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Theoretical Analysis of the Initial Stages of the Thermal Decomposition of Trinitromethane

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Abstract—The hybrid method B3LYP/6-311G* of density functional theory is used to optimize the geometries of nitroform and some intermediates of its decomposition ($CH(NO_2)_2$, $CH(NO_2)_2ONO$, $CH(NO_2)$, and HC(O)NO) and to locate the transition states of the dissociation and isomerization reactions involving these species. The heat of formation of nitroform and of the intermediates of its decomposition and the Gibbs energies of activation of the reactions examined are calculated using the modern ab initio multilevel procedures G2M(CC5) and G2. The high-pressure limits of the rate constants of these reactions in the temperature range 300–2000 K are calculated using transition state theory or its variational analogue.

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INTRODUCTION

Trinitromethane (nitroform, **1**) is used in the synthesis of high-energy materials and is an intermediate in various decomposition reactions. In particular, nitroform is formed during the thermal decomposition of hydrazine nitroformate (HNF), a promising oxidizer and a component of solid rocket fuels [1–3]. The problem of replacing ammonium perchlorate with a chlorine-free oxidizer has become a challenging issue because of the necessity of reducing the deleterious environmental effect of solid-fuel rockets. The thermodynamic characteristics of **1** and of the intermediates of its decomposition, as well as the rate constants of the elementary steps involving these species, are necessary for constructing kinetic models for the complicated processes of the combustion of high-energy materials.

The rate constants of all elementary steps are required to construct a detailed kinetic mechanism for the combustion of a high-energy substance. Experimental rate constant data available in the literature cover only a few reactions, and no such information is available for most of the hypothesized reactions. Hence, the calculation of the rate constants and their temperature and pressure dependences is an important task. The statistical Rice–Ramsperger–Kassel–Marcus (RRKM) theory has often been used in such calculations [4, 5].

To apply this theory, it is necessary to know the structure and properties of the reactants, products, and transition states for each elementary step. It is necessary to use high-level quantum-chemical methods in calculating the heat of formation, the height of the potential barrier, and the heat of reaction with an accuracy close to experimental (~1 kcal/mol). Complex multilevel theoretical procedures (for example, G1–G3 and G2M [6–9]) have been developed in the last 10–15 years.

A complex theoretical approach based on high-level quantum-chemical calculations and statistical theories is now used by several research groups [10–13] in the study of the mechanisms of gas-phase reactions. Unfortunately, multilevel quantum-chemical calculations are applicable only to small molecules containing at most ten atoms (excluding H).

In this work, we calculate the properties (geometry, the enthalpy of formation, the frequencies of normal vibrations, moments of inertia, etc.) of trinitromethane and of a number of anticipated intermediates in the thermal decomposition of this compound. The calculations are carried out with the use of two multilevel procedures in order to choose the optimal technique for the system examined. The transition states were located, and the high-pressure limit of rate constant is estimated for a number of primary monomolecular reactions involved in isomerization and dissociation.

CALCULATION PROCEDURES

Quantum-Chemical Calculations

As mentioned above, multilevel procedures such as G1 [6], G2 [7], G3 [8], and their modifications (G2M [9]) are commonly used to perform the most precise quantum-chemical calculations of energy and thermodynamic characteristics. Molecular geometry is initially optimized, and normal vibration frequencies are calculated with the use of a low-level procedure (HF, MP2, or density functional theory). After the geometry is optimized, the electron energy is calculated using a high-level procedure. Next, several additive corrections

(which are also difficult to calculate) are applied to the electron energy.

In this work, the enthalpy of formation, the Gibbs energy of activation, and other thermodynamic characteristics are mainly calculated by the G2M(CC5) method [9] and are compared with the results obtained by the G2 method [7]. The distinctions between G2M(CC5) and the well known procedure G2 are the following:

(1) The former uses the B3LYP/6-311G(d,p) method of DFT [14, 15], while the latter uses the MP2 method in geometry optimization and the Hartree–Fock (HF) method in the calculation of vibrational frequencies;

(2) The G2M(CC5) procedure employs the CCSD(T) method to take into account the electron correlation, while the G1–G3 procedures use QCISD(T);

(3) The number of additive corrections in the G2M(CC5) procedure is smaller.

We chose to use the G2M(CC5) procedure [9] in this work for the reason that DFT methods are preferable for open systems (radicals, triplet states, etc.), since the calculated wave functions do not usually contain a substantial contribution of higher spin states. Furthermore, G2M calculations are approximately 5 times less time-consuming and require less computer resources. All calculations were performed using the Gaussian 98 program package [16].

Thermodynamic potentials, such as internal energy (U), enthalpy (H), and Gibbs energy (G), were calculated according to standard formulas of statistical physics with the use of calculated vibrational frequencies and moments of inertia. The heats of formation ($\Delta H^{\mathrm{g}}_{\mathrm{f},\,298}(\mathrm{M})$) of nitroform and supposed intermediates in the gas state at $P = 1$ atm and $T = 298$ K were calculated as follows:

$$\begin{aligned}\Delta H^{\mathrm{g}}_{\mathrm{f},\,298}(\mathrm{M}) &= E_{\mathrm{el}}(\mathrm{M}) + ZPVE(\mathrm{M}) \\ &+ [H_{298}(\mathrm{M}) - H_0(\mathrm{M})] \\ -\sum_i \{E_{\mathrm{el}}(\mathrm{X}_i) &+ [H_{298}(\mathrm{X}_i) - H_0(\mathrm{X}_i)]\} \\ &+ \sum_i \Delta H^0_{\mathrm{f},\,298}(\mathrm{X}_i),\end{aligned} \qquad (1)$$

where $E_{\mathrm{el}}(\mathrm{M})$ is the total electronic energy of the molecule calculated using the multilevel procedure, $E_{\mathrm{el}}(\mathrm{X}_i)$ is the electronic energy of the ith atom calculated by the same procedure, $ZPVE$ is the zero-point vibrational energy of the molecule ($1/2\sum h\nu_i$), $[H_{298}(\mathrm{M}) - H_0(\mathrm{M})]$ is the thermal correction to the enthalpy of the molecule, and $\Delta H^0_{\mathrm{f},\,298}(\mathrm{X}_i)$ is the experimental enthalpy of formation of the ith atom.

The enthalpy of formation of the reactants, intermediate species, and transition states at an arbitrary temperature T and $P = 1$ atm were calculated using formula (1) with $H_{298}(\mathrm{M})$ and $H_{298}(\mathrm{X}_i)$ in place of $H_T(\mathrm{M})$ and $H_T(\mathrm{X}_i)$.

Estimation of the Rate Constants and Their Temperature Dependences

If a saddle point corresponding to the transition state was present on the potential energy surface (PES), the rate constant of the monomolecular decomposition or isomerization reaction at a high pressure was calculated according to transition state theory:

$$k_\infty(T) = \alpha\frac{kT}{h}\exp\left(-\frac{\Delta G^{\neq}(T)}{kT}\right), \qquad (2)$$

where α is the statistical factor (number of equivalent reaction channels) and $\Delta G^{\neq}$ is the Gibbs energy of activation in the standard state.

When the section of the potential energy surface (PES) along the reaction coordinate axis (s) had no barrier, as in the decomposition of molecules to radicals and in the inverse reaction of radical recombination, canonical variation transition state theory (CVTST) [5, 17] was used. In this theory, the transition state is viewed as the reaction coordinate $s^{\neq}$ maximizing the Gibbs activation energy $\Delta G^0(T, s)$:

$$\Delta G^{\neq}(T) = \max_s(\Delta G^0(T, s)) \qquad (3)$$

The PES section was calculated by the UB3LYP/6-311G(d,p) method (with the use of the guess = mix procedure), varying the length of the breaking bond (C–N or C–O) between 1.5 and 3.5 Å in 0.1 Å steps. For each length of the breaking bond, the other geometric parameters were fully optimized. For each structure, $(3N - 7)$ vibrational frequencies along the normal coordinates orthogonal to the reaction coordinate axis were calculated. These vibration frequencies and the calculated moments of inertia for each structure were used in the calculation of $\Delta G^0_{\mathrm{B3LYP}}(T, s)$. Unlike the PES section, the section of the free energy surface always has a maximum. It is the configuration $s^{\neq}$ corresponding to this maximum that is taken to be the transition state in variational theory. These calculations were carried out for several temperatures in the range 298–2000 K in 250-K steps, and the corresponding $\Delta G^{\neq}_{\mathrm{B3LYP}}(T)$ maximum was found for each temperature. Next, the total electron energy for each structure of the transition state $s^{\neq}(T)$ was recalculated with the use of the G2M(CC5) procedure and the refined values of Gibbs activation energy were found:

$$\begin{aligned}\Delta G^{\neq}_{\mathrm{G2M}}(T) &= \Delta G^{\neq}_{\mathrm{B3LYP}}(T) + E_{\mathrm{el}}(\mathrm{G2M}) \\ &- E_{\mathrm{el}}(\mathrm{UB3LYP}).\end{aligned} \qquad (4)$$

Table 1. Experimental and calculated heats of formation for nitro derivatives of methane and for a number of intermediates of their decomposition in the gas phase at 1 atm and 298 K

Molecule	$\Delta H^{g}_{f,298}$, kcal/mol		
	G2M(CC5) method	G2 method	experiment
$^{\bullet}NO$	19.9	21.1	21.6 [9]
$^{\bullet}NO_2$	6.1	7.4	7.9 [9]
$CH_2(NO_2)_2$	–19.5	–15.4	–14.2 ± 0.2 [21]
CH_3NO_2	–22.6	–20.5	–19.3 ± 0.3 [21]
			–16.8 [22]
$CH(NO_2)_3$	–12.4	–6.2	–0.2 ± 0.5 [23]
	–5.2[a]		–3.2 ± 0.8 [24]
	–7.7[b]		5.8 [25]
$CH(NO_2)_2ONO$	–23.2	–17.0	–
$C(NO_2)_2NOOH$	7.1	13.5	–
$^{\bullet}CH(NO_2)_2$	33.9	37.0	33.2; 37.5 [18]
$^{\bullet}C(NO_2)NOOH$	65.3	67.6	–
$CH(NO_2)$	77.3	–	–
$HC(O)NO$	–0.4	–2.8	–
$HC(O)NO_2$	–38.0	–34.9	–
$C(NO_2)NO$	57.5	59.0	–

[a,b] Estimated from the calculated enthalpy of the isodesmic reaction (V) and from the experimental enthalpy of formation of CH_3NO_2 and $CH_2(NO_2)_2$ according to data reported in (a) [23] and (b) [24].

The temperature dependences of the rate constants of the dissociation reactions in the high-pressure limit were calculated according to formula (2) with the use of the free activation energy values calculated by formula (4). The dependences calculated were then fitted to the Arrhenius equation

$$k = A\exp(-E_a/RT). \quad (5)$$

RESULTS AND DISCUSSION

The primary reaction in the thermal decomposition of **1** is dissociation [18]:

$$\underset{\mathbf{1}}{HC(NO_2)_3} \xrightarrow{k_1} \underset{\mathbf{2}}{^{\bullet}CH(NO_2)_2} + {}^{\bullet}NO_2. \quad (I)$$

As in the case of nitromethane monomolecular decomposition [18–20], the isomerization of **1** into nitrite **3** may compete with dissociation:

$$\underset{\mathbf{1}}{HC(NO_2)_3} \xrightarrow{k_2} \underset{\mathbf{3}}{HC(NO_2)_2ONO}. \quad (II)$$

In this work, the dissociation of radical **2** to radical $^{\bullet}NO_2$ and carbene **4** in the singlet state (reaction (III)), followed by the isomerization of the singlet carbene into aldehyde **5** (reaction (IV)), were analyzed along with the reactions of the starting compound **1**.

$$\underset{\mathbf{2}}{^{\bullet}CH(NO_2)_2} \xrightarrow{k_3} \underset{\mathbf{4}}{:CH(NO_2)} + {}^{\bullet}NO_2, \quad (III)$$

$$\underset{\mathbf{4}}{:CH(NO_2)} \xrightarrow{k_4} \underset{\mathbf{5}}{HC(=O)NO} \quad (IV)$$

Calculation of the Heats of Formation

Before calculating the transition states and/or PES sections for reactions (I)–(IV), we calculated the enthalpy of formation for nitroform and for the intermediates assumed for its thermal decomposition. We used two multilevel quantum-chemical procedures in order to choose the most optimal technique for the system under consideration. Furthermore, we calculated the heat of formation for a number of simpler methane derivatives for which experimental heats of formation are available from the literature. All of the calculated heats of formation refer to the gas phase. For compounds whose standard state is condensed, we used, for comparison, the experimental heat of formation in the liquid or solid phase corrected for the heat of evapora-

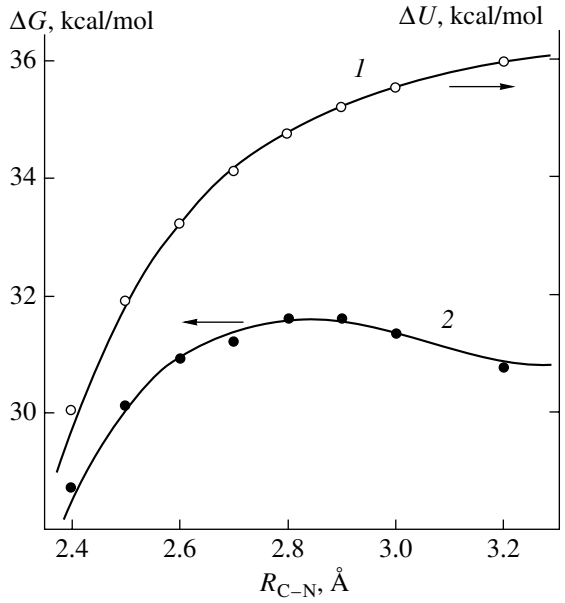

Fig. 1. (*1*) PES section and (*2*) Gibbs energy for reaction (I) calculated as a function of the reaction coordinate by the B3LYP/6-311G** method.

tion or sublimation. The calculated and experimental data are presented in Table 1.

As can be seen in Table 1, the G2 procedure allows the enthalpy of formation of nitro compounds to be calculated with a high degree of accuracy (about ~1 kcal/mol). The only exception is nitroform. However, the experimental data for nitroform are also widely scattered. For this reason, we estimated this parameter from the calculated enthalpy of the isodesmic reaction (V), in which the number of bonds of a given type is invariable.

$$2CH_2(NO_2)_2 \longrightarrow CH_3NO_2 + CH(NO_2)_3. \qquad (V)$$

The enthalpy of appropriate isodesmic reactions can be calculated with a high accuracy even using low-level procedures. For example, the enthalpy of reaction (V) calculated by the B3LYP/6-311G(d,p), G2M(CC5), and G2 methods is 5.6, 4.0, and 3.8 kcal/mol, respectively. The heat of formation of **1** derived from the enthalpy of reaction (V) (–5.2 and –7.7 kcal/mol, Table 1) is significantly lower than most of the experimental values and is close to the value calculated by the G2 method (–6.2 kcal/mol). Hence, the experimental enthalpies of formation of nitroform need to be refined.

As is clear from Table 1, the G2M(CC5) heats of formation are systematically underestimated as compared to the experimental and G2 values. The deviations increase nearly additively (by 1.5–2 kcal/mol) with increasing number of NO_2 groups in the molecule. Therefore, it can be expected that the accuracy of the calculation of heat, the Gibbs energy of activation, and the enthalpy of activation for the reactions examined will be substantially higher. For instance, the heat of reaction (I) at 298 K calculated by the G2M(CC5) method is 52.4 kcal/mol, and the same heat calculated by the G2 method is 50.6 kcal/mol.

When these quantities are calculated by the G2M(CC5) procedure, the errors are partially compensated and the calculation time is much shorter (in comparison with G2). In addition, reactions involving free radicals, for which the HF method and perturbation theory (MP2) can lead to large errors, were of great interest in this work. This is the reason why we chose the G2M(CC5) procedure.

Calculation of Transition State Structures (or PES Sections) and Reaction Rate Constants in the High-Pressure Limit

As mentioned above, the decomposition reactions yielding radicals have no energy barrier. Therefore, to calculate the rate constant of such a reaction, one should use canonical variational transition state theory (CVTST) and calculate a PES section.

1. Calculation of the rate constant of nitroform dissociation (reaction (I)). Figure 1 shows the PES section for reaction (I). The calculations were carried out by the UB3LYP/6-311G(d,p) method by varying the C–N bond length with full optimization with respect to the other coordinates. As was expected, no maximum on the PES section and, accordingly, no saddle point on the PES were found.

Figure 1 plots the Gibbs energy as a function of the reaction coordinate at 298 K. This curve has a maximum. The structure corresponding to the Gibbs energy maximum is taken to be the transition state at the specified temperature, in accordance with variational theory.

Similar calculations for the PES section were performed at various temperatures between 298 and 2000 K in 250-K steps. The calculated values of the Gibbs energy of activation were corrected according to formula (4). The Gibbs energies of activation at 298 to 2000 K are in the range 44.4–37.0 kcal/mol.

The temperature dependence of the rate constant of reaction (I) in the high-pressure limit was calculated using formula (2). As is clear from Fig. 2, this dependence is satisfactorily described by the Arrhenius law (5). Table 2 presents the corresponding parameters of the Arrhenius equation (preexponential factor A and activation energy E_a) and the rate constants at the ends of the temperature range examined. The calculated parameter $A = 10^{15.3 \pm 0.1}$ s^{-1} is in satisfactory agreement with the value $A = 10^{15.6}$ s^{-1}, which is accepted in the literature for simple C–N bond dissociation reactions [20].

2. Calculation of the rate constant of nitroform isomerization (reaction (II)). The heat of formation of nitrite **3**, a nitroform isomer, was found to be much lower ($\Delta H^g_{f,298} = -23.2$ kcal/mol) than the correspond-

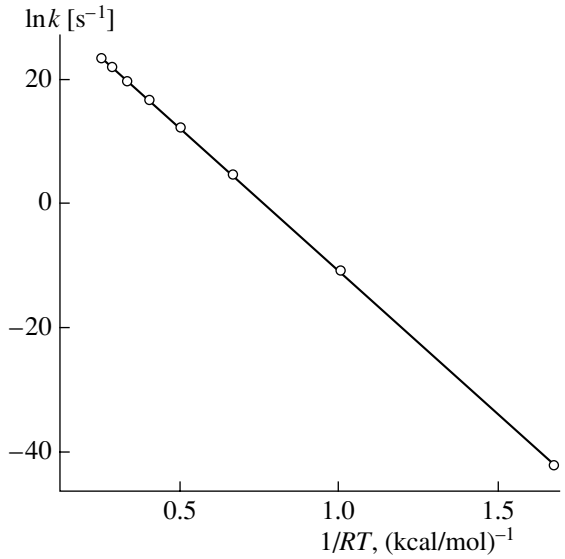

Fig. 2. Arrhenius plot of the high-pressure limit of the rate constant of reaction (I).

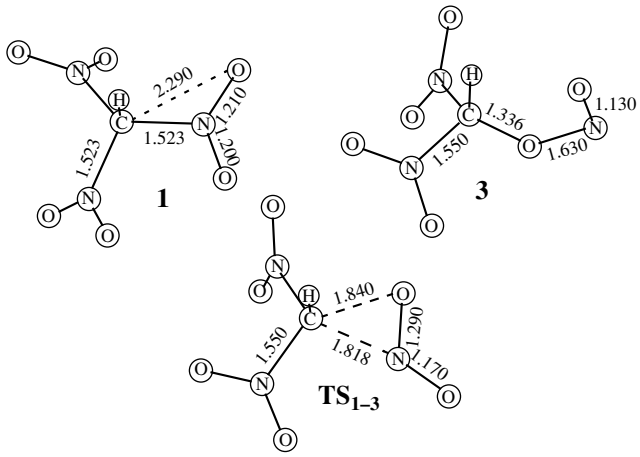

Fig. 3. Geometries (bond lengths in Å) of trinitromethane (*1*), the isomeric nitrite (*3*), and the transition state in the isomerization of **1** into **3** (**TS_{1-3}**) calculated by the B3LYP/6-311G** method.

ing value for nitroform itself. In other words, molecule **3** in the gas phase is thermodynamically more favorable than **1**. In addition, it is known that, in the case of monomolecular decomposition of nitromethane and other nitroalkanes, isomerization into the corresponding nitrite competes with dissociation [18–20]. Therefore, it is necessary to calculate the rate constant of the isomerization reaction (II) and to compare it to k_1.

We located the transition state of this reaction, whose geometrical structure is presented in Fig. 3. We confirmed (with the aid of the IRC procedure) that this structure indeed corresponds to the saddle point on the way between reactant **1** and product **3**. Furthermore, Fig. 3 shows the calculated geometries of nitroform and product **3**. Note that the transition state for the nitro–nitrite rearrangement of nitromethane has repeatedly been calculated [19, 26, 27]. In [19], the geometry of the transition state was calculated by various methods (PM3, HF, B3LYP, CASSCF, and MP2) and all of them led to the same structure of the transition state. Note that the geometry of the CNO_2 moiety in the transition state calculated by us (Fig. 3) is close to that found for the transition state of nitromethane isomerization [19].

The calculated O–N bond length in nitrite **3** (1.63 Å) is appreciably longer than was expected. HF calculations gave a "normal" length of the O–N bond (1.395 Å), while the bond length obtained by MP2 calculations (1.715 Å) was even greater than the B3LYP value. The O–N bond in the nitrite is likely to be extraordinarily long. This is due to the steric strain in this molecule. Note that all of the calculation methods used here lead to a normal O–N bond length comparing well with the experimental value (1.418 Å [28]) for nitrite CH_3ONO (HF, 1.336 Å; MP2, 1.415 Å, and B3LYP, 1.434 Å).

Although reaction (II) is exothermic, its activation barrier is very high (Table 2). The Gibbs energy of activation at 298 K is, for instance, 64.8 kcal/mol. Correspondingly, the high-pressure limit of the rate constant at 2000 K is $k_2 = 1.2 \times 10^7$ s^{-1}. This is 3 orders of magnitude lower than the rate constant of dissociation (k_1) at the same temperature. Thus, in accordance with current views [18], this reaction channel should not play an essential role in nitroform decomposition.

Table 2. Gibbs energies of activation, rate constants, and parameters of the Arrhenius equation for reactions (I)–(III) at 298 and 2000 K calculated with the use of the conventional and variational transition state approaches and the G2M method

Reaction	$\Delta G^{\neq}_{G2M}$, kcal/mol		log$k$ [s^{-1}]		log$A$[s^{-1}]	E_a, kcal/mol
	298 K	2000 K	298 K	2000 K		
(I)	44.4	37.0	–18.4	10.2	15.3 ± 0.1	47.1 ± 0.2
(II)	64.8	64.7	–30.7	7.1	13.7 ± 0.1	61.2 ± 0.4
(III)	43.8	21.4	–18.8	11.6	16.9 ± 0.1	49.1 ± 0.2

Table 3. Enthalpies and Gibbs energies of activation for reaction (IV) calculated by various methods

Method	ΔH_r(298 K), kcal/mol	$\Delta G^{\neq}$(298 K), kcal/mol
B3LYP/6–311G(d,p)	–74.8	0.25
CCSD(T)/6–311G(d,p)	–82.6	0.59
G2M(CC5)	–77.9	–0.68

3. Calculation of the rate constant of the decomposition of the radical $^{\cdot}CH(NO_2)_2$ (reaction (III)). Unlike the decomposition of molecule **1** into two radicals (reaction (I)), in this case the radical decomposes to a radical and a singlet species (singlet carbene). The heat of this reaction (ΔH_{298}) is 49.5 kcal/mol (G2M(CC5) method). Calculations have shown that there is an energy barrier in this reaction. The transition state was located by the B3LYP/6-311G(d,p) method, and the barrier height was refined by the G2M(CC5) procedure.

The Gibbs energy of activation at various temperatures was calculated with the use of the transition state configuration corresponding to the saddle point on PES. The rate constant of reaction (III) in the high-pressure limit (k_3) in the temperature range 298–2000 K was found by formula (2). The temperature-dependent activation energy data were then fitted to the Arrhenius equation (5). The A and E_a values thus found are presented in Table 2.

4. Calculation of the rate constant of singlet carbene isomerization (reaction (IV)). Singlet carbene **5** is one of the products of reaction (III). It is well known that carbene has two close-lying low electronic states, a singlet and a triplet [29, 30]. The triplet is the ground state for the simplest carbene, CH_2, and for some of its derivatives [29], whereas the singlet is the ground state for other carbenes, for example, halocarbenes [30].

We calculated the electron structure of the carbene $CHNO_2$ in both triplet and singlet electronic states by the B3LYP/6-311G(d,p) method. Note that density functional theory often provides a better description for the properties of carbenes than other, more time-consuming methods [31, 32].

According to our calculations, the singlet state is ground for the carbene $CHNO_2$. The energy of the triplet state is higher by 6.8 kcal/mol. For this reason, the formation and reactions of triplet carbene are not considered in this work.

We analyzed the isomerization of the singlet carbene $CHNO_2$ (reaction (IV)). Table 3 presents the enthalpy and the Gobbs energy of activation for this reaction calculated by various quantum-chemical methods. The isomerization reaction (IV) is highly exothermic, and, therefore, its activation barrier is very low. According to the G2M(CC5) calculations, the Gibbs energy of activation is negative. This means that carbene isomerization has a negligible (≤1 kcal/mol), if any, energy barrier; hence, the reaction is extremely fast ($k_4 \approx 10^{12}$–10^{13} s^{-1}).

Thus, the primary stage of nitroform decomposition **1** is the formation of the radicals $^{\cdot}NO_2$ and $^{\cdot}CH(NO_2)_2$ through reaction (I). Nitroform isomerization (channel (II)) is unimportant. The radical $^{\cdot}CH(NO_2)_2$ then decomposes to form $^{\cdot}NO_2$ and singlet carbene, and the carbene rapidly isomerizes to HC(O)NO. We intend to calculate the rate constants of the above reactions in a wide pressure range with the use of the kinetic networks of PPKM theory [5] instead of the transition state approach.

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