

Theoretical Study of the Nitroalkane Thermolysis. 1. Computation of the Formation Enthalpy of the Nitroalkanes, Their Isomers and Radical Products

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The gas phase enthalpies of formation of mono-, di-, tri-, tetranitromethane and nitroethane, as well as of their nitrite and aci-form isomers were calculated using different multilevel (G2, G3, G2M(CC5)) and density functional theory (DFT)-based (B3LYP, MPW1B95 and MPWB1K) techniques. The enthalpies of the C–N bond dissociation and isomerization of these nitroalkanes were also calculated. The calculated values of the formation and reaction enthalpies were compared with the experimental data when these data were available. It was found that only the G3 procedure gave accurate (within 1 kcal/mol) results for the formation enthalpy of nitroalkanes, their isomers, and radical products. The G3 procedure and two new hybrid meta DFT methods proposed by Truhlar's group (Zhao, Y.; Truhlar, D. *J. Phys. Chem. A* 2004, 108, 6908) showed good results for the reaction enthalpies of the nitromethane isomerization and the C–N bond dissociation. Our calculation results were used to analyze thermodynamics of the dissociation and isomerization reactions of the poly nitro-substituted methanes.

Introduction

Nitroalkanes, and nitrosubstituted methanes in particular, are of significant interest as the prototypes of high-energy materials. Nitromethane (**1**), which is the simplest nitroalkane, is widely used as a model substance for investigating propellant ignition, combustion phenomena, and atmospheric pollution.^{1–7} Its thermal gas phase decomposition has been intensively investigated in shock-tube^{8–11} and static reaction vessel^{12–14} experiments. The IR multiphoton dissociation (IR-MPD) of **1** in molecular beam has also been studied.^{15,16} Moreover, the thermal decomposition of **1** has been extensively investigated theoretically.^{17–22} Nevertheless, there are still open questions even for the nitromethane primary unimolecular reactions.^{18,20,21}

Trinitromethane (nitroform, **7**) appears as the intermediate in the hydrazine nitroformate decomposition, which is a promising chlorine-free oxidant for the solid rocket fuel.^{23–27} Thermodynamic characteristics of nitroform and intermediates of its decomposition as well as the rate constants of elementary reactions are crucial for modeling the complex process of the hydrazine nitroformate combustion.^{27,28}

Although the nitroalkanes have been studied extensively, there is still some disagreement among the existing experimental thermodynamic data, especially on the formation enthalpy of these species. The discrepancy exists even for the most extensively studied nitroalkane **1**. The enthalpy of **1** formation in the standard ($T = 298$ K, $p = 1$ atm) state ($\Delta_f H_{\text{liquid}}^0$) has been measured using static bomb calorimetry many times. Results of the early studies (-21.3^{29} and -22.8^{30} kcal/mol) were found unreliable,^{31,32} and these measurements were repeated in the seventies ($\Delta_f H_{\text{liquid}}^0 = -28.5^{32}$ and -26.9^{33} kcal/mol). In contrast to the enthalpy of formation, very consistent results were reported for the enthalpy of evaporation ($\Delta_{\text{vap}} H^0 = 9.1^{29}$ and $9.2^{32,34}$ kcal/mol). The gas phase formation enthalpy of **1**

($\Delta_f H_{\text{gas}}^0 = \Delta_f H_{\text{liquid}}^0 + \Delta_{\text{vap}} H^0$) has also been reported.^{29,30,32,34} At present two values of $\Delta_f H_{\text{gas}}^0$ are generally accepted for **1**. The first one (-19.3 kcal/mol) is based on the accurate measurement of $\Delta_f H_{\text{liquid}}^0$ by Knobel and Miroshnichenko (-28.5 kcal/mol)³² and listed in the NIST Chemistry webbook.³⁵ The second value (-17.8 kcal/mol)³⁴ is based on the unpublished result for $\Delta_f H_{\text{liquid}}^0$ (-27 kcal/mol) given in ref 34, and it was used in the G2³⁶ and subsequent G-family test sets.^{37–39} We also chose this value because it was supported by the latest measurements.³³

The value of $\Delta_f H_{\text{liquid}}^0$ for dinitromethane (**4**) has been measured with the static bomb calorimetry technique (-25.2 kcal/mol) and reported only in one paper.³² Authors have also obtained the gas phase formation enthalpy ($\Delta_f H_{\text{gas}}^0 = -14.1$ kcal/mol) by combining their experimental result for the liquid **4** and the $\Delta_{\text{vap}} H^0$ estimated from the empirical correlation formula.

The melting point of trinitromethane (**7**) is close to 25 °C, but the data are inconsistent ($T_{\text{fus}} = 19,^{35} \sim 25,^{29} 26.3^{40}$ and $27\text{--}28^{41}$ °C), which is the evidence of insufficient purity of the samples. The experimental enthalpy of formation has been measured calorimetrically for the solid ($\Delta_f H_{\text{solid}}^0$) and liquid ($\Delta_f H_{\text{liquid}}^0$) states. The early experimental result ($\Delta_f H_{\text{liquid}}^0 = -18.6$ kcal/mol)²⁹ had been questioned.⁴⁰ Miroshnichenko et al.⁴⁰ demonstrated that **7** is very sensitive to the moisture and the products of **7** combustion depend on the oxygen content. The calorimetric studies performed with cautions allowed the authors to measure both $\Delta_f H_{\text{solid}}^0$ (-11.5 ± 0.5 kcal/mol) and $\Delta_f H_{\text{liquid}}^0$ for the supercooled liquid (-7.9 ± 0.4 kcal/mol). The enthalpies of sublimation ($\Delta_{\text{sub}} H^0 = 11.1 \pm 0.1$ kcal/mol) and evaporation ($\Delta_{\text{vap}} H^0 = 7.8 \pm 0.1$ kcal/mol) were also measured and the gas phase enthalpy was calculated to be $\Delta_f H_{\text{gas}}^0 = -0.2 \pm 0.5$ kcal/mol.⁴⁰ Unfortunately, the later calorimetric studies^{41,42} gave significantly different results for $\Delta_f H_{\text{liquid}}^0$ (-16.3^{41} and -10.7^{42} kcal/mol), $\Delta_{\text{vap}} H^0$ (13.1 kcal/mol)⁴¹ and $\Delta_f H_{\text{gas}}^0$ (-3.15 kcal/mol).⁴¹

In contrast to the previous nitroalkanes, the experimental data on tetranitromethane (**10**) and nitroethane (**12**) are more

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consistent. The enthalpy of formation of **10** in the standard state measured by static bomb calorimetry was found to be $\Delta_f H_{\text{liquid}}^0 = 8.9^{43}$, 8.8^{44} and 9.2^{45} kcal/mol. Data in the literature for $\Delta_{\text{vap}} H^0$ are very consistent too (10.3^{46} and 10.5^{45} kcal/mol). The value of $\Delta_f H_{\text{gas}}^0 = 19.7^{45}$ kcal/mol has been accepted for the NIST database.³⁵ In the case of **12**, the $\Delta_f H_{\text{liquid}}^0$ was found with the calorimetric techniques to be -33.5 ,²⁹ -34.3 ,^{30,31} and -34.4 ,³³ kcal/mol. The enthalpy of evaporation was measured as $\Delta_{\text{vap}} H^0 = 9.9$ ²⁹ and 9.4 ³⁰ kcal/mol. The currently accepted value^{31,35} for the gas phase formation enthalpy is $\Delta_f H_{\text{gas}}^0 = -24.4$ kcal/mol.

Therefore the experimental formation enthalpies of the simple nitroalkanes are obtained mainly in the calorimetric tests and are found to be consistent for some compounds under study (**10**, **12**). At the same time some data are significantly scattered (**7**) or reported only in one paper (**4**), and even for the well-studied **1** two noticeably different values are accepted.^{35,36} The main source of the errors could be the absence of the product analysis and insufficient purity of the compounds.^{31,32} The addition of the inflammable substances to the bomb to ignite the mixture properly can also increase the error as the desired heat of formation is the difference of two big values: the heat of combustion and the sum of the product formation enthalpies.

The situation is even more complicated for the determination of the formation enthalpy of the reactive intermediates. For example, the enthalpies of formation of mono-, di- and trinitrosubstituted methyl radicals were obtained using the activation energies of the thermal decomposition of corresponding nitromethanes.^{7,8,11,47,48} The enthalpies of the C–N bond rupture reaction were estimated⁷ as $\Delta_f H^0 = E_a - RT_{\text{av}}$, assuming that the observed rate constant of thermal decomposition is equal to the rate constant of the dissociation. However, the secondary reactions of the nitro-substituted methyl radicals¹⁰ as well as contribution of other primary unimolecular reactions (e.g., isomerization to nitrites and aci-forms) could lead to overestimation of the rate constant of dissociation and therefore to the underestimation of its activation energy. Moreover, this approach does not take into account temperature dependence of the reaction enthalpy and entropy and can give only very rough estimations.

The reaction barriers of the C–N bond rupture for nitromethane and nitroethane (**1** and **12**) were also estimated from the results of IR-MPD experiments using RRKM theory, although the authors pointed out that the error of the activation barrier determination might be significant (few kcal/mol).^{15,16}

The quantum chemical calculations are the most appropriate alternative for obtaining the gas phase thermodynamic properties. A number of highly accurate multilevel procedures has been proposed recently.^{36,49–54} Unfortunately, these calculations are very time- and resource-consuming and can be performed only for the “moderate size” species containing up to 10–12 atoms of C, N and O. For the larger species, one has to use the lower level of theory, e.g., less consuming “light” multilevel procedures^{55–58} or the density functional theory. However, the problem of suitable method selection is very important.

In this paper we report results of the calculations of the nitroalkane thermodynamic properties obtained using a number of multilevel procedures and DFT-based techniques. In addition to nitroalkanes, we performed calculations of the properties of their isomers - corresponding nitrites and aci-forms, which (along with radicals) could be the primary products of the nitroalkane thermal decomposition. The main objectives of our calculations were to test the accuracy of the employed methods, to choose the most appropriate techniques for further investiga-

tions of the nitroalkane-based high-energy materials and to try to predict thermodynamic properties of the species with very scattered or unknown experimental data. Results of our calculations and available experimental data were used to analyze the thermodynamics of the primary reactions of the nitroalkane thermal decomposition.

Computational Details

Both multilevel techniques and DFT-based methods have been used in this study. Among the numerous multilevel techniques, the G2³⁶ and G3⁴⁹ procedures and G2M(CC5)⁵⁶ method (a typical “light” multilevel technique) were chosen. DFT calculations were performed using the widespread hybrid B3LYP method^{59,60} with the 6-311G(d,p) basis set and two new hybrid meta DFT methods (MPWB95/6-31+G(d,p) and MPWB1K/6-31+G(d,p)) proposed by Truhlar’s group.⁶¹ All equilibrium structures were ascertained to be at the minima on the potential energy surfaces. Corresponding thermal corrections were included to obtain the values of the enthalpies at 298 K. All calculations have been performed using Gaussian 03⁶² suite of programs.

The gas phase enthalpies of formation in the standard state ($p = 1$ atm and $T = 298$ K, $\Delta_f H_{\text{gas}}^0$) were obtained using the atomization energy approach. The calculated atomization energies at 298 K were subtracted from the well-known enthalpies of formation of the isolated atoms. For any molecule M the enthalpy of formation was calculated as follows:

$$\Delta_f H_{\text{gas}}^0(\text{M}) = E_{\text{el}}(\text{M}) + \text{ZPVE}(\text{M}) + [H_{298}(\text{M}) - H_0(\text{M})] - \sum_i^{\text{atoms}} \{E_{\text{el}}(\text{X}_i) + [H_{298}(\text{X}_i) - H_0(\text{X}_i)]\} + \sum_i^{\text{atoms}} \Delta_f H_{\text{gas}}^0(\text{X}_i)$$

where $E_{\text{el}}(\text{M})$ is the electronic energy of the molecule calculated at the chosen level of theory; $E_{\text{el}}(\text{X})$ is the electronic energy of the atom X_i calculated using the same technique; ZPVE is the energy of molecule’s zero-point vibrations; $[H_{298}(\text{M}) - H_0(\text{M})]$ is a thermal correction to enthalpy obtained by means of simple Gibbs’ statistical mechanics. The NIST Chemistry webbook³⁵ was used as a source of the atomic enthalpies $\Delta_f H_{\text{gas}}^0(\text{X}_i)$.

In some cases isodesmic reaction technique was implemented to provide an independent estimation of $\Delta_f H_{\text{gas}}^0$.

Results and Discussion

1. Calculations of the Gas Phase Enthalpies of Formation.

Most of nitroalkanes under study and their isomers have two or more conformers. Geometries of all these conformers were optimized and their enthalpies of formation were calculated at different levels of theory. Only properties of the lowest energy conformers will be discussed in this paper. The properties of other conformers, including their relative formation enthalpies (Table 1S), could be found in the Supporting Information.

Figure 1 represents the geometries of the lowest energy conformers of nitroalkanes optimized at MP2(Full)/6-31G(d) and B3LYP/6-311G(d,p) levels. The geometries of other compounds under study are presented in Figure 2 and in the Supporting Information (Figure 1S, 2S). Figure 1 demonstrates that both methods predict similar geometry. However, the C–N bond lengths predicted by the B3LYP method are about 0.02 Å longer than those optimized at MP2 level and vice versa for the NO bond lengths. The well-known experimental bond lengths for **1** in a gas phase ($R_{\text{CN}} = 1.49 \pm 0.02$ Å, $R_{\text{NO}} = 1.22 \pm 0.01$ Å)⁶³ are in good agreement with the theoretical

TABLE 1: Gas Phase Enthalpies of Formation ($\Delta_f H_{\text{gas}}^0$) of Methane, Nitroalkanes, Their Nitrite Isomers and Aci-Forms

molecule	$\Delta_f H_{\text{gas}}^0$, kcal/mol						expt
	G2	G3	G2M(CC5)	B3LYP	MPW1B95	MPWB1K	
CH ₄	-18.5	-18.1	-17.6	-17.2	-19.3	-18.0	-17.89 ³⁵
CH ₃ NO ₂ , 1 ^a	-20.2	-17.5	-21.8	-12.3	-16.1	1.2	-17.8 ³⁴
CH ₃ ONO, 2	-18.4	-15.4	-20.3	-10.9	-13.3	3.7	-15.6 ± 0.2 ⁶⁵
CH ₂ NOOH, 3	-5.3	-3.1	-7.4	1.7	-2.0	15.4	
CH ₂ (NO ₂) ₂ , 4 ^b	-15.1	-10.2	-19.2	-0.1	-3.8	30.0	-14.1 ± 1.0 ³²
CH ₂ (NO ₂)ONO, 5	-23.4	-18.1	-27.5	-9.2	-11.0	22.4	
CH(NO ₂)NOOH, 6	-4.6	-0.3	-8.9	4.2	0.2	35.2	
CH(NO ₂) ₃ , 7 ^c	-5.9	1.3	-12.1	17.7	14.6	65.4	-0.2 ± 0.5 ⁴⁰
CH(NO ₂) ₂ ONO, 8		-12.0		-0.1	0.9	51.8	
C(NO ₂) ₂ (NOOH), 9	10.0	16.4	3.6	27.5	23.3	75.1	
C(NO ₂) ₄ , 10				43.0	39.8	108.6	19.7 ± 0.5 ⁴⁵
C(NO ₂) ₃ (ONO), 11				14.5	16.3	85.2	
CH ₃ CH ₂ (NO ₂), 12	-27.3	-24.7	-28.5	-16.8	-24.9	-6.7	-24.4 ± 1.0 ³¹
CH ₃ CH ₂ (ONO), 13	-25.6	-22.9	-27.0	-15.1	-21.4	-3.4	
CH ₃ CH(NO ₂), 14	-15.1	-13.0	-17.0	-5.3	-13.6	4.6	

^a Two noticeably different experimental values are generally accepted.^{35,36} ^b Only one experimental result is known. ^c Available experimental results are very scattered; the most trustworthy one was chosen for the comparison.

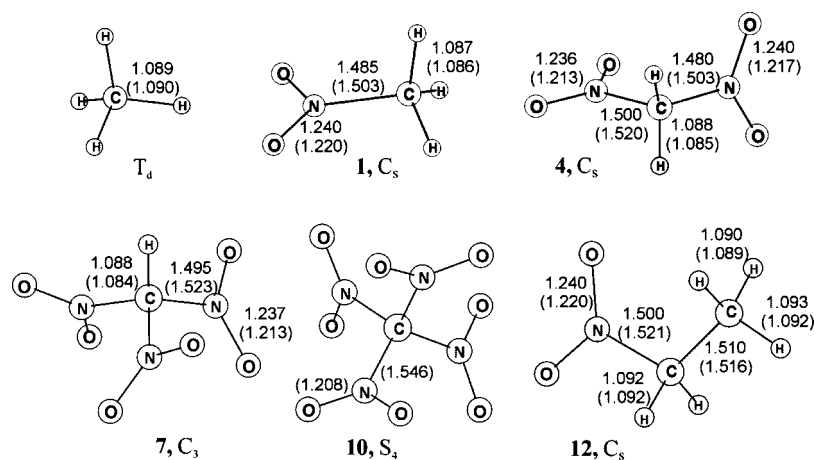


Figure 1. Geometries (bond lengths in Å) of methane and nitroalkanes under study optimized by MP2(Full)/6-31G(d) and B3LYP/6-311G(d,p) (in parentheses) methods.

predictions by both methods. Solid state data for **7** ($R_{\text{CN}} = 1.505$ Å, $R_{\text{NO}} = 1.219$ Å)⁶⁴ are also in fairly good agreement with the calculations.

Table 1 shows the gas phase formation enthalpies of the nitroalkanes and their isomers predicted at different levels of theory. In addition, this table contains the calculated $\Delta_f H_{\text{gas}}^0$ of methane and the experimental data available in the literature. The most reliable literature values are shown in Table 1. The calculated values of $\Delta_f H_{\text{gas}}^0$ for methane agree well with the experiment for all theoretical methods. For the multilevel techniques the deviation is less than 0.6 kcal/mol, whereas among the DFT-based methods only the MPW1B95 procedure demonstrates noticeable discrepancy (-1.4 kcal/mol).

Unfortunately, the inspection of Table 1 shows that the values of $\Delta_f H_{\text{gas}}^0$ for nitroalkanes and their isomers predicted by all methods differ tremendously. Even two most accurate procedures, the G2 and G3, gave significantly different values of $\Delta_f H_{\text{gas}}^0$ for nitroalkanes and their isomers. Moreover, the difference increases with the number of -NO₂, -ONO and -NOOH groups (up to ~6-7 kcal/mol for **7** and **9**).

As it was pointed out in the Introduction, the reliable experimental data are available only for nitroalkanes **1**, **10** and **12**. The enthalpy of formation is also known for methyl nitrite **2** (Table 1).⁶⁵ It was determined by measuring the heat of reaction between methyl alcohol and nitrosyl chloride and was found to be in good agreement with the previous results.⁶⁵ One

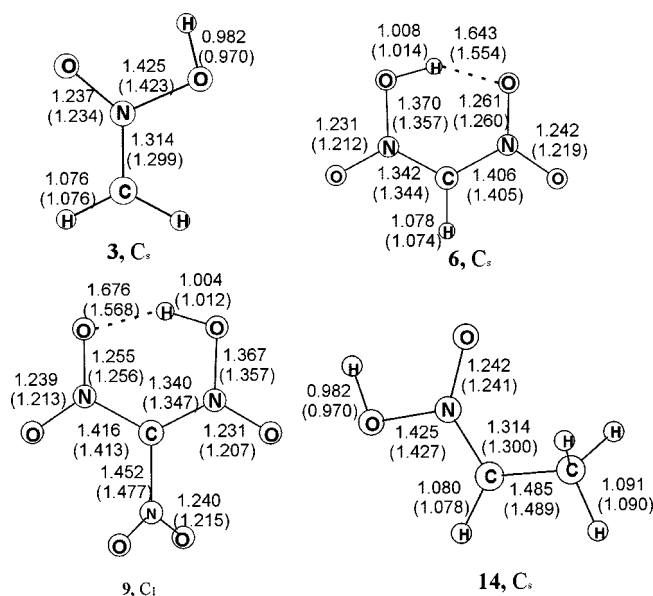


Figure 2. Geometries (bond lengths in Å) of the aci-forms of nitroalkanes optimized by MP2(Full)/6-31G(d) and B3LYP/6-311G(d,p) (in parentheses) methods.

can conclude from these reliable experimental data that only G3 procedure reproduces the formation enthalpies of compounds

TABLE 2: Calculated (Using Atomization Approach) and Experimental Gas Phase Formation Enthalpies ($\Delta_f H_{\text{gas}}^0$) of the Selected Radicals

molecule	$\Delta_f H_{\text{gas}}^0$, kcal/mol						expt
	G2	G3	G2M(CC5)	B3LYP	MPW1B95	MPWB1K	
•NO	21.0	21.9	19.9	22.1	25.6	34.7	21.58 ³⁵
•NO ₂	7.4	8.4	6.1	7.6	10.5	27.6	7.91 ³⁵
•CH ₃	35.2	34.1	36.1	34.4	34.5	35.4	34.82 ³⁵
•CH ₂ CH ₂	30.1	28.8	31.2	29.8	25.7	27.9	28.9 ± 0.4 ⁶⁶
•CH ₂ (NO ₂), R1	30.6	31.5	29.0	34.1	32.5	49.9	24.7 ^a
•CH(NO ₂) ₂ , R2	37.3	40.5	34.2	46.3	45.2	80.2	33.2 ^a
•C(NO ₂) ₃ , R3				66.2	65.8	118.9	47.9 ^a

^a Experimental enthalpies of **R1–R3** given in ref 7 could be considered as very rough estimates.

well. Unfortunately, this comparison could be done only for compounds with one NO₂ or ONO group. In the case of nitroalkanes **4** and **7** the agreement is not as good, but the experimental results are not reliable in this case.

Table 1 shows that the G2 and G2M(CC5) predictions are significantly lower than the experimental and G3 values. The G2M(CC5) demonstrates the worst performance among the used multilevel techniques. Discrepancy between results of the G2M(CC5) and G3 calculations increases approximately additively with respect to the number of NO₂, ONO and NOOH groups (about 5 kcal/mol per group). Most likely, the number of basis set corrections in the G2M(CC5) procedure⁵⁶ is not sufficient for the accurate calculation of atomization energies. In the G3 theory, contrary to G2 and G2M, core-related correlation contributions were taken into account, a spin-orbit corrections were added to the energies of atomic species, and the “higher level corrections” (HLC) for atoms and molecules were separately reoptimized against the bigger G2/97 training set.⁴⁹ In our opinion these improvements led to more accurate description of the atomization energies of the compounds under study by the G3 technique.

All tested DFT methods have shown poor performance in calculations of the formation enthalpy (by means of atomization energy approach). The largest disagreement is for the MPWB1K method, which overestimates the formation enthalpy by ~20 kcal/mol even for **1** (see Table 1). Note that for the hydrocarbon species (shown in Tables 1 and 2) the MPWB1K procedure gives accurate results. The accuracy of the B3LYP and MPW1B95 calculations is not satisfactory either. These methods significantly overestimate the enthalpy of formation. Discrepancy with the G3 and experiment increases approximately additively with respect to the number of NO₂, ONO and NOOH groups. Our data demonstrate that these methods cannot be used reliably to calculate atomization energies of nitroalkanes and their formation enthalpies by the atomization approach. This might be due to the errors in the calculation of electronic energies for atoms rather than an intrinsic failing of the methods for nitro compounds. It should be also noted that MPWB1K method was not specially meant for the atomization energy calculations and the test set against which MPWB1K and MPW1B95 were optimized did not include nitrocompounds.⁶¹

2. Calculations of the Isomerization Enthalpies. In contrast to the formation enthalpies of **1** and **2**, all levels of theory predict accurately that **1** is thermodynamically slightly more favorable (by 1.5–2.8 kcal/mol) than methylnitrite **2**. The difference predicted by G3 procedure (2.1 kcal/mol) agrees with experiment (2.2 kcal/mol). Very similar results were obtained for nitroethane and its isomer (**12**, **13**). Note that the enthalpy differences between **12**, **13** and **14** were calculated previously by B3LYP/6-311+G(3df,2p) method.²² According to these calculations, the enthalpy difference is 1.9 kcal/mol between

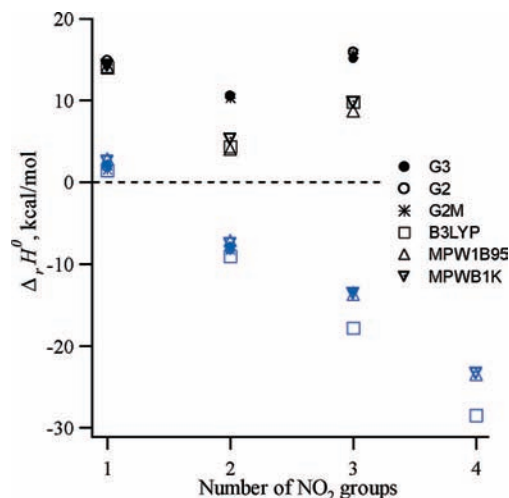


Figure 3. Dependence of the calculated values of the reaction enthalpies ($\Delta_r H^0$, kcal/mol) on the number of nitro groups: nitro–nitrite isomerization (blue points); isomerization to aci-form (black points).

13 and **12** and 9.9 kcal/mol between **14** and **12**, which is close to our B3LYP/6-311G(d,p) results (see Table 1). This indicates that the basis set augmentation does not influence the DFT results significantly.

There are no experimental data on the formation enthalpies of the nitrite isomers of the other nitroalkanes under study. However, the enthalpies of nitro-nitrite isomerization calculated by different methods agree very well (Figure 3, blue points). The differences in the calculated values are less than 1 kcal/mol with the only exception of the B3LYP technique, which gives noticeably lower values of $\Delta_r H^0$ (Table 1, Figure 3).

Therefore, we can analyze the dependence of the enthalpy of nitro–nitrite isomerization on the number of nitro groups using the results of calculations. In contrast to the nitrite **2**, the nitro-substituted nitrites (**5**, **8**, **11**) are significantly more stable than their counterpart nitromethanes (**4**, **7**, **10**). Figure 3 demonstrates clearly the growth of the enthalpy difference between nitro and nitrite forms with the increase of the number of the NO₂ groups (by about 8–9 kcal/mol per group). This effect could be easily explained by the considerable growth of a strain in the nitromethanes upon introducing bulky nitro groups. This strain manifests itself in the noticeable lengthening of the CN bonds in **7** and especially in **10** (Figure 1). The strain is smaller in the case of changing the bulky NO₂ group to a more elongated O–N=O group (Supporting Information, Figure 1S).

There are no experimental data on the formation enthalpies of the aci-forms of nitroalkanes. The $\Delta_r H^0$ values for the isomerization of nitromethanes to aci-forms were calculated theoretically and were found to be positive for all compounds under study (Figure 3). In the case of **1** → **3** isomerization the

TABLE 3: Enthalpies of the C–N Bond Rupture Reactions at 298 K ($\Delta_r H^0$) and at 0 K ($\Delta_r H_{0K}$, in Parentheses), the Experimental Enthalpies of Reactions Determined in IR-MPD Experiments¹⁶ ($\Delta_r H_{0K}$) and Activation Energies of Nitroalkanes Thermal Decomposition (E_a , Temperature Interval in Parentheses)

reactions	$\Delta_r H^0$ ($\Delta_r H_{0K}$), kcal/mol						expt	
	G2	G3	G2M	B3LYP	MPW1B95	MPWB1K	E_a , kcal/mol (T , K)	$\Delta_r H_{0K}$, kcal/mol
$\text{CH}_3\text{NO}_2 \rightarrow \bullet\text{CH}_3 + \bullet\text{NO}_2$	62.8 (61.0)	60.0 (58.2)	64.1 (62.4)	54.3 (52.6)	61.1 (59.4)	61.8 (60.1)	58.5 (900–1500) ⁸	59.4 ¹⁶
$\text{CH}_2(\text{NO}_2)_2 \rightarrow \bullet\text{CH}_2(\text{NO}_2) + \bullet\text{NO}_2$	53.1	50.1	54.3	41.8	46.7	47.5	59.7 (1050–1400) ¹¹	
$\text{CH}(\text{NO}_2)_3 \rightarrow \bullet\text{CH}(\text{NO}_2)_2 + \bullet\text{NO}_2$	50.6	47.6	52.4	36.2	41.1	42.4	42.4 (450–470) ⁴⁸	
$\text{C}(\text{NO}_2)_4 \rightarrow \bullet\text{C}(\text{NO}_2)_3 + \bullet\text{NO}_2$				30.8	36.5	37.9	38.2 (360–450) ⁴⁷	

reaction enthalpies calculated by different methods agree very well and the differences in $\Delta_r H^0$ are less than 1 kcal/mol (Figure 3, black points). In the case of di- and trinitromethanes (**4**, **7**), the $\Delta_r H^0$ values calculated by different multilevel techniques agree very well (the difference is less than 0.8 kcal/mol) and differ significantly (by ~ 6 kcal/mol) from the values obtained by DFT-based methods (Figure 3). However, all methods reproduce approximately the dependence of the $\Delta_r H^0$ values on the number of nitro groups (Figure 3, black points). The decrease of $\Delta_r H^0$ for **4** comparing to **1** (predicted by all methods) could be explained by the stabilization of aci-form **6** due to the formation of intramolecular hydrogen bond (Figure 2). In turn, the growth of $\Delta_r H^0$ for **7** could be explained by the considerably larger strain in the aci-form **9** comparing to the tetrahedral trinitromethane **7** (Figures 1 and 2).

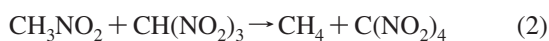
Most likely, the difference in $\Delta_r H^0$ calculated by multilevel and DFT-based techniques (~ 6 kcal/mol for **4** and **7**) originates mainly from the difference in accounting for the intramolecular hydrogen bond. The $\Delta_r H^0$ values calculated by multilevel techniques are more trustworthy whereas the DFT based techniques overestimate the energy of intramolecular hydrogen bonds in the aci-forms **6** and **9**.

3. Calculations of the Enthalpies of the Isodesmic Reactions. Because of large scattering of experimental values (for **7**) or their scarcity (for **4**), we have also used the isodesmic reactions for the estimation of $\Delta_f H_{\text{gas}}^0$ of these species because the enthalpy of appropriate isodesmic reactions can be calculated with a reasonable accuracy even using low-level procedures. We chose isodesmic reaction (1) for the estimation of the formation enthalpy of **4**.



Unfortunately, the enthalpies of reaction (1) at 298 K calculated by MPW1B95 and MPWB1K methods differ noticeably (28.1 and 30.5 kcal/mol, respectively). Using these reaction enthalpies and experimental $\Delta_f H_{\text{gas}}^0$ for methane and **10** (Table 1), we have estimated $\Delta_f H_{\text{gas}}^0$ of **4** as -13.2 and -14.4 kcal/mol, respectively. These values are close to the experimental one and lie between G2 and G3 predictions obtained by the use of atomization approach (Table 1).

The isodesmic reaction (2) was employed to estimate $\Delta_f H_{\text{gas}}^0$ of **7**:



The enthalpy of reaction (2) at 298 K was predicted to be 22.0 and 24.0 kcal/mol at MPW1B95 and MPWB1K levels, respectively. Using these values and experimental $\Delta_f H_{\text{gas}}^0$ of methane and **10** (Table 1) the $\Delta_f H_{\text{gas}}^0$ of **7** was estimated as -2.4 and -4.4 kcal/mol, respectively. Again these values lie between G2 and G3 predictions obtained using atomization approach (Table 1). Unfortunately, the discrepancy between the MPW1B95 and MPWB1K predictions of the isodesmic reaction enthalpies is about 2 kcal/mol. More accurate results could be achieved

applying the G3 or G2 procedures to the above-mentioned isodesmic reactions, but we were unable to perform these resource-consuming calculations for **10** containing 13 “heavy” atoms.

4. Calculation of the Reaction Enthalpies of the C–N Bond Rupture. It is commonly accepted^{7,20,21,27,28} that the C–N bond dissociation is the primary reaction of the thermal decomposition of nitromethanes. Therefore, we also calculated the enthalpy of dissociation of the nitromethanes and the enthalpy of formation of the radical products (by atomization approach) using the spin-unrestricted versions of the above-mentioned methods. The results are summarized in Tables 2 and 3. Table 2 also contains calculated and well-known experimental formation enthalpies of methyl, ethyl, NO_2 and NO radicals.

Table 2 demonstrates that all methods (with the exception of G2M(CC5)) predict the enthalpy of formation of methyl radical with the accuracy better than 1 kcal/mol. The accuracy of prediction for ethyl radical is worse (up to 3 kcal/mol). Only G2, G3 and B3LYP techniques reproduce the formation enthalpies of all radicals (alkyl, NO and NO_2) well. The MPW1B95 and MPWB1K meta DFT methods overestimate tremendously the formation enthalpy of NO and NO_2 radicals similar to the case of nitroalkanes (Table 1). G3 performs slightly better than G2, and it is probably not surprising because the NO_2 and C_2H_5 radicals were added to the G3 training set⁴⁹ whereas only CH_3 and NO species were presented in the initial G2 set.³⁶ At the same time it should be noted that there are no radical species similar to **R1–R3** in these test sets.

As mentioned in the Introduction, the enthalpies of formation of mono-, di- and trinitrosubstituted methyl radicals (Table 2, **R1–R3**) have been obtained previously^{7,8,11,47,48} from the enthalpies of the C–N bond rupture reaction. The latter were estimated through the activation energies of the thermal decomposition of nitromethanes (**4**, **7**, **10**) as $\Delta_r H^0 = E_a - RT_{\text{av}}$ (T_{av} is the average temperature of the pyrolysis experiment).

The calculated enthalpies of C–N bond dissociation at 298 K (and at 0 K for **1**) as well as related experimental data are listed in Table 3. The enthalpy of dissociation of nitromethane ($\Delta_r H^0$) can be also obtained from the well-known formation enthalpies of reagents and products (Tables 1 and 2) as 60.5 kcal/mol. This value is in good agreement with the G3, MPW1B95 and MPWB1K predictions, whereas the results of G2 and G2 M methods are less accurate and the B3LYP method underestimates the $\Delta_r H^0$ significantly (Table 3). The reaction enthalpies estimated using the activation energies of thermolysis (56.5 and 57.7 kcal/mol)^{8,11} are noticeably lower than more accurate data. It could be an indication of the underestimation of E_a as mentioned in the Introduction.

There is no accurate experimental data for the dissociation enthalpy of other nitroalkanes **4**, **7** and **10**. Activation energies of their thermal decomposition can only be used for very rough estimates. Table 3 and Figure 4 demonstrate significant differ-

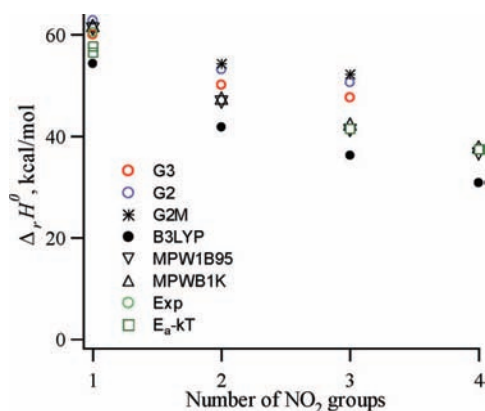


Figure 4. Dependence of the calculated and experimental values of the enthalpies ($\Delta_r H^0$) of the nitro-substituted methane dissociation on the number of nitro groups.

ence between the predictions of $\Delta_r H^0$ at different levels of theory. Unfortunately, the very good agreement of the reaction enthalpies calculated at the MPW1B95 and MPWB1K levels with experimental estimations cannot be considered as the indication of the high accuracy of these calculations. Most likely, the enthalpies of dissociation of **7** and **10** are higher than their experimental estimations by few kcal/mol, as in the case of **1**.

Nevertheless, all calculations demonstrate pronounced decrease (up to 20 kcal/mol) of the enthalpy of dissociation with a number of nitro groups. This effect correlates well with the experimental data on the activation energy of the thermal decomposition (Table 3, Figure 4) and can be explained by a considerable release of strain upon the dissociation of poly nitro-substituted methanes. It is also clear that the B3LYP technique underestimates the enthalpy of dissociation considerably. The MPW1B95 and MPWB1K meta DFT methods give more reasonable results.

Conclusion

In summary, we conclude that only the very resource-consuming G3 procedure gives accurate results (within 1 kcal/mol) for the formation enthalpies of nitro-substituted methane and ethane, their isomers as well as alkyl and NO₂ radicals. On the other hand, the enthalpies of the isomerization and C–N bond rupture reaction of nitromethane is predicted well not only by the G3 procedure but also by two new hybrid meta DFT methods proposed by the Truhlar's group. Therefore, these methods can be used for calculations of the thermodynamic and kinetic properties of the mononitro-substituted alkanes.

The reliable thermodynamic data for the poly nitro-substituted methanes are still insufficient. Therefore, it was impossible to test the accuracy of the calculations of formation and reaction enthalpies for these compounds. However, the enthalpies of tri- and tetranitroalkane dissociation calculated at the MPW1B95 and MPWB1K levels were found to be in good agreement with experimental estimations.

It is commonly accepted,^{7,20,21,27,28} that the C–N bond dissociation with NO₂ elimination is the primary reaction of the thermal decomposition of nitromethanes. Nevertheless, the results of IR-MPD experiments^{15,16} indicate that isomerization of **1** into nitrite **2** should be taken into account. There are no experimental data on the enthalpy of the nitro–nitrite isomerization of nitromethanes with the only exception of nitromethane **1**. Also, no data are available on the isomerization of nitroalkanes to their aci-forms. Our calculations demonstrate that the nitro-substituted nitrites (**5**, **8**, **11**) are significantly more stable

than their counterpart nitromethanes (**4**, **7**, **10**), and the enthalpy difference between nitro and nitrite forms rises significantly with a number of NO₂ groups (by about 8–9 kcal/mol per group). On the contrary the aci-forms are thermodynamically less favorable than nitromethanes. To estimate the contribution of the isomerization reactions to the process of nitroalkane thermal decomposition, kinetics of these reactions should be known. Calculations of the barriers for the isomerization reactions are now in progress and will be published elsewhere.

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Supporting Information Available: Cartesian coordinates of all compounds under study and the enthalpy of formation of the different conformers of the species under study and geometry of the nitrite isomers and radicals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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