref. 24.
[d] — = no experimental data.
[e] —— = no reliable experimental data.
[f] Ref. 29.
[g] Ref. 30.
[h] Ground state.
[i] Ref. 27 at 0 K.

obtained using the CBS-Q and G2 methods are expected to be accurate to within ±1 to 2 kcal mol^{-1}. For the well-known species included here (CH_4, NH_3, CH_3, NH_2), mean absolute deviations of about 0.4 kcal mol^{-1} are obtained here for both the CBS-Q and G2 methods compared to experimental values. For MMH itself experimental values reported in the literature at 298.15 K are 22.75 (Ref. 22), 22.20 (Ref. 23), and 22.20 (Ref. 24) kcal mol^{-1}. The value predicted by the G2 method, 22.9 kcal mol^{-1}, is closest to the experimental values, the CBS-Q value being too large by about 2 kcal mol^{-1}. Therefore for all of the species derived from MMH the G2 values are preferred. The enthalpies of formation obtained in Table 1 for CH_2NHNH_2, CH_3NHNH, CH_3NNH_2, $CH_2{=}NNH_2$, triplet NNH_2, triplet CH_3N, CH_3NH and N_2H_3 are within about ±1 kcal mol^{-1} of those obtained by Melius by using the BAC-MP4 method. Data available on-line at http://z.ca.sandia.gov/~melius/bac/bac082897.eng0 [cited Aug. 1997].

For methylhydrazyl radicals only rough experimental values, or values derived indirectly from experiments, are available. These disagree with the present calculations, as 95 kcal mol^{-1} and 83 kcal mol^{-1} are reported for CH_3NNH_2 and CH_3NHNH, respectively, by Franklin et al.[25] based on experiments performed by Dibeler et al.[26] In such a case experimental data should usually prevail. However, the same authors[26] proposed, based on experiments using the same techniques, a value of 87 kcal mol^{-1} for the enthalpy of formation of N_2H_3, which is also in disagreement with our calculations (about 57 kcal mol^{-1} at 0 K). More importantly, their value also disagrees with the more recent experimental determination of Ruscic and Berkowitz[27] (55.3 ± 0.3 kcal mol^{-1} at 0 K), which is in reasonable agreement with our calculated result. We therefore conclude that the procedure of Dibeler et al.,[26] at least applied to neutrals, is not valid for these species.

For N_2H_3 (or $NHNH_2$) Armstrong et al.[28] computed, using ab initio methods, an enthalpy of formation of 56.17 kcal mol^{-1} at 0 K and 53.77 kcal mol^{-1} at 298 K. Our calculations are consistent with these values as well as with the ones given by Melius and also with the experimental value at 0 K just reported. Melius' data available on-line at http://z.ca.sandia.gov/~melius/bac/bac082897.eng0 [cited Aug. 1997].

Table 2 Computed enthalpies of formation at 0 and 298.15 K and 1 bar for $CHNHNH_2$ (singlet and triplet states) and CH_3NHN (singlet and triplet states) (Units are kcal mol^{-1})

Species	CBS-Q (0 K)	CBS-Q (298.15 K)	G2 (0 K)	G2 (298 K)	Exp
$CHNHNH_2$ (singlet)[a]	83.29	80.16	82.24	79.06	—[b]
$CHNHNH_2$ (triplet)	124.49	121.3	124.62	121.47	—
CH_3NHN (triplet)	91.82	88.50	91.78	88.50	—
CH_3NHN (singlet)[a]	70.12	66.78	68.85	65.54	—

[a] Ground state. [b] — = no experimental data.

For methyldiazene CH_3NNH Foner and Hudson[29] give for the enthalpy of formation a value of 37.4 ± 3 kcal mol^{-1} in slight disagreement with our calculations, which are more consistent with the value of 45 ± 2 kcal mol^{-1} given by Lias et al.[30]

The knowledge of these formation enthalpies allows the calculations of the reaction enthalpies for all of the possible initiation reactions during the thermal decomposition of MMH. Data for the singlet CH_3N have not been computed here and have been taken as given by Dean and Bozzelli[31]: ΔH_f^0 $^1CH_3N$ (298 K) = 112.47 kcal mol^{-1}.

For the thermal decomposition subsequent reactions can include the information in the following sections.

Decomposition of the Methylhydrazyl Radicals

The methylhydrazyl radicals can decompose through C—N or N—N bond scission or by loss of an H atom. In some of these cases, bivalent radicals are formed. Even though these reactions are not likely to be of importance, the thermochemistry of the species $CHNHNH_2$ and CH_3NHN is included here for completeness (see Table 2). Data for the other bivalent radical $C^{\bullet}H_2NHN^{\bullet}H$ have just been computed, as this species can form during the initiation. The only other new species formed in these reactions is CH_2, for which accurate thermochemical data are available.

Decomposition Reactions of $CH_3N{=}NH$, $CH_2{=}NNH_2$, $CH_2{=}NH$ and Derived Radicals

These decomposition reactions add new species to the list already given. Thermodynamic data are to be evaluated for the species $C^{\bullet}H_2N{=}NH$, $CH_3NN^{\bullet}$, $^{\bullet}CH{=}NNH_2$, $CH_2{=}NN^{\bullet}H$, $C^{\bullet}H{=}NH$, and $CH_2{=}N^{\bullet}$ (see Table 3). The radicals just formed can further decompose, and these reactions lead to the formation of the following bivalent radicals (see Table 4): $^{\bullet}CH_2N{=}N^{\bullet}$, $CHN{=}NH$, $^{\bullet}CH{=}NN^{\bullet}H$, $CH_2{=}NN$, $C{=}NNH_2$. All of the species formed can further decompose to small species with three or less atoms. However, the thermochemistry for such small species is sufficiently well known that no further computational work is needed.

Isomerization of Biradicals and Decomposition of the Species Formed

The biradicals $^{\bullet}CH_2NHN^{\bullet}H$ (formed during one of the possible initiation reactions), $^{\bullet}CH_2N{=}N^{\bullet}$, $H^{\bullet}C{=}NN^{\bullet}H$ can also isomerize to give three-membered rings, as shown in Fig. 1: a) diaziridine, b) 3H-diazirine, and c) 1H-diazirine, respectively. Three-membered heterocycles are highly reactive molecules. Because of this high reactivity, these species are not expected to be formed in high amounts in the products, but can be present in small amounts as potentially important intermediates. In fact, the formation of diaziridine appears much more probable than the formation of the two preceding

Table 3 Computed enthalpies of formation at 0 and 298.15 K and 1 bar for $C^{\bullet}H_2N{=}NH$, $CH_3NN^{\bullet}$, $^{\bullet}CH{=}NNH_2$, $CH_2{=}NN^{\bullet}H$ and $CH_2{=}N^{\bullet}$ (Units are kcal mol^{-1})

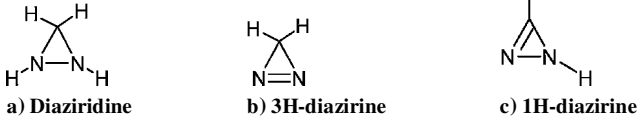
Species	CBS-Q (0 K)	CBS-Q (298.15 K)	G2 (0 K)	G2 (298 K)	Exp
$C^{\bullet}H_2N{=}NH$ (doublet)	82.36	79.80	83.00	80.48	—[a]
$CH_3NN^{\bullet}$ (doublet)	58.69	56.35	59.20	56.88	—
$^{\bullet}CH{=}NNH_2$ (doublet)	93.96	91.50	94.44	92.01	—
$CH_2{=}NN^{\bullet}H$ (doublet)	86.96	84.41	87.68	85.16	—
$CH_2{=}N^{\bullet}$ (doublet)	58.56	57.69	58.75	57.88	—

[a]— = no experimental data.

Table 4 Computed enthalpies of formation at 0 and 298.15 K and 1 bar for $^{\bullet}CH_2N{=}N^{\bullet}$ (singlet and triplet state), $CH_2{=}NN$ (singlet and triplet state), $CHN{=}NH$, $^{\bullet}CH{=}NN^{\bullet}H$ and $C{=}NNH_2$ (Units are kcal mol^{-1})

Species	CBS-Q (0 K)	CBS-Q (298.15 K)	G2 (0 K)	G2 (298 K)	Exp
$^{\bullet}CH_2N{=}N^{\bullet}$ $CH_2{=}NN$ (singlet)	65.42	63.88	65.68	64.15	—[a]
$^{\bullet}CH_2N{=}N^{\bullet}$ $CH_2{=}NN$ (triplet)	100.41	98.80	102.34	100.76	—
$CHN{=}NH$ (triplet)	137.11	135.54	138.25	136.69	—
$^{\bullet}CH{=}NN^{\bullet}H$ (triplet)	132.35	130.78	133.59	132.05	—
$C{=}NNH_2$ (singlet)	79.43	78.02	78.85	77.47	—

[a]— = no experimental data.



a) Diaziridine **b) 3H-diazirine** **c) 1H-diazirine**

Fig. 1 Three-membered rings.

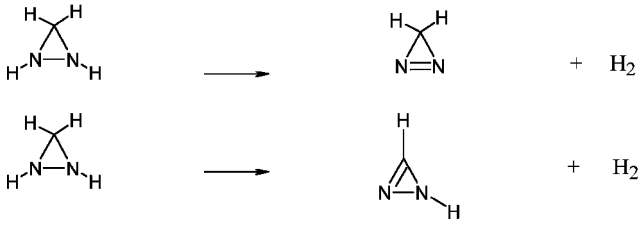


Fig. 2 Elimination reactions.

Fig. 3 Diaziridine radicals.

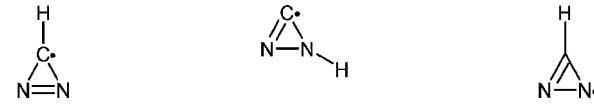


Fig. 4 Diazirinyl radicals.

	CBS-Q (0 K)	CBS-Q (298.15 K)	G2 (0 K)	G2 (298 K)	Exp (298 K)
(singlet)	66.46	62.64	64.47	60.67	-
(singlet)	77.99	76.11	75.96	74.10	79.3±2.3[a] 61.7-66[b]
(singlet)	97.85	96.06	96.14	94.36	-
(doublet)	119.42	116.62	118.47	115.88	-
(doublet)	94.57	91.76	94.03	91.23	-
(doublet)	136.07	135.16	134.68	133.77	-
(doublet)	148.05	147.30	147.73	147.00	-
(doublet)	116.73	115.89	117.02	116.20	-

Fig. 5 Computed enthalpies of formation at 0 K and at 298.15 K and 1 bar for species resulting from the cyclization of $^{\bullet}CH_2NHN^{\bullet}H$: ——, no experimental data; a, Ref. 33; and b, Ref. 34. Units used are kcal mol^{-1}.

diazirines as the biradical $C^{\bullet}H_2NHN^{\bullet}H$ forms in one step. However, once the diaziridine forms, this species can lead to the diazirines through the elimination reactions of Fig. 2. Diaziridine can also form, through simple C—H or N—H bond breaking, two diaziridinyl radicals (see Fig. 3). It can also decompose through N—N or C—N bond breaking to give NNC or NCN acyclic species.

Diazirines can form, through simple C—H or N—H bond breaking, three diazirinyl radicals (see Fig. 4). Or decompose through N—N or C—N bond breaking to give acyclic species.

No experimental data have been found in the literature for diaziridine. Nielsen[32] obtained a value of 55.8 kcal mol^{-1} for the heat of formation at 298.15 K using ab initio calculations. If one considers that the accuracy of both Nielsen's calculations and ours is ±2 kcal mol^{-1}, then Nielsen's result (56 ± 2) and ours (60 ± 2) are consistent (see Fig. 5).

Paulett and Ettinger[33] obtained experimentally a heat of formation of 3H diazirine of 79.3 ± 2.3 kcal mol^{-1}, whereas Laufer

and Okabe[34] obtained an enthalpy of formation between 61.7 and 66 kcal mol^{-1}. Our result is consistent with the value of Paulett and Ettinger.

To our knowledge no experimental data for the heat of formation of the diaziridinyl and diazirinyl radicals are available in the literature. Ab initio calculations using the CBS-Q method, one of the methods also used here, have been formed by Clifford et al.[35] Their results are exactly the same as ours.

Bimolecular Reactions

$$MMH + X \rightarrow C^{\bullet}H_2NHNH_2 + Y$$

$$MMH + X \rightarrow CH_3N^{\bullet}NH_2 + Y$$

$$MMH + X \rightarrow CH_3NHN^{\bullet}H + Y$$

for which no other species than those already studied are concerned.

Other reactions to be considered are

$$CH_3N{=}NH + X \rightarrow C^{\bullet}H_2N{=}NH + Y$$

$$CH_3N{=}NH + X \rightarrow CH_3NN^{\bullet} + Y$$

$$CH_2{=}NNH_2 + X \rightarrow {}^{\bullet}CH{=}NNH_2 + Y$$

$$CH_2{=}NNH_2 + X \rightarrow CH_2{=}NN^{\bullet}H + Y$$

$$CH_2{=}NH + X \rightarrow C^{\bullet}H{=}NH + Y$$

$$CH_2{=}NH + X \rightarrow CH_2{=}N^{\bullet} + Y$$

where X = H, NH_2, CH_3, N_2H_3, for instance, and Y the corresponding products H_2, NH_3, CH_4, and N_2H_4, respectively. Many more chain-propagating bimolecular reactions can further be written. However, the species set just given, together with other species available in the open literature, is expected to be sufficiently exhaustive to allow the writing of all of the potentially important bimolecular reactions.

Chain-Terminating Reactions

A huge number of homogeneous gas-phase reactions are, in principle, relevant to this subsection. The whole list cannot be given here. Radical-radical chain-terminating reactions can eventually lead to the formation of high molecular weight products. Some radicals, formed by different reaction pathways, are resonant structures, as shown in Fig. 6. From a mechanistic point of view, such resonantly stabilized free radicals are less reactive than ordinary radicals, as a result of the delocalization of the unpaired electron, and they can therefore reach comparatively high concentrations. These concentrations, together with rapid recombination kinetics, make possible reactions between resonant structures to form species with high molecular weight species.

Neither of these two cases appears to be of major significance during the homogeneous gas-phase thermal decomposition of MMH, as the major products are essentially CH_4, H_2, HCN, NH_3, and C_2H_6. However, high molecular weight species usually form in small amounts, and, even if not reported, these formations are likely.

Catalytic (Heterogeneous) Decomposition of MMH

All of the reactions and species given in the MMH Homogeneous Gas-Phase Thermal Decomposition subsection are also relevant to the Catalytic Decomposition subsection. However, some species have to be added because of the existence of heterogeneous reaction pathways. For MMH surface-catalyzed decomposition on titanium,

$CH_2{=}NN^{\bullet}H \longleftrightarrow C^{\bullet}H_2N{=}NH$

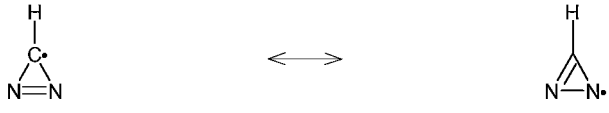


Fig. 6 Radicals that are resonant structures.

Table 5 Computed enthalpies of formation at 0 and 298.15 K and 1 bar for species observed during the surface-catalyzed decomposition of MMH (Units are kcal mol^{-1})

Species	CBS-Q (0 K)	CBS-Q (298.15 K)	G2 (0 K)	G2 (298 K)	Exp (298 K)
$CH_3N{=}NCH_3$ (singlet)	43.30	38.49	41.17	36.41	35.6[a]
$C^{\bullet}H_2N{=}NCH_3$ (doublet)	78.24	73.92	78.83	74.56	—[b]
$C_2H_5N{=}NCH_3$ (singlet)	38.52	32.24	36.35	30.12	27.2[c]
$CH_3N(H)N{=}CH_2$ (singlet)	46.51	41.57	44.84	39.94	—

[a]Ref. 36. [b]— = no experimental data. [c]Ref. 37.

Davis and Wedlich[7] observed nitrogen, ammonia, methylamine, methane, and ethane as major products, but also dimethylamine, dimethyldiazene, and traces of nine other compounds. Among these nine compounds, the authors consider the formation of ethylmethyldiazene $C_2H_5N{=}NCH_3$. Data can be found in the literature for methylamine and dimethylamine, and no computational work is needed for these species. On the other hand, ab initio calculations are of interest for dimethyldiazene, ethylmethyldiazene, and also the dimethyldiazenylradical following the chemical kinetic scheme given by Davis and Wedlich.[7]

Lee and Stringfellow[8] studied the pyrolysis of MMH on a SiO_2 surface in the 573–973 K temperature range. The major decomposition products they found were methane, nitrogen, ammonia, hydrogen, and traces of monomethylamine, hydrogen cyanide, methanimine, methyldiazene, and $CH_3N(H)N{=}CH_2$. Therefore, thermodata for this last species have been computed (see Table 5).

For dimethyldiazene, also called azomethane, an experimental value of 35.6 kcal mol^{-1} is reported by Pamidimukkala et al.[36] For ethylmethyldiazene $C_2H_5N{=}NCH_3$ an experimental value of 27.2 kcal mol^{-1} is given by Rossini.[37] This value is consistent with our calculations (see Table 5).

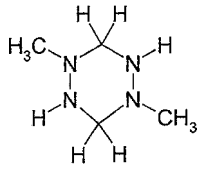
Gas-Phase One-Step and Two-Steps Oxidation of MMH (by O_2)

All of the species from the homogeneous gas-phase thermal decomposition set are also relevant to the high-temperature oxidation of MMH. They are, however, much more important for the two-step oxidation of MMH because the first step consists of an oxidative pyrolysis of MMH, that is, O_2 induces the decomposition. No other H/C/N species are expected to form in the two-step oxidation regime. For the one-step oxidation regimes[18] some other species C/H/N/O are likely, such as peroxides, but these species are beyond the scope of the present study. Some new H/C/N species are also expected in the low-temperature oxidation of MMH, as described in the following subsection.

Low-Temperature Gas-Phase Oxidation of MMH by Oxygen

Molinet et al.[38] performed an exprimental study of the oxidation of gaseous MMH by oxygen at 323 K. They propose a reaction scheme to explain the formation of the products and some of the intermediates they observed. The intermediates of interest to model the low-temperature oxidation of MMH are $CH_3N{=}NN{=}NH$, $CH_3N(H)N{=}NN(H)CH_3$, and $CH_3N{=}NN(H)N{=}CH_2$. These species can also form at higher temperature as they form from $CH_3N{=}NH$, which is supposed to be an intermediate at high temperature for both the thermal decomposition and the oxidation. They can play a role in terms of ignition at low temperature and also at high temperature. Therefore, thermodynamic data are needed for these species (see Table 6). No experimental or theoretical data have been found in the literature for these species. Concerning the products, together with CH_4, N_2, O_2, CH_3OH, and H_2O, some six-membered heterocyclic species have been observed as, for instance, 1,4-dimethylperhydrotetrazine (see Fig. 7). These compounds can also form at higher temperature in small amounts. The likelihood of these species being important, compared to the computational expense of studying such large species, does not justify their detailed consideration here. However, for completeness the one cyclic species just shown has been introduced in the computations (see Table 6). Two acyclic products have been observed: $CH_3N(H)N{=}CH_2$ and $CH_2{=}NN{=}NCH_3$ for

Table 6 Computed enthalpies of formation at 0 and 298.15 K and 1 bar for species observed during the low-temperature MMH oxidation by oxygen (Units are kcal mol^{-1})

Species	CBS-Q (0 K)	CBS-Q (298.15 K)	G2 (0 K)	G2 (298 K)	Exp
$CH_3N{=}NN{=}NH$ (singlet)	109.48	105.09	107.55	103.20	—[a]
$CH_3N(H)N{=}NN(H)CH_3$ (singlet)	79.51	71.96	78.03	70.56	—
$CH_3N{=}NN(H)N{=}CH_2$ (singlet)	105.85	99.94	104.47	98.62	—
$CH_2{=}NN{=}NCH_3$ (singlet)	86.00	81.48	87.49	79.77	—
 (singlet)	76.01	64.27	——[b]	——	—

[a] — = no experimental data. [b] —— = too computationally expensive at this level.

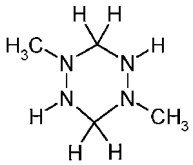


Fig. 7 1,4-dimethyl perhydrotetrazine.

which thermodynamic data are needed to complete the low-temperature oxidation chemistry of MMH by oxygen (see Table 6). Note that the species $CH_3N(H)N{=}CH_2$ is also produced during the catalytic decomposition of MMH (see the Catalytic Decomposition subsection).

Hypergolic MMH/NTO Reaction

This bipropellant combination is the one widely used for the thrusters onboard satellites. The two gases ignite spontaneously upon contact at low temperature[39] (about 298 K or lower). Gas-phase reactions have been shown to be important for ignition when hydrazine and NTO come into contact in the liquid state.[40] The same probably holds for liquid MMH and liquid NTO. The gas-phase initiation reactions in that case are

$$CH_3NHNH_2 + NO_2 \rightarrow C^{\bullet}H_2NHNH_2 + HONO$$

$$CH_3NHNH_2 + NO_2 \rightarrow CH_3N^{\bullet}NH_2 + HONO$$

$$CH_3NHNH_2 + NO_2 \rightarrow CH_3NHNH^{\bullet} + HONO$$

No H/C/N species other than the ones given in the preceding subsections appear to be needed to model this chemistry. This is not the case for the corresponding H/C/N/O chemistry because at low temperature nitrate, nitro, nitrito, nitroso, and also azido compounds can form.

Tropospheric Oxidation

As explained in the Introduction, the fate of gaseous MMH released in the troposphere has also been studied.[3–5] The atmospheric oxidation of monomethylhydrazine in the troposphere is probably initiated by reactions with OH radicals, as reaction with hydroxyl radicals is the most important atmospheric sink process for most chemical species with available H atoms:

$$CH_3NHNH_2 + OH \rightarrow C^{\bullet}H_2NHNH_2 + H_2O$$

$$CH_3NHNH_2 + OH \rightarrow CH_3N^{\bullet}NH_2 + H_2O$$

$$CH_3NHNH_2 + OH \rightarrow CH_3NHNH^{\bullet} + H_2O$$

Under atmospheric conditions the three methylhydrazyl radicals initially produced then react with molecular oxygen to give peroxy radicals. These oxygenated species are beyond the scope of the present study, which focuses exclusively on the H/C/N species.

Table 7 Computed enthalpies of formation at 0 and 298.15 K and 1 bar for ions formed at low-Earth orbital altitude (Units are kcal mol^{-1})

Species	CBS-Q (0 K)	CBS-Q (298.15 K)	G2 (0 K)	G2 (298 K)	Exp
(doublet) $CH_3NHNH_2^+$	204.74	199.94	204.94	200.15	222[a] 207[b]
(singlet) $N_2H_3^+$	232.84	230.14	231.40	228.71	230[a,c,d]
(singlet) CH_3NH^+	183.02	180.16	181.86	179.01	178[e,f]

[a]Ref. 26. [b]Ref. 43. [c]Ref. 44. [d]Ref. 45. [e]Ref. 46. [f]Ref. 47.

Stone[3] also studied the fate of MMH in the presence of ozone. The products observed and the chemical kinetic scheme proposed to explain the formations of the products do not need complementary thermochemistry for H/C/N species. Note that surface reactions are also likely for this chemistry as the MMH/O_2 gas-phase reactions at room temperature can be surface catalyzed.[41,42]

Low-Earth Orbital Altitude Oxidation of MMH

The interest concerning this chemistry has been addressed in the Introduction. Although the ion density is much lower than the neutral species density at 250-km altitude, the ionic reactions between MMH and atmospheric species have been identified as significant. At this altitude 98% of the ions are O^+, and the initiation reaction is[6]

$$CH_3NHNH_2 + O^+ \rightarrow CH_3NHNH_2^+ + O$$

The process will continue through the fragmentation of the methylhydrazine ion, which is briefly discussed by Gardner et al.[6] These authors found that the C—N or N—N bond breaking is preferred over the C—H and N—H bond breaking. Consequently, the ionic species $N_2H_3^+$ and CH_3NH^+ are of interest for this chemistry (see Table 7).

Two experimental values for the enthalpy of formation of MMH ion, 207 (Ref. 43) and 222 kcal mol^{-1} (Ref. 26), are reported in the literature. Our value of 200 kcal mol^{-1} is roughly consistent with these (see Table 7). For the N_2H_3 ion eight experimental values, ranging from 208–243 kcal mol^{-1}, are reported, with three of them around 230 kcal mol^{-1}.[26,44,45] Our calculations are consistent with these experimental results (see Table 7). Chupka[46] reports a value of 178 kcal mol^{-1} for the enthalpy of formation of CH_4N^+ without specifying the exact nature of CH_4N^+ (CH_3NH^+ or $CH_2NH_2^+$). Rosenstock et al.[47] consider this experimental value to apply to the CH_2NH_2 ion. However, this experimental value is also consistent with our calculations for CH_3NH^+.

Vibrational Frequencies

Scaled B3LYP/6-31G(d) vibrational frequencies, from which heat capacities can be derived, are given in the Table 8. The scaling factor is 0.9613, as recommended by Wong[48] for frequencies calculated at the B3LYP/6-31G(d) level. The agreement between experimental data and ab initio computations of vibrational frequencies and bond lengths at this level of theory has been shown to be good for a wide range of molecules.[49,50] Scott and Radom report that one of the most successful procedures for obtaining fundamental vibrational frequencies is to use scaled frequencies computed at the B3LYP/6-31G(d) level of theory as done here. Ma et al.[51] also observed good agreement between experiments and ab initio calculations for the structures and vibrational frequencies of hydrazines. Bond lengths in the molecules given next are not reported here, but can be obtained from the authors upon request. In Table 8 the computed frequencies are given and compared to the experimental frequencies (in parenthesis), when available.

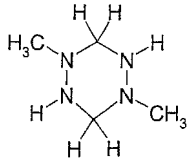
Good agreement between experiment and theory is clearly shown here for such an elusive species as methyldiazene ($CH_3N{=}NH$) (Ref. 52). With MMH itself good agreement is obtained between theory and experiment,[53] except for one of the 21 vibrational frequencies of the molecule. This needs to be studied further, but is beyond the scope of the present paper. Murase et al.[54] pointed out that the experimental assigment of one of the N-N-H bending modes is questionable. For $CH_3N{=}NCH_3$ the agreement is also reasonably good between experiment and theory, except for one of the 24 vibrational frequencies of the molecule.[55] Concerning the singlet state of

Table 8 Computed and experimental (if any) vibration frequencies (in cm^{-1}) and computed moments of inertia (in amu $bohr^2$) for the species under consideration in this study (Frequencies given in parenthesis are experimental values)

Species	Spin state	Vibrational frequencies, cm^{-1}	Moments of inertia, amu $bohr^2$
MMH[a]	Singlet	252(257) 278(315) 432(425) 778(777) 925(888) 950(968) 1109(1108) 1139(1118) 1181(1210) 1289(1282) 1413(?) 1449(1449) 1455(1465) 1488(1479) 1638(1597) 2846(2784) 2965(2951) 3019(2967) 3244(3314) 3271(3358) 3401(3366)	47 188 212
CH_2NHNH_2	Doublet	278 368 445 679 752 886 991 1144 1213 1301 1411 1463 1635 3035 3147 3261 3293 3410	38 177 202
CH_3NHNH	Doublet	175 400 507 648 953 1095 1105 1249 1356 1414 1450 1476 1498 2901 2986 3032 3248 3321	38 177 202
CH_3NNH_2	Doublet	155 429 462 712 929 1031 1073 1241 1288 1397 1449 1453 1618 2833 2892 3013 3246 3450	39 173 199
CH_2NHNH	Singlet	425 525 604 711 936 1033 1197 1346 1415 1450 1666 3098 3214 3250 3314	26 162 188
CH_2NHNH	Triplet	259 396 495 550 648 995 1097 1153 1340 1412 1478 3025 3166 3220 3358	36 162 188
$CH_3N{=}NH$[b]	Singlet	199(170) 535(557) 831(844) 898(920) 1114(1120) 1136(1140) 1375(1382) 1440(1430) 1441(1435) 1463(1457) 1604(1559) 2923(2925) 3000(2988) 3011(2992) 3109(3127)	30 163 182
$CH_2{=}NNH_2$	Singlet	413 500 684 770 893 1042 1151 1287 1443 1625 1652 2935 3099 3285 3467	28 158 184
NNH_2	Triplet	776 1068 1172 1552 3229 3334	6.1 54 58
$NHNH_2$	Doublet	623 712 1118 1190 1455 1629 3245 3307 3460	9.0 59 67
CH_3N	Triplet	940 940 1020 1355 1399 1399 2842 2900 2900	11 65 65
CH_3NH	Doublet	252 928 980 1011 1310 1369 1452 1457 2852 2888 2994 3219	15 71 75
$CH_2{=}N$	Doublet	914 951 1353 1670 2885 2935	6.3 46 53
$CH_2{=}NN$	Triplet	443 450 773 1046 1096 1354 1482 3016 3158	19 140 159
$CH_2{=}NNH$	Doublet	255 536 559 876 1044 1145 1207 1443 1478 2932 2948 3116	27 142 169
$CH_2{=}NN(H)CH_3$	Singlet	169 194 328 517 668 760 878 923 1110 1122 1134 1228 1406 1426 1459 1471 1496 1628 2890 2936 2985 3031 3102 3280	49 388 416
$CH_2N{=}N$	Triplet	442 450 772 1047 1096 1354 1482 3016 3159	19 140 159
$CH_2N{=}N$[c]	Singlet	410(406) 410(421) 561(564) 1084(1109) 1182(1170) 1406(1414) 2138(2102) 3092(3077) 3204(3184)	6.5 160 166
$CH_2N{=}NCH_3$	Doublet	69 94 349 567 579 876 880 1012 1077 1112 1167 1299 1380 1436 1442 1478 2903 2955 2996 2998 3127	40 373 402
$CH_3CH_2N{=}NCH_3$	Singlet	81 181 208 213 340 444 554 787 870 935 1005 1027 1089 1122 1178 1246 1321 1375 1379 1443 1444 1450 1463 1477 1611 2921 2923 2940 2969 2996 3008 3009 3013	97 741 769
$CH_3N{=}NN{=}CH_2$	Singlet	57 201 252 284 508 558 751 894 992 1027 1067 1137 1174 1380 1405 1442 1445 1585 1648 2925 2978 2999 3010 3096	53 677 719
$CH_3N{=}N{-}N{=}NH$	Singlet	81 202 246 284 426 580 811 983 989 1074 1138 1378 1406 1439 1444 1602 1646 2932 2984 3009 3021	51 686 726
$CH_3N{=}NNHN{=}CH_2$	Singlet	19 161 183 225 343 383 515 520 630 739 887 984 1061 1079 1139 1161 1235 1392 1395 1446 1453 1476 1555 1628 2920 2960 2984 3001 3118 3255	59 1191 1239
CH_3NH+		900 934 1034 1120 1303 1409 1549 1718 3059 3172 3343 3433	12 58 70
CH_3NHN	Triplet	192 383 650 937 1086 1095 1206 1363 1414 1453 1477 2915 3000 3037 3273	37 166 189
$CH_3NHN{=}NNHCH_3$	Singlet	83 150 176 185 210 369 370 524 537 752 756 945 1005 1104 1107 1119 1138 1181 1256 1407 1416 1428 1453 1459 1461 1484 1489 1541 2892 2893 2988 2988 3030 3030 3315 3317	86 1251 1294

(**Continued**)

Table 8 Computed and experimental (if any) vibration frequencies (in cm^{-1}) and computed moments of inertia (in amu $bohr^2$) for the species under consideration in this study (Frequencies given in parenthesis are experimental values) Continued

Species	Spin state	Vibrational frequencies, cm^{-1}	Moments of inertia, amu $bohr^2$
$CH_3N{=}N$	Doublet	153 441 726 1013 1058 1352 1441 1444 1835 2950 3047 3048	25 162 176
$CH{=}NNH$	Triplet	406 470 758 936 1151 1295 1476 2995 3204	13 151 164
$CH{=}NNH_2$	Doublet	349 455 627 764 974 1102 1281 1617 1723 3018 3307 3451	18 161 177
$CHNHNH_2$	Singlet	283 534 627 879 981 1112 1200 1314 1392 1517 1626 2850 3256 3274 3373	30 164 188
cyc-$CH_2N{=}N$	Singlet	816 957 976 1026 1115 1463 1674 3032 3139	44 76 107
cyc-$CH_2N{=}N$ radical	Doublet	629 910 1032 1086 1588 3013	41 61 98.5
cyc-CH2NHNH diaziridine	Singlet	722 810 914 943 1118 1144 1149 1203 1306 1350 1499 2991 3083 3236 3271	76 77 129
rad diaziridine (H abstraction from C)	Doublet	684 780 826 901 1084 1084 1196 1307 1307 3016 3187 3210	61 76 122
rad diaziridine (H abstraction from N)	Doublet	735 856 935 978 1053 1086 1182 1273 1486 2988 3075 3278	61 75 118
cyc-$NHN{=}CH$	Singlet	532 774 941 1005 1148 1319 1735 3109 3205	45 81 120
cyc-$NHN{=}CH$ rad (H abstraction on C from cyc-$NHN{=}CH$)	Doublet	514 795 997 1008 1420 3314	44 59 100
cyc-$NHN{=}CH$ rad (H abstraction on N from cyc-$NHN{=}CH$)	Doublet	690 829 881 1159 1579 3116	44 63 106
Ion MMH	Doublet	124 337 423 508 589 901 1063 1082 1249 1359 1416 1436 1446 1514 1622 2945 3028 3071 3380 3417 3502	40 191 218
$N_2H_3^+$	Singlet	1030 1163 1214 1436 1583 1715 3183 3222 3312	8.6 51 60
	Singlet	115 224 235 244 278 321 369 401 411 484 521 645 759 776 877 904 964 1024 1029 1050 1069 1093 1117 1125 1156 1169 1213 1220 1262 1286 1345 1371 1409 1411 1433 1439 1448 1451 1457 1475 1476 1483 2746 2823 2878 2908 2961 2969 2976 2987 3003 3030 3145 3308	379 1217 1497
$C{=}NNH_2$	Singlet	259 338 854 1038 1312 1629 2138 3324 3417	6.4 169 172
$CH_3N{=}NCH_3$ [d]	Singlet	160(222) 220(223) 280(312) 338(352) 572(589) 895(916) 982(1009) 1007(1010) 1104(?) 1109(1109) 1174(1176) 1375(1380) 1378(1393) 1442(1434) 1443(1438) 1444(1445) 1448(1447) 1616(1580) 2922(2916) 2923(2926) 2996(2966) 2996(2977) 3009(2982) 3009(2982)	43 408 428
CH_3NHN	Singlet	143 524 738 806 1076 1106 1350 1438 1446 1501 1624 2758 2936 3011 3073	31 170 190
$CHNHNH_2$	Triplet	239 381 476 635 871 1036 1112 1222 1267 1390 1642 2957 3276 3374 3395	36 167 188
NNH_2	Singlet	950 1288 1574 1711 2805 2875	5.4 47 52
$CH_2N{=}NH$	Doublet	382 442 755 882 1090 1133 1246 1454 1606 2995 3119 3226	19 158 174
$CHN{=}NH$	Triplet	279 424 723 935 980 1301 1636 2949 3199	18 144 160

[a]Ref. 53. [b]Ref. 52. [c]Ref. 56. [d]Ref. 55.

diazomethane, good agreement is obtained between experimental data[56] and the calculations performed here.

Summary and Conclusions

Gas-phase thermochemical properties of more than 50 C/H/N species expected to play a role in the chemistry of monomethylhydrazine under various conditions have been computed and presented here. These were obtained from high-level ab initio quantum chemistry calculations. Groups of them have been discussed in terms of the conditions under which they are expected to be of potential importance. Where comparisons with previous experimental and theoretical work are possible, the agreement ranges from satisfactory to excellent. The results summarized here can therefore be used as a starting point for the construction of detailed chemical kinetic models of the combustion, pyrolysis, and atmospheric chemistry of monomethylhydrazine and related species. The next steps in the development of such a model will be to investigate, theoretically and experimentally when possible, the kinetics of those elementary reactions that are, on thermodynamic grounds, most favorable and therefore most likely to be of importance.

Appendix: Thermodata in the CHEMKIN Format

The thermochemical data described in the main text are summarized here in the format of the CHEMKIN Thermodynamic Database[57] and also of the Thermodynamic Database of Burcat.[12] Data can be obtained for MMH and for few of the species studied here in the Tables of Burcat. Data available on-line at ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics. Both the ab initio calculations and the subsequent thermochemical calculations (to get the heat capacity, etc.) were carried out using the GAUSSIAN94 (Ref. 58) and GAUSSIAN98 (Ref. 59) computational chemistry programs.

CH2NHNH2 C 1N 2H 5 G 300.000 4000.000 1000.00 1
0.51875187E+01 0.16424971E−01 −0.69575960E−05 0.14001429E−08 −0.10887917E−12 2
0.30737385E+05 −0.21029307E+01 0.34843171E+00 0.33316585E−01 −0.30349002E−04 3
0.16864462E−07 −0.42343190E−11 0.31886809E+05 0.22004974E+02 4

CH3NHNH C 1N 2H 5 G 300.000 4000.000 1000.00 1
0.41468561E+01 0.18084142E−01 −0.78773524E−05 0.16193939E−08 −0.12800410E−12 2
0.24264569E+05 0.35029786E+01 0.15068302E+01 0.23155589E−01 −0.92753760E−05 3
−0.23879616E−09 0.69678850E−12 0.25134468E+05 0.17780395E+02 4

CH3NNH2 C 1N 2H 5 G 300.000 4000.000 1000.00 1
0.42736067E+01 0.17954702E−01 −0.78218163E−05 0.16081979E−08 −0.12713411E−12 2
0.23218478E+05 0.28943714E+01 0.12921131E+01 0.24749760E−01 −0.12520872E−04 3
0.25471106E−08 −0.18055516E−12 0.24144750E+05 0.18744654E+02 4

CH2NHNHs C 1N 2H 4 G 300.000 4000.000 1000.00 1
0.46045514E+01 0.14294422E−01 −0.61347753E−05 0.12472869E−08 −0.97773395E−13 2
0.29239960E+05 −0.13539277E+00 0.20858615E+00 0.29142750E−01 −0.26254946E−04 3
0.14526506E−07 −0.37091840E−11 0.30320962E+05 0.21919063E+02 4

CH3N═NH C 1N 2H 4 G 300.000 4000.000 1000.00 1
0.34916582E+01 0.16145884E−01 −0.71757708E−05 0.14969867E−08 −0.11962001E−12 2
0.19040338E+05 0.61232288E+01 0.17230468E+01 0.17036262E−01 −0.14468384E−05 3
−0.55575662E−08 0.20842340E−11 0.19776984E+05 0.16386073E+02 4

CH2═NNH2 C 1N 2H 4 G 300.000 4000.000 1000.00 1
0.44681079E+01 0.14494729E−01 −0.62432884E−05 0.12729474E−08 −0.10000400E−12 2
0.18072510E+05 0.57547358E+00 0.18617631E+00 0.28852636E−01 −0.25765147E−04 3
0.14370670E−07 −0.37518436E−11 0.19138712E+05 0.22104084E+02 4

CHNHNH2s C 1N 2H 4 G 300.000 4000.000 1000.00 1
0.43591516E+01 0.14681863E−01 −0.63527774E−05 0.13001718E−08 −0.10246094E−12 2
0.37602863E+05 0.14188009E+01 0.84383599E+00 0.24372035E−01 −0.16110585E−04 3
0.58065333E−08 −0.10258712E−11 0.38583787E+05 0.19619205E+02 4

CH3NHNs C 1N 2H 4 G 300.000 4000.000 1000.00 1
0.37096282E+01 0.16017633E−01 −0.71478120E−05 0.14952147E−08 −0.11970090E−12 2
0.30946729E+05 0.54383507E+01 0.18501517E+01 0.18078637E−01 −0.47560553E−05 3
−0.20334060E−08 0.81563515E−12 0.31673539E+05 0.15968649E+02 4

CH2N═NH C 1N 2H 3 G 300.000 4000.000 1000.00 1
0.45782144E+01 0.10220151E−01 −0.43487706E−05 0.87903262E−09 −0.68632421E−13 2
0.38492350E+05 0.13875690E+01 0.90678797E+00 0.22189618E−01 −0.19302648E−04 3
0.95640926E−08 −0.20978554E−11 0.39398248E+05 0.19868642E+02 4

CH3N═N C 1N 2H 3 G 300.000 4000.000 1000.00 1
0.41265016E+01 0.12326552E−01 −0.54640739E−05 0.11373571E−08 −0.90714279E−13 2
0.26694928E+05 0.46864663E+01 0.27283611E+01 0.14276429E−01 −0.48421308E−05 3
−0.36359771E−09 0.23656104E−12 0.27220600E+05 0.12502130E+02 4

CH═NNH2 C 1N 2H 3 G 300.000 4000.000 1000.00 1
0.50711257E+01 0.10765209E−01 −0.45918622E−05 0.92923437E−09 −0.72578946E−13 2
0.44145857E+05 −0.10482432E+01 0.12871386E+01 0.24760649E−01 −0.25619889E−04 3
0.16134914E−07 −0.44616854E−11 0.45017867E+05 0.17637903E+02 4

CH2═NNH C 1N 2H 3 G 300.000 4000.000 1000.00 1
0.51340835E+01 0.11254805E−01 −0.49827301E−05 0.10364506E−08 −0.82633113E−13 2
0.40611175E+05 −0.13202465E+01 0.12995657E+01 0.24073095E−01 −0.22579157E−04 3
0.13112506E−07 −0.35460338E−11 0.41575690E+05 0.17988086E+02 4

CH2═N C 1N 1H 2 G 300.000 4000.000 1000.00 1
0.29474434E+01 0.73169537E−02 −0.32389157E−05 0.67314418E−09 −0.53610967E−13 2
0.27863434E+05 0.79458697E+01 0.26244283E+01 0.66932556E−02 −0.38484145E−06 3
−0.18718493E−08 0.58402160E−12 0.28055662E+05 0.10062763E+02 4

CHN═NH C 1N 2H 2 G 300.000 4000.000 1000.00 1
0.55300370E+01 0.76638738E−02 −0.33694983E−05 0.69732668E−09 −0.55385319E−13 2
0.66636183E+05 −0.24073262E+01 0.19582973E+01 0.21064437E−01 −0.23898133E−04 3
0.15839865E−07 −0.44981123E−11 0.67453431E+05 0.15192301E+02 4

CH═NNH C 1N 2H 2 G 300.000 4000.000 1000.00 1
0.53828909E+01 0.78530409E−02 −0.34683638E−05 0.72062017E−09 −0.57425676E−13 2
0.64302844E+05 −0.22465637E+01 0.13866403E+01 0.22206439E−01 −0.24303717E−04 3
0.15316134E−07 −0.41747339E−11 0.65242097E+05 0.17586992E+02 4

C═NNH2 C 1N 2H 2 G 300.000 4000.000 1000.00 1
0.44592598*E*+01 0.83729080*E*−02 −0.35570552*E*−05 0.71745452*E*−09 −0.55889262*E*−13 2
0.37220264*E*+05 0.23249767*E*+01 0.34849816*E*+01 0.10862882*E*−01 −0.60960585*E*−05 3
0.22226530*E*−08 −0.53777989*E*−12 0.37515969*E*+05 0.74533199*E*+01 4

diaziridine C 1N 2H 4 G 300.000 4000.000 1000.00 1
0.37550184*E*+01 0.15633216*E*−01 −0.68848287*E*−05 0.14284659*E*−08 −0.11377099*E*−12 2
0.28364998*E*+05 0.32316028*E*+01 −0.13109010*E*+01 0.28988035*E*−01 −0.18470409*E*−04 3
0.47988483*E*−08 −0.18747231*E*−12 0.29787513*E*+05 0.29558671*E*+02 4

3H-diazirine C 1N 2H 2 G 300.000 4000.000 1000.00 1
0.39518117*E*+01 0.95930432*E*−02 −0.43276727*E*−05 0.91364253*E*−09 −0.73698177*E*−13 2
0.35437312*E*+05 0.27593121*E*+01 0.69045895*E*+00 0.17937202*E*−01 −0.11562601*E*−04 3
0.33964330*E*−08 −0.40436678*E*−12 0.36383664*E*+05 0.19816314*E*+02 4

1H-diazirine C 1N 2H 2 G 300.000 4000.000 1000.00 1
0.45529445*E*+01 0.87572696*E*−02 −0.38862485*E*−05 0.81060029*E*−09 −0.64799166*E*−13 2
0.45521386*E*+05 0.69905435*E*+00 0.78164048*E*+00 0.21028919*E*−01 −0.19827574*E*−04 3
0.10963517*E*−07 −0.27767368*E*−11 0.46474799*E*+05 0.19742991*E*+02 4

diaziridine rad (H abst. from C) C 1N 2H 3 G 300.000 4000.000 1000.00 1
0.48218157*E*+01 0.11465236*E*−01 −0.50492975*E*−05 0.10474869*E*−08 −0.83408203*E*−13 2
0.56049829*E*+05 −0.10047425*E*+01 −0.12431761*E*+01 0.31943957*E*−01 −0.32085723*E*−04 3
0.17944141*E*−07 −0.43573666*E*−11 0.57518230*E*+05 0.29366500*E*+02 4

diaziridine rad (H abst. from N) C 1N 2H 3 G 300.000 4000.000 1000.00 1
0.43824780*E*+01 0.12036385*E*−01 −0.53410383*E*−05 0.11142556*E*−08 −0.89099845*E*−13 2
0.43746016*E*+05 0.11981958*E*+01 −0.98428337*E*+00 0.28538705*E*−01 −0.24582380*E*−04 3
0.11557024*E*−07 −0.24260851*E*−11 0.45132103*E*+05 0.28492144*E*+02 4

3H-diazirine rad C 1N 2H 1 G 300.000 4000.000 1000.00 1
0.47706474*E*+01 0.57220686*E*−02 −0.26388901*E*−05 0.56579866*E*−09 −0.46146500*E*−13 2
0.65432561*E*+05 0.52603884*E*+00 0.13842395*E*+01 0.16534598*E*−01 −0.16422667*E*−04 3
0.92413979*E*−08 −0.23640895*E*−11 0.66301986*E*+05 0.17685495*E*+02 4

1H-diazirine rad (H abst. from C) C 1N 2H 1 G 300.000 4000.000 1000.00 1
0.53482098*E*+01 0.48593592*E*−02 −0.21741228*E*−05 0.45683681*E*−09 −0.36747348*E*−13 2
0.71960113*E*+05 −0.23306409*E*+01 0.12334289*E*+01 0.19497758*E*−01 −0.22804177*E*−04 3
0.14260872*E*−07 −0.37343467*E*−11 0.72920891*E*+05 0.18092942*E*+02 4

1H-diazirine rad (H abst. from N) C 1N 2H 1 G 300.000 4000.000 1000.00 1
0.49132153*E*+01 0.54840666*E*−02 −0.25048062*E*−05 0.53364374*E*−09 −0.43338777*E*−13 2
0.56560662*E*+05 −0.12897884*E*+00 0.11766413*E*+01 0.18286533*E*−01 −0.20157562*E*−04 3
0.12378052*E*−07 −0.33008836*E*−11 0.57470662*E*+05 0.18572521*E*+02 4

CH3N═NCH3 C 2N 2H 6 G 300.000 4000.000 1000.00 1
0.49863152*E*+01 0.24070809*E*−01 −0.10732555*E*−04 0.22441162*E*−08 −0.17961655*E*−12 2
0.15409582*E*+05 −0.15606158*E*+01 0.19013815*E*+01 0.27280859*E*−01 −0.53752194*E*−05 3
−0.57609693*E*−08 0.23430172*E*−11 0.16600457*E*+05 0.15898338*E*+02 4

CH2N═NCH3 C 2N 2H 5 G 300.000 4000.000 1000.00 1
0.62642367*E*+01 0.19534972*E*−01 −0.86934631*E*−05 0.18156270*E*−08 −0.14521541*E*−12 2
0.34411213*E*+05 −0.52185438*E*+01 0.82573312*E*+00 0.34930517*E*−01 −0.25594610*E*−04 3
0.11185299*E*−07 −0.25707822*E*−11 0.35928354*E*+05 0.22887504*E*+02 4

C2H5N═NCH3 C 3N 2H 8 G 300.000 4000.000 1000.00 1
0.62499041*E*+01 0.32218385*E*−01 −0.14385039*E*−04 0.30110632*E*−08 −0.24120641*E*−12 2
0.11342798*E*+05 −0.67423535*E*+01 0.93190193*E*+00 0.41582862*E*−01 −0.15623413*E*−04 3
−0.13336099*E*−08 0.12953660*E*−11 0.13170207*E*+05 0.22311896*E*+02 4

CH2═NN(H)CH3 C 2N 2H 6 G 300.000 4000.000 1000.00 1
0.52825928*E*+01 0.23484552*E*−01 −0.10385219*E*−04 0.21587953*E*−08 −0.17205364*E*−12 2
0.17106937*E*+05 −0.28016279*E*+01 0.53951358*E*+00 0.35025912*E*−01 −0.20188260*E*−04 3
0.61131122*E*−08 −0.11216110*E*−11 0.18548349*E*+05 0.22241846*E*+02 4

CH3N═NN═NH C 1N 4H 4 G 300.000 4000.000 1000.00 1
0.73128686*E*+01 0.18849976*E*−01 −0.85239567*E*−05 0.18011780*E*−08 −0.14531458*E*−12 2
0.48519937*E*+05 −0.10352630*E*+02 0.27214587*E*+01 0.29570046*E*−01 −0.17083375*E*−04 3
0.51254424*E*−08 −0.10388216*E*−11 0.49952086*E*+05 0.14038633*E*+02 4

CH3NHN═NNHCH3 C 2N 4H 8 G 300.000 4000.000 1000.00 1
0.83255167*E*+01 0.32942105*E*−01 −0.14641727*E*−04 0.30562089*E*−08 −0.24438820*E*−12 2
0.30967760*E*+05 −0.16284151*E*+02 0.14898205*E*+01 0.47559157*E*−01 −0.22708354*E*−04 3
0.26810908*E*−08 0.41600073*E*−12 0.33145508*E*+05 0.20311369*E*+02 4

CH3N=NNHN=CH2 C 2N 4H 6 G 300.000 4000.000 1000.00 1
0.90885363E+01 0.26171233E−01 −0.11716638E−04 0.24583174E−08 −0.19731530E−12 2
0.45196023E+05 −0.18435232E+02 0.12203887E+01 0.48450499E−01 −0.36639511E−04 3
0.16938855E−07 −0.41660985E−11 0.47405784E+05 0.22263527E+02 4

CH3N=NN=CH2 C 2N 3H 5 G 300.000 4000.000 1000.00 1
0.71927488E+01 0.21971505E−01 −0.98696977E−05 0.20755010E−08 −0.16684940E−12 2
0.36569879E+05 −0.10422126E+02 0.13345116E+01 0.37284783E−01 −0.24978672E−04 3
0.97865654E−08 −0.22239799E−11 0.38291462E+05 0.20230280E+02 4

1,4-dimethylperhydrotetrazine C 4N 4H 12 G 300.000 4000.000 1000.00 1
0.96259600E+01 0.51165067E−01 −0.23018112E−04 0.48466814E−08 −0.39003928E−12 2
0.26087270E+05 −0.28742650E+02 −0.45242715E+01 0.87099947E−01 −0.55636451E−04 3
0.18879645E−07 −0.35893125E−11 0.30274455E+05 0.45500139E+02 4

MMH+ C 1N 2H 6 G 300.000 4000.000 1000.00 1
0.44592197E+01 0.20118763E−01 −0.85421575E−05 0.17224238E−08 −0.13415937E−12 2
0.98311907E+05 0.23247376E+01 0.18850285E+01 0.25492196E−01 −0.10751026E−04 3
0.31662703E−09 0.68126440E−12 0.99124035E+05 0.16102365E+02 4

N2H3+ N 2H 3 G 300.000 4000.000 1000.00 1
0.17732245E+01 0.11134320E−01 −0.47744546E−05 0.97019892E−09 −0.76031122E−13 2
0.11402473E+06 0.13932221E+02 0.30166405E+01 0.11362769E−02 0.17669569E−04 3
−0.18897383E−07 0.61021543E−11 0.11403026E+06 0.91970198E+01 4

CH3NH+ C 1N 1H 4 G 300.000 4000.000 1000.00 1
0.20085263E+01 0.13692290E−01 −0.58105637E−05 0.11712988E−08 −0.91220093E−13 2
0.88772065E+05 0.11404167E+02 0.14491338E+01 0.11043496E−01 0.51549313E−05 3
−0.10575738E−07 0.38985084E−11 0.89139503E+05 0.15352607E+02 4

Acknowledgment

The computations upon which this work were based were partially supported by generous grants of supercomputer time from the State University of New York at Buffalo Center for Computational Research, for which we are grateful.

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