

THEORETICAL STUDY OF THE THERMODYNAMIC PROPERTIES OF NITROGEN- AND OXYGEN-CONTAINING HIGH-ENERGY MATERIALS

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ABSTRACT

Different multi-level [G2, G3, G2M(CC5)] and DFT-based (B3LYP, MPW1B95, and MPWB1K) techniques were tested for the calculations of the gas-phase formation enthalpy of nitromethanes as well as C-N bond dissociation energies of these species. The calculated values of the formation and reaction enthalpies were compared with the experimental data if these data were available. It was found that only the G3 procedure gave accurate (within 1 kcal/mol) results. Two new hybrid meta-DFT methods proposed by Truhlar's group showed good results for the reaction enthalpies of the C-N bond dissociation. Using the G3 procedure, the accurate formation enthalpies of some nitro-alkanes with remarkably scattered experimental data were obtained. The gas-phase formation enthalpies of hydrazinium (HNF) and ammonium nitroformate (ANF) were calculated. These data gave an opportunity to predict the dominating vaporization pathway of these compounds. The standard-state enthalpy of formation of a new perspective high-energy compound, [1,2,5]oxadiazolo[3,4-e][1,2,3,4]tetrazine-4,6-di-N-dioxide (furazano-1,2,3,4-tetrazine-1,3-dioxide), was computed using the theoretically calculated gas-phase formation enthalpy and the experimentally measured sublimation enthalpy.

INTRODUCTION

Detailed chemical mechanisms of energetic material combustion are very complicated and usually contain hundreds of elementary reactions. The thermodynamic parameters of these reactions (compounds heat of formation, heat of reaction) as well as kinetic ones (activation energies, rate constants) are crucial for advanced understanding and modeling of physical and chemical phenomena, which take place during the combustion process.

The standard-state heat of formation $\Delta_f H^0$ can be determined experimentally by means of calorimetric tests, but there are some problems, for example, with identification of the short-lived intermediates. At the same time, serious attention should be paid to the purification of the species under study and careful measurement of the combustion product concentrations. The small available amounts of the analyzed compound can also be a serious obstacle. The addition of inflammable substances to the bomb in order to ignite the mixture properly can also increase the error as the desired heat of formation is the difference between two big values: the heat of combustion and the sum of the product formation enthalpies. As a result of these facts, reliable experimental data are available for only a small number of known species.

At present, all the necessary data (electronic energy levels of the molecule, its normal frequencies, etc.) for calculations of the gas-phase enthalpies of formation ($\Delta_f H_{gas}^0$), reaction enthalpies, and activation barriers can be obtained from the first principles (*ab initio*) by means of quantum chemical calculations. The accuracy closest to the experimental one (~ 1 kcal/mol) for the enthalpies and activation barriers can be achieved using multi-level techniques.¹⁻⁴ Unfortunately, these calculations are very time and resource consuming and can be performed only for "moderate size" species, containing up to 12–15 atoms of C, N, and O. For the larger species, one has to use the lower level of theory, e.g. less consuming "light" multi-level procedures⁵ or the density functional theory (DFT).⁶ Therefore, the problem of a suitable method selection is very important.

One of the goals of this paper was to choose the most appropriate procedure for the calculation of the thermodynamic properties of the nitrogen- and oxygen-containing compounds. For this purpose, we performed a series of gas-phase formation enthalpy calculations of mono-, di-, tri-, and tetranitromethane, and nitroethane. We also calculated the enthalpy of the C-N bond dissociation in the nitromethanes in order to test the spin-unrestricted versions of the employed methods. These compounds were chosen as they are simple enough prototypes of the high-energy compounds and reliable experimental data for some of them are available.

However, the discrepancy amongst the experimental data exists even for some extensively studied nitro-alkanes. For instance, two different values $\Delta_f H_{gas}^0 = -19.3$ kcal/mol^{7,8} and $\Delta_f H_{gas}^0 = -17.8$ kcal/mol^{9,10} are commonly accepted for nitromethane (CH₃NO₂, NM). For trinitromethane [CH(NO₂)₃, nitroform (NF)], the experimental data are scattered significantly (from -5 to 5 kcal/mol).¹¹⁻¹³ Note that NF is an important intermediate of thermal decomposition of

hydrazinium nitroformate (HNF, $N_2H_5^+C(NO_2)_3^-$) – the promising high-energy material.¹⁴ The situation is even more complicated for the determination of the formation enthalpy of the reactive intermediates (e.g., nitrosubstituted methyl radicals).

Thus, our second goal was to predict thermodynamic properties of the species with very scattered or unknown experimental data using the chosen reliable computational methods. The investigated compounds are the above-mentioned NM and NF; hydrazinium (HNF) and ammonium nitroformate ($NH_4^+C(NO_2)_3^-$, ANF). In addition, the standard-state formation enthalpy of [1,2,5]oxadiazolo[3,4-e][1,2,3,4]tetrazine-4,6-di-N-dioxide (furazano-1,2,3,4-tetrazine-1,3-dioxide, FTDO), a new high-energy material synthesized at the Zelinsky Institute of Organic Chemistry (RAS), was calculated. A series of papers has been devoted to the study of the spectroscopic and thermochemical properties of FTDO,¹⁵⁻¹⁷ but there has been no reliable information on its formation enthalpy; only some contradictory estimations exist (730 and 995 kcal/kg).¹⁸

COMPUTATIONAL PROCEDURES

Both multi-level techniques and DFT-based methods have been used in this study. Among the numerous multi-level techniques, the most wide-spread G2¹ and G3² procedures proposed by Pople's group were used. In some cases Peterson's CBS-QB3³ and Weizmann-1 (W1)⁴ procedures were employed. A typical "light" multi-level technique G2M (CC5)⁵ was also tested. It is known that the accuracy of these multi-level methods is sufficient for thermodynamic calculations. For instance, for the G3 theory, the average absolute deviation from the experiment for the calculated 148 enthalpies of formation is 0.94 kcal/mol.² The most accurate W1 procedure showed the mean absolute derivation 0.3 kcal/mol on a smaller subset of the species with the most reliable experimental data.⁴ However, to the best of our knowledge, there is no information on testing these methods particularly for the nitrogen- and oxygen-containing compounds.

DFT calculations were performed using the very wide-spread hybrid B3LYP method¹⁹ with the 6-311G(d,p) basis set and two new hybrid meta-DFT methods [MPW1B95/6-31+G(d,p) and MPWB1K/6-31+G(d,p)], proposed by Truhlar's group for thermodynamic and kinetic computations.²⁰ All equilibrium structures were ascertained to be the minima on the potential energy surfaces. Corresponding thermal corrections were included in order to obtain the values of the enthalpies at 298 K. All calculations have been performed using Gaussian 03²¹ suite of programs.

The standard state of NM and NF is liquid; HNF, ANF and FTDO are solid. However, the above-described high-accuracy calculations are possible for the gas phase only. Therefore, we calculated first the enthalpy of formation of these species in the gas phase at 298 K and a pressure of 1 bar ($\Delta H_{f,298}^{gas}$) at the chosen levels of the theory, using the atomisation energy approach. The calculated atomisation 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:

$$\Delta_f H_{gas}^0(M) = E_{el}(M) + ZPVE(M) + [H_{298}(M) - H_0(M)] - \sum_i^{atoms} \{E_{el}(X_i) + [H_{298}(X_i) - H_0(X_i)]\} + \sum_i^{atoms} \Delta_f H_{gas}^0(X_i), \quad (1)$$

where $E_{el}(M)$ is an electronic energy of the molecule calculated at the chosen level of theory; $E_{el}(X)$ is the electronic energy of the atom X_i calculated using the same technique; $ZPVE$ is the energy of molecule's zero-point vibrations; $[H_{298}(M) - H_0(M)]$ is a thermal correction to enthalpy obtained by means of simple Gibbs' statistical mechanics. The NIST Chemistry web book⁸ was used as a source of the atomic enthalpies $\Delta_f H_{gas}^0(X_i)$. In some cases, the isodesmic reaction technique (i.e. the usage of reactions where the number of bonds of a given formal type is conserved) was implemented in order to provide an independent estimation of $\Delta_f H_{gas}^0$.

The standard-state enthalpy of formation of FTDO was calculated using the theoretically calculated value and experimentally measured sublimation enthalpy ΔH_{subl} :

$$\Delta H_f^0 = \Delta H_{f,298}^{gas} - \Delta H_{subl} \quad (2)$$

The sublimation enthalpy of FTDO was determined from the temperature dependence of its vapor pressure. Samples of 100 mg were put into a measuring vessel equipped with a Bourdon manometer. The vessel was evacuated up to 1 Torr. The temperature dependence of FTDO vapor pressure was approximated then by the Clausius-Clapeyron equation:

$$\ln P = -\frac{\Delta H_{subl}}{RT} + C \quad (3)$$

where ΔH_{subl} is the sublimation enthalpy.

RESULTS AND DISCUSSION

Testing the Computational Methods: Calculations of the Gas Phase Enthalpies of Formation

Table 1 contains the gas phase formation enthalpies of the nitroalkanes predicted at different levels of theory. In addition, this table contains calculated $\Delta_f H_{gas}^0$ values of methane, some radical species and the most reliable experimental data available in the literature.

Table 1: The gas phase enthalpies of formation ($\Delta_f H_{gas}^0$) of methane, nitroalkanes, methyl nitrite, and some radical compounds

Molecule	$\Delta_f H_{gas}^0$, kcal/mol						
	G2	G3	G2M(CC5)	B3LYP	MPW1B95	MPWB1K	Expt
CH ₄	-18.5	-18.1	-17.6	-17.2	-19.3	-18.0	-17.89 ⁸
CH ₃ NO ₂ ^a	-20.2	-17.5	-21.8	-12.3	-16.1	1.2	-17.8 ^{9,10} -19.3±0.3 ^{7,8}
CH ₃ ONO	-18.4	-15.4	-20.3	-10.9	-13.3	3.7	-15.6±0.2 ⁸
CH ₂ (NO ₂) ₂ ^b	-15.1	-10.2	-19.2	-0.1	-3.8	30.0	-14.1±1.0 ⁷
CH(NO ₂) ₃ ^c	-5.9	-1.3	-12.1	17.7	14.6	65.4	-0.2±0.5 ¹²
C(NO ₂) ₄	–	19.6	–	43.0	39.8	108.6	19.7±0.5 ^{8,22}
C ₂ H ₅ (NO ₂)	27.3	24.7	-28.5	-16.8	-24.9	-6.7	-24.4±1.0 ⁸
•NO	21.0	21.9	19.9	22.1	25.6	34.7	21.58 ⁸
•NO ₂	7.4	8.4	6.1	7.6	10.5	27.6	7.91 ⁸
•CH ₃	35.2	34.1	36.1	34.4	34.5	35.4	34.82 ⁸
•CH ₃ CH ₂	30.1	28.8	31.2	29.8	25.7	27.9	28.9±0.4 ⁸

^aTwo noticeably different values are generally accepted.^{8,9}

^bOnly one experimental result is known.

^cAvailable experimental results are very scattered; the most trustworthy one was chosen for the comparison.

Unfortunately, the inspection of Table 1 shows that the values of $\Delta_f H_{gas}^0$ for the nitroalkanes predicted by all methods differ tremendously. Even the two most accurate procedures, G2 and G3, gave significantly different values of $\Delta_f H_{gas}^0$. Moreover, the difference increases with the number of NO₂-groups (up to ~6-7 kcal/mol for NF). The discrepancy between the results of G2M (CC5) and G3 calculations increases approximately additively with respect to the number of NO₂ groups (about 5 kcal/mol per group). Most likely, the number of basis set corrections in the G2M (CC5) procedure⁵ is not sufficient for the accurate calculation of atomization energies.

All tested DFT methods have shown poor performance in the formation enthalpy calculations. The largest disagreement is for the MPWB1K method, which overestimates the formation enthalpy by about 20 kcal/mol even for NM (see Table 1). The accuracy of B3LYP and MPW1B95 calculations is not satisfactory either. These methods significantly overestimate the enthalpy of formation, the discrepancy between experimental and theoretically calculated values increases with the number of nitro groups.

Previously,²³ we have also compared the accuracy of the B3LYP and multi-level methods in kinetic calculations. Activation barriers for the primary reactions of thermal decomposition of simple nitroalkanes were calculated and compared with the experimental data if this data were available. The best agreement with the experiment was also achieved using the G3 procedure (the discrepancy was ~1-2 kcal/mol), whereas B3LYP noticeably underestimated the values of reaction barriers (the discrepancy ~10 kcal/mol).

All methods [with the exception of G2M(CC5)] predict the enthalpy of formation of methyl radical with an accuracy rate better than 1 kcal/mol. The accuracy of prediction for the ethyl radical is worse (up to 3 kcal/mol). Only the G2, G3, and B3LYP techniques reproduce the formation enthalpies of all radicals (alkyl, NO, and NO₂) well. The MPW1B95 and MPWB1K meta-DFT methods tremendously overestimate the formation enthalpy of NO and NO₂ radicals similar to the case of nitroalkanes (Table 1). G3 performs slightly better than G2 and this is probably not surprising since NO₂ and C₂H₅ radicals were added to the G3 training set,² whereas only CH₃ and NO species were presented in the initial G2 set.¹

Thus, the results of the desired accuracy (~1 kcal/mol) can only be obtained using the G3 technique. Of course, an inevitable cost for the accuracy is the large amount of required time and computational resources. G3 calculations for molecules even slightly bigger than C(NO₂)₄ are impossible.

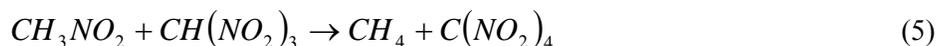
Pinpointing the Formation Enthalpies of Some Nitroalkanes: High-Accurate Methods and the Isodesmic Reactions Technique

In order to resolve the discrepancy in the NM gas phase formation enthalpy (Table 1), we performed very accurate W1⁴ calculations of atomization energy for this compound. The obtained value $\Delta_f H_{gas}^0 = -18.0$ kcal/mol is very close to one of the experimental results,^{9,10} $\Delta_f H_{gas}^0 = -17.8$ kcal/mol, and G3 prediction (Table 1). Thus, we opted for the latter experimental value for NM in the subsequent isodesmic calculations.

Due to the large scattering of experimental values for NF or their scarcity for dinitromethane (DNM),⁷ we have also used the isodesmic reactions technique for the estimation of $\Delta_f H_{gas}^0$ of these species. The enthalpy of appropriate isodesmic reactions can be calculated with a reasonable accuracy even using low-level procedures. We chose the isodesmic reaction in Eq. (4) for the estimation of the formation enthalpy of DNM:



The isodesmic reaction (5) was employed to estimate $\Delta_f H_{gas}^0$ of NF:



Using the reaction enthalpy values calculated at the different levels of theory and experimental $\Delta_f H_{gas}^0$ of methane, NM and C(NO₂)₄ (Table 1), the formation enthalpies of NF and DNM were obtained (Table 2). The most reliable G3 values are $\Delta_f H_{gas}^0 = 1.8$ kcal/mol for NF and $\Delta_f H_{gas}^0 = -10.1$ kcal/mol for DNM. The origin of a significant discrepancy (~4 kcal/mol) between the calculated and experimental values for DNM might be the use of the $\Delta_{vap} H^0$, estimated from the empirical correlation formula rather than the measured value.⁷ The existing experimental data on the formation enthalpy of NF are quite contradictory (see Introduction).

It should be also noted that the formation enthalpies of DNM and NF calculated at the G3 level of theory using isodesmic reaction technique (Table 2) are in good agreement with the ones calculated using the atomization energy approach (Table 1). This fact also confirms the reliability of the G3 atomization energy calculations. The use of the isodesmic reaction technique allowed one to reduce significantly the scattering of the values obtained using different DFT methods, but unfortunately the accuracy of these procedures is still not sufficient.

We believe that our G3 results for $\Delta_f H_{gas}^0$ of NF, obtained by atomization energy approach (1.3 kcal/mol) and isodesmic reaction method (1.8 kcal/mol), are the most reliable values.

Table 2: The enthalpy of formation of di- and tetranitromethane calculated using isodesmic reaction technique (the most reliable values are in bold)

Molecule	$\Delta H_{f,298}^{gas}$, kcal/mol			
	G3	B3LYP	MPW1B95	MPWB1K
$\text{CH}_2(\text{NO}_2)_2^a$	-10.1	-12.1	-13.2	-14.4
$\text{CH}(\text{NO}_2)_3^b$	1.8	-0.8	-2.4	-4.4

^a The formation enthalpy was obtained using the calculated heat of the Isodesmic Reaction (4) and the experimental values of the formation enthalpy of CH_4 and $\text{C}(\text{NO}_2)_4$ from Table 1.

^b The formation enthalpy was obtained using the calculated heat of the Isodesmic Reaction (5) and the experimental values of the formation enthalpy of CH_4 and NM from Table 1.

Calculations of the Reaction Enthalpies of the C-N Bond Rupture

It is commonly accepted²⁴ that the C-N bond dissociation is the primary reaction in the thermal decomposition of nitromethanes. Therefore, we also calculated the enthalpy of dissociation of the nitromethanes using the spin-unrestricted versions of the above-mentioned methods. The results are summarized in Table 3.

The activation barrier at 0 K for the NM dissociation reaction was found to be $\Delta_r H_{0K} = 59.4$ kcal/mol in very thorough IR-multiphoton dissociation experiments.²⁵ The enthalpy of dissociation of NM ($\Delta_r H^0$) can also be obtained from the well-known formation enthalpies of reagents and products as 60.5 kcal/mol. This value is in good agreement with the W1, G3, MPW1B95, and MPWB1K predictions, while the results of the G2 method 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 as $E_a - RT_{\text{aver}}$ (56.5 and 57.7 kcal/mol)²⁴ are noticeably lower than the more accurate data. This fact might be an indication of the significant contribution of the secondary reactions to the measured value of E_a .

Table 3: The 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), and the activation energies of nitroalkanes thermal decomposition (E_a , temperature interval in parentheses). The most trustworthy values are in bold.

Reactions	$\Delta_r H^0$ ($\Delta_r H_{0K}$), kcal/mol						Experiment ²⁴
	G2	G3	W1	B3LYP	MPW1B95	MPWB1K	E_a , kcal/mol (T, K)
CH ₃ NO ₂ → •CH ₃ +•NO ₂	62.8 (61.0)	60.0 (58.2)	61.4 (59.8)	54.3 (52.6)	61.1 (59.4)	61.8 (60.1)	58.5 (900-1500) 59.7 (1050-1400)
CH ₂ (NO ₂) ₂ → •CH ₂ (NO ₂)+•NO ₂	53.1	50.1	–	41.8	46.7	47.5	–
CH(NO ₂) ₃ → •CH(NO ₂) ₂ +•NO ₂	50.6	47.6	–	36.2	41.1	42.4	42.4 (450-470)
C(NO ₂) ₄ → •C(NO ₂) ₃ +•NO ₂	–	45.0	–	30.8	36.5	37.9	38.2 (360-450)

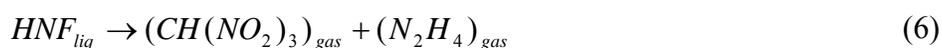
There is no accurate experimental data for the dissociation enthalpy of other nitroalkanes DNM, NM, and C(NO₂)₄. Activation energies of their thermal decomposition can only be used for very rough estimates. Table 3 demonstrates a significant difference between the predictions of $\Delta_r H^0$ at different levels of theory. Unfortunately, a very good agreement between the reaction enthalpies calculated at MPW1B95 and MPWB1K levels and experimental estimations cannot be considered as indication of the high accuracy of these calculations. Most likely, the enthalpies of dissociation of NM and C(NO₂)₄ are higher than their experimental estimations by few kcal/mol, as in the case of NM. The G3 predictions again seem to be the most accurate.

Thus, only the G3 method is suitable for the formation enthalpy calculations of nitroalkanes. Other resource-consuming multi-level procedures do not provide the desirable (~1 kcal/mol) accuracy and the DFT methods fail completely in this case. In the meantime, the average error of the DFT techniques for C-N bond cleavage reactions is not so high, so these methods can be used for the estimations of reaction enthalpies. In order to obtain the accurate results, one still has to use the G3 technique.

Calculations of the HNF and ANF Formation Enthalpy and Analysis of Their Vaporization Pathways

Taking into account the results of the testing of different techniques' performance, the G3 procedure was chosen for the calculations of HNF and

ANF formation enthalpies. The gas-phase formation enthalpy of HNF was found to be 28.9 kcal/mol, the corresponding value for ANF is $\Delta_f H_{gas}^0 = -1.6$ kcal/mol. Meanwhile, the standard state of these compounds is solid. Because of this fact, it is interesting to compare the calculated gas-phase formation enthalpies of HNF and ANF, their experimentally measured solid-state formation enthalpies,²⁶ and the phase change data obtained by Sinditskii et al.²⁷ The authors measured the vapor pressure above the melted HNF. They found the proportionality coefficient $\beta=19.2$ kcal/mol between $\ln P$ and $\left(-\frac{1}{RT}\right)$ in Eq. (3). Two different vaporization pathways can be proposed for HNF:



For the dissociative vaporization channel in Eq. (6), $\beta = \frac{\Delta H_{vap}}{2}$; and for the channel (7), $\beta = \Delta H_{vap}$. Using the experimental formation enthalpy of HNF²⁶ $\Delta_f H_{solid}^0 = -18.4$ kcal/mol, an estimation of melting enthalpy $\Delta H_{melt} = 2.7$ kcal/mol²⁷ and the calculated values of $\Delta_f H_{gas}^0$ for HNF, $CH(NO_2)_3$ (Table 1) and N_2H_4 (G3 value is 24.9 kcal/mol), one can immediately find that the vaporization occurs through the dissociative pathway [Eq. (6)]. In the meantime, the discrepancy between the sum of the solid-state formation enthalpy and melting enthalpy on the one side and the sum of the gas phase formation enthalpies of $CH(NO_2)_3$ and N_2H_4 on the other side is still significant (3.6 kcal/mol). The main source of such inconsistency might be the empirical estimation of the HNF melting enthalpy. The analogous calculations for ANF also indicate the domination of the dissociative vaporization pathway. Thus, using the highly accurate G3 procedure, the gas-phase formation enthalpies of HNF and ANF were calculated and the evidence of their dissociative vaporization pathway was obtained.

Calculations of the Structure, Vibrational Frequencies and Formation Enthalpy of FTDO

As mentioned in the Introduction, there is no reliable information on the formation enthalpy of FTDO. However, its structure and IR spectra are well known.^{15,16} Prior to the formation enthalpy calculations, we had tested different methods used for geometry optimization and frequency calculations. The optimized geometry of FTDO is shown in Fig. 1. The molecule is planar, bond

lengths calculated at the MP2/6-31G(d) (used in G2 and G3 methods), and B3LYP/6-31G(d) (used in CBS-QB3) levels are close to each other and are in good agreement with the X-ray diffraction data¹⁵ (maximum discrepancy is less than 0.03 Å). It should be noted that the B3LYP geometry fits the experimental data slightly better.

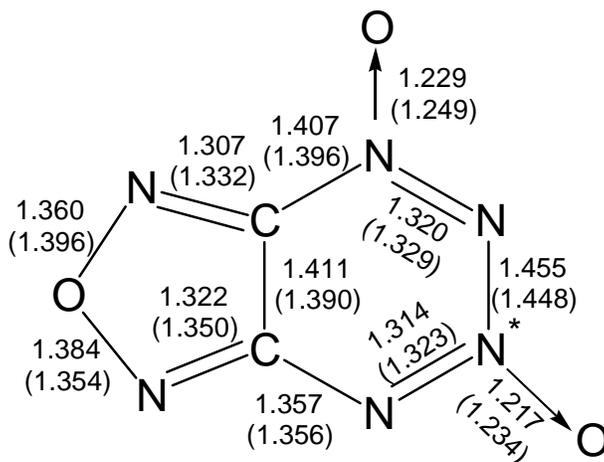


Figure 1: Bond lengths (Å) of FTDO computed at the B3LYP/6-31G(d) and MP2/6-31G(d) (in parenthesis) levels of theory.

The IR spectra of the FTDO molecule and its isotope analogue (atom ¹⁴N, marked by an asterisk in Fig. 1, was substituted by ¹⁵N) calculated at B3LYP level were compared with the experimental ones (Table 4).¹⁵ The intense lines with the most noticeable isotope shifts were used for comparison. Table 4 demonstrates good agreement between the calculations and experiment.

Table 4: Maxima of the most intense lines in the IR spectra of FTDO and its isotope analogue (cm⁻¹); the calculated frequencies were scaled by the standard factor 0.9614.²⁸

Number	B3LYP/6-31G(d)		Experiment ¹⁵	
	FTDO	¹⁵ N - FTDO	FTDO	¹⁵ N - FTDO
1	1556	1538	1548	1538
2	1507	1502	1517	1507
3	1411	1409	1420	1415
4	1123	1116	1148	1141
5	1592	1583	1589	1589
6	668	655	676	662

The gas-phase formation enthalpy of FTDO was calculated using the atomization reaction:



and another reaction:



The results of $\Delta H_{f,298}^{gas}(FTDO)$ calculations are shown in Table 5. The calculated values range from ~169 kcal/mol to ~174 kcal/mol, the G3 value obtained using the atomization reaction [Eq. (8)] is slightly higher (178.5 kcal/mol).

Table 5: Results of $\Delta H_{f,298}^{gas}(FTDO)$ calculations at different levels of theory

Reaction	$\Delta H_{f,298}^{gas}(FTDO)$, kcal/mol		
	G2	G3	CBS-QB3
6	173.9	178.5	170.5
7	172.2	171.7	168.8

Thus, the average value of the formation enthalpy of FTDO is $\Delta H_{f,298}^{gas} = 173.0$ kcal/mol. The error can be estimated as the average scattering of the results of different techniques (± 3 kcal/mol).

It has been mentioned above that the accuracy of B3LYP calculations is not satisfactory for the N,O-containing systems. For the sake of comparison and completeness, we have calculated FTDO formation enthalpy at the B3LYP/6-311G(d,p) level of theory: for Reaction (8), $\Delta H_{f,298}^{gas} = 185.0$ kcal/mol and for Reaction (9), $\Delta H_{f,298}^{gas} = 164.4$ kcal/mol. In accord with previous results, the deviation from the average value 173 kcal/mol is more than 10 kcal/mol.

The temperature dependence of the FTDO vapor pressure was measured in the temperature range of 40–80°C with the step 10°C and the results were approximated by Eq. (3). The value of sublimation enthalpy ($\Delta H_{sub}(FTDO)$) was found to be 15.1 ± 0.8 kcal/mol. Therefore, FTDO standard state enthalpy of formation is $\Delta H_f^0 = 158 \pm 4$ kcal/mol or 1010 ± 30 kcal/kg.

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