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Multilevel Quantum Chemical Calculation of the Enthalpy of Formation of [1,2,5]Oxadiazolo[3,4-e][1,2,3,4]-Tetrazine-4,6-Di-N-Dioxide

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The enthalpy of formation in the standard state for the promising novel energetic material [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 calculated using a theoretically calculated value of the heat of formation in the gas phase and am experimentally measured value of the heat (enthalpy) of sublimation. The theoretical calculations were performed using the G2, G3, and CBS-QB3 high-accuracy multilevel quantum chemical techniques.

Key words: furazano-1,2,3,4-tetrazine-1,3-dioxide, enthalpy of formation, enthalpy of sublimation, quantum chemical calculations.

INTRODUCTION

The creation of energetic materials is one of the main current trends in the search for substances and compositions that would provide a considerable improvement in the performance of various gas-generating devices. In particular, it has been shown [1, 2] that the use of oxidizers with a high enthalpy of formation in rocket propellants allows one to eliminate metallic fuel as a propellant component and to attain extremely high values of the specific impulse. At the same time, materials with a high enthalpy of formation, as a rule, are characterized by high detonation velocities and pressures. A detailed analysis of the production conditions and energetic characteristics of modern energetic materials, including DNAF ($C_4N_8O_8$) and ONC ($C_8N_8O_{16}$) with calculated detonation velocities of 10.0 and 10.1 km/sec, respectively, was performed in [3]. Even higher calculated detonation velocities were obtained for hypothetical polynitrogen compounds [3], for example, N_8 (14.86 km/sec) and N_{60} (17.31 km/sec).

Actually, the above-mentioned compounds have not received widespread acceptance since they have been synthesized in small quantities (DNAF and ONC) or currently exist only hypothetically (N_x). Nevertheless, an analysis of their properties is of significant interest, at least, from a viewpoint of seeking general relationships between the constitution of a material and the energetic parameters of its physicochemical transformations. Among promising energetic compounds are tetrazine dioxides (TDOs) synthesized at the Zelinskii Institute of Organic Chemistry of the Russian Academy of Sciences [4, 5]. A calculated value of the specific impulse for a propellant containing 1,2,3,4-tetrazine-1,3-dioxide is given in [6]. It is markedly higher than that for other propellants containing high-enthalpy oxidizers based on CNO compounds or for propellants containing promising chlorine-free oxidizers (ammonium dinitramide and hydrazinium nitroformate) [7].

Furazano-1,2,3,4-tetrazine-1,3-dioxide (FTDO) is a typical representative of the new type of stable nitrogen compounds containing a unique combination of two diazene oxide groups directly bound to each other. The synthesis of FTDO and investigation of its spectroscopic and thermochemical properties have been a subject of extensive studies [4, 5, 8–10]. However, there are no reliable data on such an important parameter as the

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enthalpy of formation of FTDO; there are only some contradictory estimates (730 and 995 kcal/kg [6]). This reflects the lack of detailed and reliable information on the energetic characteristics (enthalpy of formation, reaction barriers) for recently synthesized high-energy compounds. In view of great difficulties in dealing with these materials (high sensitivity, ability to react with unsaturated hydrocarbons, bases, epoxies, and free radicals, and limited available quantities of the materials), it is reasonable to perform detailed theoretical studies directed toward determining the structure of these compounds and their energetic characteristics.

Recent great progress in computer technology has enabled high-level quantum chemical calculations which provide sufficient information (on the electronic energy of molecules, vibrational frequencies, etc.) to determine the required thermodynamic parameters. Modern multilevel quantum chemical methods allow one to achieve accuracy similar to the experimental one for the calculation of the thermodynamic parameters, including the enthalpy of formation. In the present work, the geometry of IR spectrum and the enthalpy of formation of FTDO are calculated using modern quantum chemical methods and multilevel techniques.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Computational Methods

The most accurate quantum chemical calculations of the energetic and thermodynamic characteristics of materials are currently conducted using the so-called multilevel quantum chemical techniques. The best of them enable calculations of properties such as heat of formation, activation barrier, heat of reaction, with a nearly experimental accuracy (≈1–2 kcal/mol) [11–13].

In such calculations, as a rule, one first optimizes the molecular geometry and determines the normal vibrational frequencies using low-level methods [HF, MP2 or one of the density functional techniques, DFT] acceptable from a viewpoint of computation costs. Next, one of the high-level post Hartree–Fock methods with a standard basis set is used to calculate the electronic energy for the optimized geometry, which is followed by some additive corrections for the incompleteness of the basis set. These calculations are also rather complicated. At present, the most widely used are the G1–G3 methods proposed by Pople [11, 12]; the set of CBS-Q methods [13] developed by the group of Peterson is also fairly accurate.

The results obtained using multilevel techniques have accuracy sufficient for calculations of the thermodynamic characteristics of compounds and processes. For example, calculations [11] performed using the G3 method for the G2 standard test set of molecules gave a mean absolute deviation of 1.02 kcal/mol for the atomization energy [12]. According to CBS-QB3 calculations [13], this value is 0.87 kcal/mol.

The standard state of FTDO is the solid state, but the high-accuracy quantum chemical calculations described above are feasible only for gases. Therefore, the enthalpy of formation of FTDO was calculated for the gas phase at a temperature of 298 K and a pressure $p = 1$ atm ($\Delta H^{\text{gas}}_{f,298}$) using the most accurate methods — G2 [11], G3 [12], and CBS-QB3 [13]. The enthalpy of formation of FTDO in the standard state (ΔH^0_f) was determined using a theoretically calculated value of $\Delta H^{\text{gas}}_{f,298}$ and an experimentally measured value of the heat (enthalpy) of sublimation ΔH_{subl}:

$$\Delta H^0_f = \Delta H^{\text{gas}}_{f,298} - \Delta H_{\text{subl}}. \tag{1}$$

The enthalpy of formation in the gas phase was calculated as follows:

$$\begin{aligned}\Delta H^{\text{gas}}_{f,298}(M) &= E_{\text{el}}(M) + \text{ZPVE}(M) \\ &\quad + [H_{298}(M) - H_0(M)] \\ &\quad - \sum_i^{\text{products}} \Big\{ E_{\text{el}}(X_i) + \text{ZPVE}(X_i) \\ &\quad + [H_{298}(X_i) - H_0(X_i)] \Big\} \\ &\quad + \sum_i^{\text{products}} \Delta H^0_{f,298}(X_i).\end{aligned}$$

Here $E_{\text{el}}(M)$ is the total electronic energy of the molecule calculated using quantum chemical techniques; $E_{\text{el}}(X_i)$ is the electronic energy of the final decomposition product i calculated using the same technique; ZPVE is the zero-point vibrational energy ($\sum h\nu_i/2$, where h is Planck's constant and ν_i are the vibrational frequencies of the molecule); $H_{298}(X) - H_0(X)$ is the thermal correction to the enthalpy; $\Delta H^0_{f,298}(X_i)$ is the experimental enthalpy of formation of the ith product.

Thus, to calculate $\Delta H^{\text{gas}}_{f,298}(M)$ using the indicated technique, one should simply subtract the heat of the reaction $M \to \sum X_i$ from the total enthalpy of formation of the reaction products $\sum_i^{\text{products}} \Delta H^0_{f,298}(X_i)$. The values of $\Delta H^0_{f,298}(X_i)$ are taken from the database of the National Institute of Standards and Technology [14].

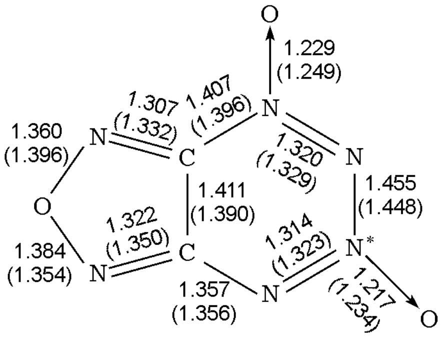

Fig. 1. Bond lengths (in Å) of the FTDO molecule computed at the B3LYP/6-31G(d) and MP2/6-31G(d) (in parentheses) levels of theory.

The usual approach is to use the atoms constituting the molecule as X_i. In this case, it is the atomization reaction

$$\text{FTDO} \rightarrow 2\text{C} + 6\text{N} + 3\text{O}. \qquad (2)$$

We also calculated the value of $\Delta H^{\text{gas}}_{f,298}(M)$ using another reaction:

$$\text{FTDO} \rightarrow 2\text{CO} + 3\text{N}_2 + 0.5\text{O}_2. \qquad (3)$$

To check the accuracy of the frequency calculations, we compared IR spectra of FTDO and its isotope substituted derivatives calculated using the MP2 and B3LYP techniques [15, 16] with available literature data [4]. These methods are used for geometry optimization in the G2, G3, and CBS-QB3 procedures. All calculations were performed using the Gaussian-98 suit of programs [17].

Measurement of the Enthalpy of Sublimation

To determine the enthalpy of sublimation of FTDO experimentally, its vapor pressure was measured on a setup with a Burdon manometer. A 100-mg sample was placed in the reaction vessel, which was evacuated to a residual pressure below 1 torr. The temperature dependence of the FTDO vapor pressure was approximated by the Clausius–Clapeyron equation

$$\ln p = -\frac{\Delta H_{\text{subl}}}{RT} + \text{const.} \qquad (4)$$

RESULTS AND DISCUSSION

Geometry Optimization and Calculation of IR Spectra

TABLE 1

The Most Intense Lines of the IR Spectrum of FTDO and Its Isotope Substituted Analog, cm^{-1}

B3LYP/6-31G(d) calculation		Experiment [4]	
FTDO	^{15}N (FTDO)	FTDO	^{15}N (FTDO)
1556	1538	1548	1538
1507	1502	1517	1507
1411	1409	1420	1415
1123	1116	1148	1141
1592	1583	1589	1589
668	655	676	662

Note. For the calculated frequencies, a standard scaling factor of 0.9614 was used [13].

TABLE 2

Enthalpy of Formation of FTDO Calculated Using Various Quantum Chemical Techniques

Reaction	$\Delta H^{\text{gas}}_{f,298}$, kcal/mol		
	G2	G3	CBS-QB3
2	173.9	178.5	170.5
3	172.2	171.7	168.8

Figure 1 gives the results of geometry optimization for FTDO; the molecule is planar. The bond lengths calculated at the MP2/6-31G(d) level (used in the G2 and G3 approaches) and at the B3LYP/6-31G(d) level (used in the CBS-QB3) are fairly close to each other (the largest deviation does not exceed 0.03 Å). The characteristic bond lengths (Fig. 1) are also in good agreement with X-ray structural data [4]; the difference does not exceed 0.03 Å. The results of the B3LYP calculations are in better agreement with experiment.

IR spectra of the FTDO molecule and its isotope analog calculated at the B3LYP level were compared with experimental values [4]. The comparison was performed for the most intense lines, for which a considerable isotopic shift was observed in the case of substitution of the ^{15}N isotope for the nitrogen atom in the tetrazine fragment (marked by an asterisk in Fig. 1). The results of the comparison are given in Table 1. As follows from the table, the calculated vibrational frequencies are in good agreement with experimental data.

Calculations of the Gas-Phase Enthalpy of Formation

Results of calculations of $\Delta H^{\text{gas}}_{f,298}$ (FTDO) using reactions (2) and (3) are given in Table. 2. The results

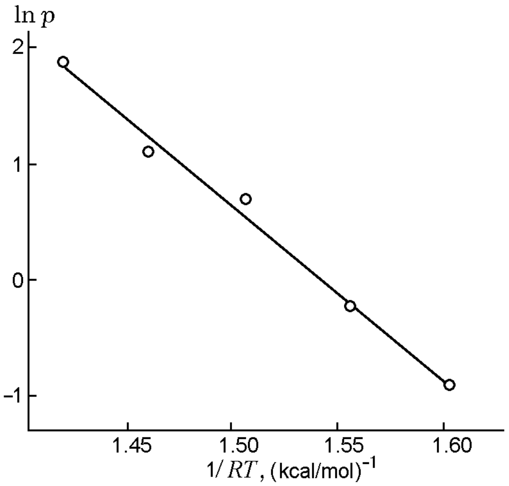

Fig. 2. FTDO vapor pressure versus temperature in Clausius–Clapeyron coordinates.

are in the range from ≈169 to ≈174 kcal/mol. The G3 calculation using the atomization reaction drops out from this range (2) (178.5 kcal/mol). Thus, the average value of gas-phase formation enthalpy of FTDO is $\Delta H^{\rm gas}_{f,298} = 172.6$ kcal/mol. The accuracy of this value can be estimated as the scattering of results obtained using different techniques (±3 kcal/mol).

As noted above, we employed the currently most accurate computational techniques. However, they cannot be used to calculate the enthalpy of formation for more complicated compounds, for example, the derivatives of FTDO. To test the accuracy of the density functional techniques and the capability for calculations of the properties of more complicated systems, we also performed a B3LYP/6-311G(d,p) calculation of the enthalpy of formation of FTDO using the atomization reaction (2). The obtained value $\Delta H^{\rm gas}_{f,298} = 185.0$ kcal/mol is 10 kcal/mol higher than the average value for the high-level calculations. Using the calculated enthalpy of reaction (3), we obtained $\Delta H^{\rm gas}_{f,298} = 164.4$ kcal/mol. It should be noted that the B3LYP technique also considerably overestimates the enthalpies of formation in the case of nitroalkanes [18]. Thus, the B3LYP calculations give a large scatter of data and these quantitative estimates differ considerably from the results of the most accurate techniques; therefore, the application of DFT techniques is appropriate only for semiquantitative estimations.

Sublimation Enthalpy Measurement

The temperature dependence of the FTDO vapor pressure was measured in the temperature range 40–80°C with a step of 10°C, and the results were approximated by equation (4) (Fig. 2). The enthalpy of sublimation of FTDO was found to be $\Delta H_{\rm subl}(\rm FTDO) = 15.1 \pm 0.8$ kcal/mol.

CONCLUSIONS

Thus, calculations using formula (1) give the standard-state enthalpy of formation of FTDO $\Delta H^0_f(\rm FTDO) = 158 \pm 4$ kcal/mol or 1010 ± 26 kcal/kg. This value agrees with one of the values used in [6] (995 kcal/kg). One might expect that the specific impulse of a FTDO based propellant should be close to that calculated in [6].

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