Theoretical study of the trinitromethane thermal decomposition: thermodynamics and rate constants of elementary reactions

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Density functional theory at the B3LYP/6-311G** level has been used to optimise geometry of nitroform $CH(NO_2)_3$ and some intermediates of its decomposition ($CH(NO_2)_2$, $CH(NO_2)_2ONO$, $CH(NO_2)$, $HC(O)NO$). Transition states for some dissociation and isomerization reactions involving those intermediates were located. The heat of formation for nitroform and its decomposition intermediates as well as free energies of activation of the reactions were calculated using up-to-date *ab initio* multilevel quantum chemical approaches G2M(CC5) and G2. Rate constants of the reactions at high pressure limit in the temperature range of 300 to 2000 K were calculated using transition state theory or its variation analogue.

INTRODUCTION

Trinitromethane (nitroform, **1**) is used to synthesise some high energy materials (HEM) and is involved as an intermediate in the decomposition of HEM. Specifically, it is formed under thermal decomposition of hydrazine nitroformate, a promising oxidant being a component of solid rocket fuel [1–3]. Note that the problem of replacement of ammonium perchlorate by a chlorine-free oxidant is of special significance at present in connection with a task of reducing ecological damage arising from launching solid fuel missiles. Information on thermodynamic characteristics of **1** and intermediates of its decomposition as well as rate constants of elementary reactions involving those intermediates is required to create kinetic models for complex processes of HEM combustion.

To construct detail kinetic mechanisms of combustion of HEM one has to know rate constants of all elementary reactions. Unfortunately, there are experimental data for only a few rate constants; the information on most part of the proposed reactions is lacking. That is why the problem of theoretical calculation of rate constants as well as their temperature and pressure dependencies is urgent nowadays. Such calculations are frequently being accomplished using Rice — Ramsperger — Kassel — Marcus (RRKM) statistical theory [4, 5].

Its application, in turn, demands to know structure and properties of reagents, products, intermediates and transition states of each elementary reaction. One has to use high-level quantum-chemical methods in order to calculate such properties as formation enthalpy, height of potential barriers, heats of reactions with accuracy close to the experimental one (~1 kcal/mol). During last

10–15 years complicated multilevel theoretical procedures have been developed, e. g. G1-G3 or G2M [6–9].

Several research groups are studying now mechanisms of gas phase reactions using high-level quantum chemical calculations [10–13]. Unfortunately, multilevel quantum chemical calculations can be carried out only for small molecules with number of atoms (other than H) of order of ten or less.

This work presents calculations of properties (geometry, enthalpy of formation, frequencies of normal vibrations, moments of inertia and so on) of trinitromethane and series of proposed intermediates of its thermal decomposition. The calculations were carried out using two multilevel procedures to choose the most optimal one for the system under consideration. Furthermore, transition states were localised and rate constants at high pressure limit of some primary unimolecular isomerization and dissociation reactions were estimated.

COMPUTATIONAL PROCEDURES

Quantum chemical calculations

The most accurate quantum chemical calculations of energy and thermodynamic characteristics are carried out using such multilevel procedures as G1 [6], G2 [7] and G3 [8] or their modification (G2M [9]). In the course of those calculations geometry of molecule is optimised first of all and frequencies of normal vibrations are calculated using HF or DFT procedures. Then the electron energy is calculated for an optimised geometry using one of the high-level methods. After that the electronic energy is corrected on some additive terms which calculation is also sufficiently complicated.

In this work calculations of formation enthalpy, free energy of activation and other thermodynamic characteristics were carried out mainly by method G2M(CC5) [9], results obtained using method G2 being used for comparison [7].

Heats of formation ($\Delta H_{f,298}^{gas}(M)$) for nitroform (**1**) and proposed intermediates in gas phase at pressure *p*=1 atm and temperature *T*=298 K were calculated as follows.

$$\Delta H_{f,298}^{gas}(M) = E_{el}(M) + ZPVE(M) + \left[H_{298}(M) - H_0(M)\right] -$$
$$- \sum_i^{atoms} \left\{E_{el}(X_i) + \left[H_{298}(X_i) - H_0(X_i)\right]\right\} + \sum_i^{atoms} \Delta H_{f,298}^0(X_i), \tag{1}$$

where $E_{el}(M)$ is a complete electronic energy of a molecule calculated using multilevel technique; $E_{el}(M)$ is an electronic energy of *i*-th atom calculated using the same technique; *ZPVE* is an energy of molecule's zero-point oscillations ($\frac{1}{2}\sum h\nu_i$); $\left[H_{298}(M) - H_0(M)\right]$ is a thermal

correction to molecule's enthalpy; $\Delta H^0_{f,298}\left(X_i\right)$ is an experimental value of i-th atom enthalpy of formation.

Estimations of rate constants at high pressure limit and their temperature dependence

In the case when there is a saddle point on the potential energy surface (PES) corresponding to a transition state, calculation of rate constants of monomolecular reactions of decomposition or isomerization was carried out for high pressure limit according to the transition state theory (2):

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

where α is a statistical factor (number of equivalent reaction channels), ΔG^* is activation free energy in a standard state.

If there is no barrier on the PES along the reaction coordinate (s) (this situation is typical for reactions of closed-shell molecule decomposition into radicals or reverse reaction of radical recombination), canonical variational transition state theory (CVTST) was used [5]. According to this theory the transition state is assumed to correspond to the point $s^{\ddagger}$ on the cross-section of PES where free energy of activation $\Delta G^0(T,s)$ reaches a maximum.

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

To find $\Delta G^{\neq}$ for each temperature, we first scanned the potential energy surface for dissociation into products. The dissociating C-N distance was varied from 1.5 to 3.5 Å at intervals of 0.1 Å; other geometric parameters were optimized for each value of C-N at B3LYP level. For each structure, we calculated the (3N-7) vibrational frequencies, projected out of the gradient direction. To obtain more reliable energies, we also performed G2M(CC5) calculations for each structure, corresponding to transition state at a fixed temperature. The G2M(CC5) potential energy, computed moments of inertia, and vibrational frequencies were used for calculation of $\Delta G^{\neq}$ at temperatures in the range 300-2000 K with step 250K.

Temperature dependences of the dissociation reactions rate constants at high-pressure limit were calculated according to (2), using the maximum $\Delta G^{\neq}$. Then the obtained temperature dependences were approximated with Arrhenius equation

$$k = A\exp(-E_a / RT). \qquad (4)$$

RESULTS AND DISCUSSION

Dissociation reaction (I) is a primary reaction at thermal decomposition of **1**.

$$HC(NO_2)_3 \xrightarrow{k_1} \bullet CH(NO_2)_2 + \bullet NO_2 \quad (I)$$
$$\textbf{1} \qquad\qquad\qquad \textbf{2}$$
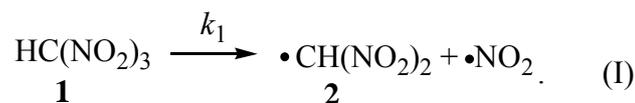
Isomerization reaction giving nitrite **3** may compete with dissociation (just as in the case of nitromethane decomposition [14])

$$HC(NO_2)_3 \xrightarrow{k_2} HC(NO_2)_2ONO \quad (II)$$
$$\textbf{1} \qquad\qquad \textbf{3}$$
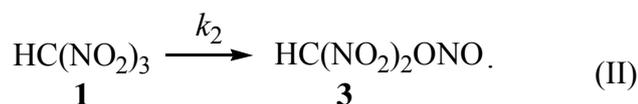
In addition to reactions of sturting material **1**, we have investigated the dissociation of radical **2** into radical NO_2 and carbene **4** in its singlet state (III) and subsequent isomerization of singlet carbene into aldehyde **5** (IV).

$$\bullet CH(NO_2)_2 \xrightarrow{k_3} \text{:}CH(NO_2) + \bullet NO_2 \quad (III)$$
$$\textbf{2} \qquad\qquad \textbf{4}$$

$$\text{:}CH(NO_2) \xrightarrow{k_4} HC\overset{O}{\underset{NO}{\diagup}} \quad (IV)$$
$$\textbf{4} \qquad\qquad \textbf{5}$$
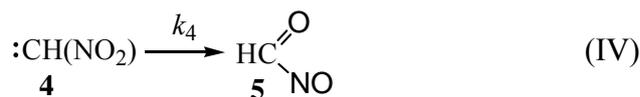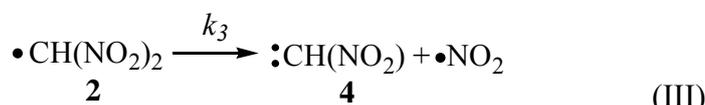
Calculation of formation enthalpy

Before proceeding calculations of transition states and/or cross-sections of PES for reactions (I) to (IV) we had calculated enthalpies of formation for nitroform **1** and a series of proposed intermediates of its thermal decomposition using two multilevel quantum chemical procedures in order to select the most optimal one for the system under consideration. Enthalpies of formation for a series of more simple nitro-derivatives of methane for which experimental data are known from the literature were also calculated. All the calculated data refer to gas phase. If a standard state of a substance is a condensed phase, experimental values of formation enthalpy were calculated from the data for liquid or solid phase using evaporation or sublimation heats. Results of calculations along with experimental data are given in Table 1.

Table 1 demonstrates that, indeed, G2 method allows one to calculate formation enthalpy of nitrocompounds with fairly good accuracy of about 1 kcal/mol. The only exception is nitroform **1**. Nevertheless, experimental values for nitroform also differ from each other dramatically. Therefore we estimate this magnitude using the calculated value of enthalpy for isodesmic (i. e. without changing the number of the same type bonds) reaction (V).

Table 1. Experimental and calculated values of formation heat in gas phase ($\Delta H_{f,298}^{\text{gas}}$) for nitro-derivatives of methane and intermediates at pressure 1 atm and temperature 298 K

Molecule	$\Delta H_{f,298}^{\text{gas}}$, kcal/mol		
	Method G2M(CC5)	Method G2	Experiment
$\cdot NO$	19.9	21.1	21.6 [9]
$\cdot NO_2$	6.1	7.4	7.9 [9]
$CH_2(NO_2)_2$	−19.5	−15.4	$−14.2 \pm 0.2$ [15]
CH_3NO_2	−22.6	−20.5	$−19.3 \pm 0.3$ [15]
			−16.8 [16]
$CH(NO_2)_3$	−11.5	−6.2	$−0.2 \pm 0.5$ [17]
	−5.2[a]		$−3.2 \pm 0.8$ [18]
	−7.7[b]		5.8 [19]
$CH(NO_2)_2ONO$	−23.2	−17.0	—
$C(NO_2)_2NOOH$	7.1	13.5	—
$\cdot CH(NO_2)_2$	33.9	37.0	—
$\cdot C(NO_2)NOOH$	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 a calculated value of enthalpy for isodesmic reaction (V) and experimental values of enthalpy of formation of CH_3NO_2 and $CH_2(NO_2)_2$ according to [15] (a) and [16] (b), respectively.

$$2\ CH_2(NO_2)_2 \longrightarrow CH_3NO_2 + CH(NO_2)_3 \qquad (V)$$
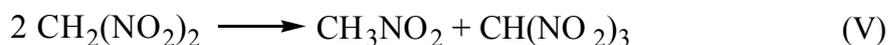
If the choice of isodesmic reactions is correct, one can compute the enthalpy of reaction with the good accuracy even by low level quantum chemical methods. For example, the enthalpy of reaction (V) is 5.6, 4.0 and 3.8 kcal/mol at B3LYP/6-311G(d,p), G2M(CC5) and G2 levels, respectively. Calculated in this way the enthalpy of formation for **1** (-5.2 and -7.7 kcal/mol, table 1) is significantly smaller than experimental ones and it is close to G2 value (-6.2 kcal/mol). So it is necessary to perform additional experiments to define the enthalpy of formation of nitroform more precisely.

As it follows from the Table 1, G2M(CC5) procedure systematically underestimates the enthalpies of formation of investigated species in comparison with both experimental and G2 methods. It is seen also, that errors grow additively with the number of NO_2 groups in the molecule. So, one should expect more precise results for the reaction enthalpies and activation enthalpies for the investigated reactions. For instance the enthalpy of reaction (I) at 298 K is 51.5 kcal/mol at G2M(CC5) level of theory and 50.6 kcal/mol at G2 level.

Taking into account that the reactions involving radicals (for which Hartree — Fock level and Moller-Plesset perturbation theory give significant errors) were of significant interest in the present work, that the errors of procedure G2M(CC5) are partly compensated and time of calculation essentially decreases (as compared to G2), the G2M(CC5) method had been chosen for calculations. All the calculations have been performed using Gaussian-98 suit of programs [20].

Calculations of transition state structures (or PES cross-sections) and rate constants at high-pressure limit

1. Calculation of rate constant for nitroform dissociation reaction (I)
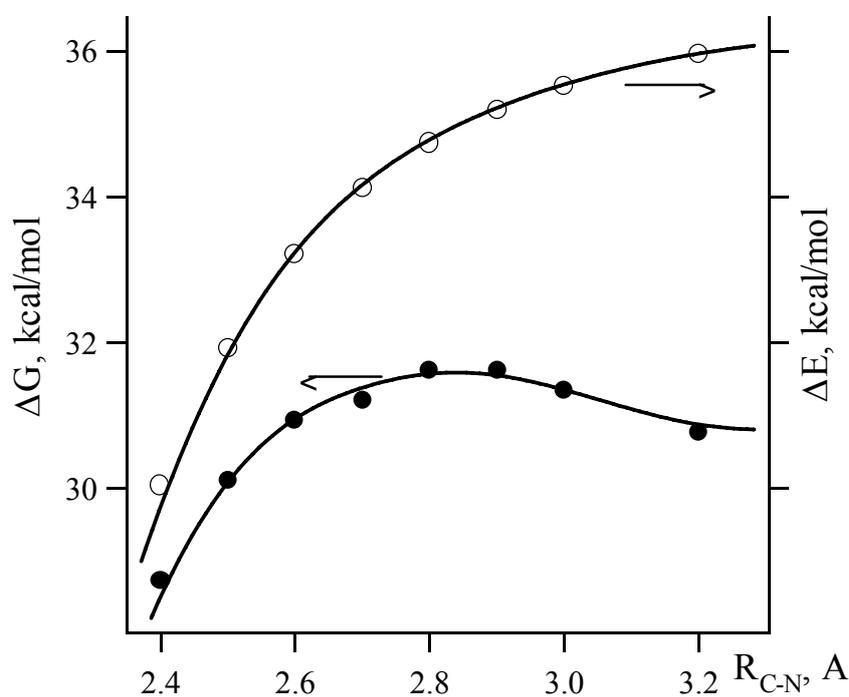
Figure 1. PES cross-section for reaction (I) (hollow circles) and dependence of free energy on the reaction co-ordinate (solid circles) as calculated using B3LYP/6-311G** procedure

Fig. 1 shows the PES cross-section for reaction (I). Calculations were carried out using B3LYP/6-311G(d,p) procedure with variation of C–N bond length and full optimisation over all other co-ordinates. As one could expect, there is no maximum on the curve and hence there is no saddle point on the PES.

Fig. 1 shows as well Gibbs free energy dependence on reaction co-ordinate at 298 K. One can see that there is a maximum in this case. The structure corresponding to the maximum of free energy is proposed to be a transition state at this temperature, according to the canonical variational TST.

At high-pressure limit (2) temperature dependence of rate constant of reaction (I) $k_1(T)$ had been calculated. Table 2 shows Arrhenius parameters (A and E_a) for this reaction along with the rate constant change within the range of temperatures under consideration. The calculated value of $A = 10^{15.3 \pm 0.1}$ parameter agrees fairly well with the value $A = 10^{15.6}$ accepted in the literature for reactions of C–N bond dissociation [14].

Table 2. Calculated values of the activation free energy ($\Delta G^{\#}_{G2M}(T)$) and rate constants for reactions (I) - (III) at various temperatures. The values of pre-exponential factors (A) and activation energies (E_a) obtained by Arrhenius approximation of the calculated rate constants temperature dependences for the reactions are also shown.

Reaction	$\Delta G^{\#}_{G2M}(T)$		lg k		lg A	$E_{a,}$ kcal/mol
	298 K	2000 K	298 K	2000 K		
(I)	43.5	36.1	−18.4	10.2	15.3 ± 0.1	46.2 ± 0.3
(II)	75.0	75.1	−41.8	5.4	13.7±0.1	76.4±0.4
(III)	43.8	21.4	−18.8	11.6	16.9±0.1	49.1± 0.2

2. Calculation of the rate constant for nitroform isomerisation reaction (II)

It was founded that for the nitroform isomer, nitrite **3**, heat of formation turned out to be essentially lower ($\Delta H^{gas}_{f,298} = -23.2$ kcal/mol) than the corresponding value for nitroform. Therefore in gas phase substance **3** is thermodynamically more preferable than **1**. Besides, it was reported that in the case of monomolecular decomposition of nitromethane the isomerization reaction giving nitrite competes with dissociation [14]. Because of these facts, it is necessary to calculate rate constant for isomerisation reaction (II) and compare it with k_1.

The transition state for this reaction was localized (Fig. 2). According to the calculation O–N bond in nitrite **3** was found to be noticeably longer than one could expect reasoning from the characteristic values. At the same time, calculations at Hartree — Fock level give the "normal" length of O–N bond (1.395 Å). However, according to the results obtained with MP2 procedure this bond proves to be even longer (1.715 Å) than one obtained with B3LYP. Apparently for nitrite **3** an abnormally long O–N bond should be observed due to a steric tension in this molecule. Note that for nitrite CH_3ONO all the applied computational procedures give the normal length of O–N bond (HF — 1.336 Å, MP2 — 1.415 Å, B3LYP — 1.434 Å) which is in good agreement with experimental data (1.418 Å [21]).
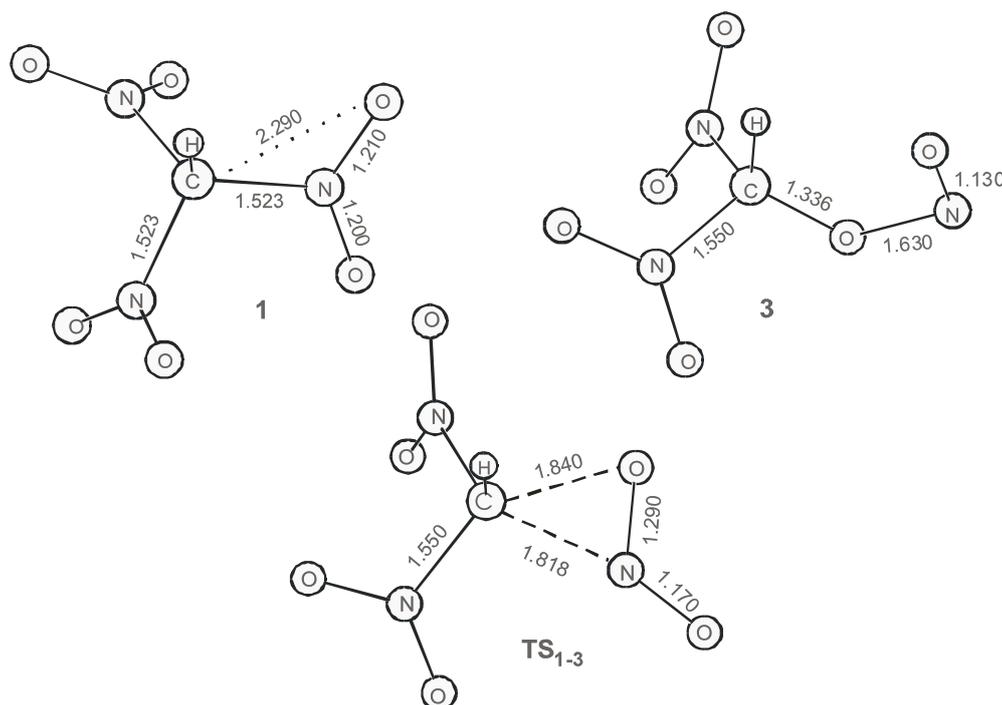
Figure 2. Geometry (bond lengths in Å) of trinitromethane (**1**), its isomer - nitrite **3** and transition state for the isomerization of **1** into **3** (**TS$_{1-3}$**) calculated at the B3LYP/6-311G** level.

In spite of the fact that reaction (II) is exothermic its activation barrier proved to be very high (Table 2). Respectively, the value of rate constant at high-pressure limit (2), e. g. at 2000 K, is $k_2 = 3.9 \cdot 10^4$ c^{-1}. One can see (Table 1) that it is about 5 orders of magnitude lower than the value of dissociation rate constant (k_1) at this temperature. Thus, this reaction channel cannot play an important role in nitroform decomposition.

3. Calculation of the rate constant for radical •CH(NO$_2$)$_2$ dissociation

In contrast to the reaction of molecule **1** decomposition into two radicals (I), in this case the decomposition of radical into radical and a singlet particle (singlet carbene) takes place.

$$CH(NO_2)_2\bullet \rightarrow CHNO_2 + \bullet NO_2 \qquad\qquad (III)$$
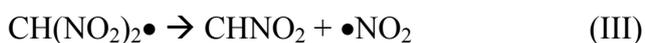
Enthalpy of this reaction (ΔH_{298}) amounts 49.5 kcal/mol (G2M(CC5) procedure). Calculations show that this reaction has a barrier. Transition state had been localised using B3LYP/6-311G(d,p) level of theory and then the barrier height was recalculated using G2M(CC5) procedure.

Rate constant of reaction (III) in the temperature range of 298–2000 k at high-pressure level (k_3) was calculated according to (2). Then the obtained temperature dependence was approximated with Arrhenius equation (4). The values of pre-exponential factor and activation energy for k_3 are shown in Table 2.

4. Calculation of the rate constant for singlet carbene isomerization reaction (IV)

One of the products of reaction (III) is singlete carbene **5**. It is well known for carbenes that two rather close to each other lowest electronic states exist, a singlet and a triplet one [22, 23].

Carbene $CHNO_2$ electronic structure both in singlet and in triplet electronic state were optimized using B3LYP/6-311G(d,p) procedure. Note that the carbenes can be described fairly well by density functional theory; often such description is even better than that made using high levels of theory [24, 25].

According to the calculations carried out in this work the ground state of carbene $CHNO_2$ is a singlet one. Triplet state is 6.8 kcal/mol higher in energy at B3LYP/6-311G(d,p) level, so we do not consider formation and reactions of triplet carbene here.

The singlet carbene $CHNO_2$ isomerization reaction was investigated.

$$CHNO_2 \rightarrow HC(O)NO \qquad\qquad (IV)$$

Table 3 shows the values of enthalpy of reaction and free energy of activation for this reaction calculated using various quantum chemical procedures.

Procedure	ΔH_r(298 K), kcal/mol	$\Delta G^{\#}$(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

Table 3. Calculated values of the reaction enthalpy ΔH_r (298 K) and activation free energy $\Delta G^{\#}$ (298 K) for singlet carbene (**4**) isomerisation (IV).

It has been found that isomerization reaction is highly exothermic, therefore barrier for this reaction is very low. G2M(CC5) method even delivers negative value of free energy of activation.

This is the evidence of the fact, that carbene isomerization should occur either with a negligible barrier (≤ 1 kcal/mol), or without any barrier at all and hence extraordinary fast ($k_4 \approx 10^{12} - 10^{13} c^{-1}$).

Thus it is found that primary stage of nitroform **1** decomposition is reaction of its decomposition giving radicals NO_2 and $CH(NO_2)_2$ (I). Nitroform isomerization (channel II) has no significance. Then $CH(NO_2)_2$ radical decomposes giving NO_2 and singlet carbene (**4**). The latter undergoes isomerization giving HC(O)NO. Further we intend to carry out calculation of rate constants for the reactions at wide pressure range, when one should use kinetic schemes of RRKM theory [5] instead of TST or its variational analogues.

REFERENCES

1. *J. Louwers,A.E.D.M van der Heijden* // Hydrazinium nitroformate based high performance solid propellants, EP 0 959 085, May 20, 1998.

2. *H.F.R. Schoyer,W.H.M.Welland-Veltmans, J. Louwers, P.A.O.G. Korting, A.E.D.M. van der Heijden, H.L.J. Keizers, R.P. van der Berg* // Journal of Propulsion and Power. 2002. V. 18. P. 131.

3. *H.F.R Schoyer, W.H.M. Welland-Veltmans, J. Louwer, P.A.O.G. Korting, A.E.D.M. van der Heijden, H.L.J. Keizers, R.P. van der Berg* // Journal of Propulsion and Power. 2002. V. 18. P. 138.

4. *P. Robinson, K. Holbrook* Unimolecular reactions. Wiley-Interscience. 1972.

5. *K. Holbrook, M. Pilling, S. Robertson.* Unimolecular reactions. Chichester: Wiley.1996.

6. *J.A. Pople, M. Head-Gordon, D. Fox, K. Raghavachari, L.A. Curtiss* // J. Chem.Phys. 1989. V. 90. P. 5622.

7. *L.A. Curtiss, K. Raghavachari, G.W. Trucks, J.A. Pople* // J. Chem.Phys. 1991. V. 94. P. 7221.

8. *L.A. Curtiss, K. Raghavachari, et. al.* // J. Chem.Phys. 1998. V. 109, P.7764.

9. *A.M. Mebel, K. Morokuma, M.C. Lin* // J. Chem. Phys. 1995. V. 103. P. 7414.

10. *E.W.G. Diau, M.C. Lin* // J. Phys. Chem. 1995. V. 99. P. 6589.

11. *C.-C. Hsu, A.M. Mebel, M.C. Lin* // J. Chem. Phys. 1996. V. 105. P. 2346.

12. *G.S. Kim, T.L. Nguyen, A.M. Mebel, S.H. Lin, M.T. Nguyen* // J. Phys. Chem. A. 2003. V. 107. P. 1788.

13. *R.S. Zhu, M.C. Lin* // J. Chem. Phys. 2003. V. 119. P. 10667.

14. *A. M. Wodtke, E. J. Hintsa, Y. T. Lee* // J. Phys. Chem. 1986. V. 90. P. 3549.

15. *U. K. Knobel, E. A. Miroshnichenko,U. A. Lebedev* // Izvestia, Chemistry, 1971, V.3. P. 485.

16. *C.F. Melius* // J. Physique IV. 1995. V. 5. C4-535.

17. *E. A. Miroshnichenko,U. A. Lebedev, S. A. Shevelev, V. I. Gulevskaya, A.A. Fainzilberg, A. Y. Apin* // Russian Journal of Physical Chemistry. 1967. V. 41., P.1477.

18. *A.Carpenter, M.F. Zimmer, E.E.Baroody, R.A.Robb* // J. Chem. Eng. Data. 1970. V. 15. P. 553.

19. *Y.N. Matyushin, V.P Lebedev, E.A. Miroshnichenko, L.M. Kostina, Y.O. Inozemcev* // Energetic Materials. Analysis, Diagnostics and Testing, Meterials of 31 International Annual Conference of ICT, Karlsruhe. 2000. 51.

20. Gaussian 98, Revision A.6, *M.J Frisch, G.W. Trucks, H.B Schlegel, et al*. Gaussian, Inc., Pittsburgh PA. 1998.

21. *B.J. van der Veken, R. Maas, G.A. Guirgis, H.D. Stidham, T.G. Sheeham, J.R. Durig* // J. Phys. Chem. 1990. V. 94. P. 4029.

22. *S. Matzinger, M. P. Fulscher* // J. Phys. Chem., 1995, V. 99, P. 10747.

23. *R. L. Schwartz, G. E. Davico, T. M. Ramond and W. C. Lineberger* // J. Phys. Chem. A., 1999, V. 103, P. 8213.

24. *J. C. Poutsma, J. J. Nash, J. A. Paulino and R. R. Squires* // J. Amer. Chem. Soc. 1997. V. 119. P. 4686.

25. *C. J. Cramer, D. G. Truhlar and D. E. Falvey* // J. Amer. Chem. Soc. 1997. V. 119. P. 12338.