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New application of kinetic data of the low-temperature thermolysis of nitroparaffins

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Abstract

A relationship has been derived between the activation energies E_a of low-temperature non-autocatalyzed thermolysis of nitroparaffins and their oxygen balances. An analogous relationship has also been found for pre-exponents of log A of this thermolysis. The direct relationship existing between E_a values and the impact sensitivity of the nitrocompounds in a condensed state is confirmed by the first relationship. From these two relationships, the molecular–structural dependences of the thermal reactivity of nitroparaffins in both gaseous and liquid states are discussed. For the thermolysis of mononitromethane in the liquid state, primary homolytic pseudo-monomolecular fragmentation decomposition is hypothesized.

Keywords: Decomposition; Nitroparaffin; Thermolysis

1. Introduction

As early as twenty years ago, the thermal reactivity of nitroparaffins and their derivatives was studied from the point of view of the influence exercised by the molecular structure [1–7]. The results obtained, however, correspond almost exclusively to thermolysis in the gaseous state. Data on the thermal reactivity of these nitrocompounds in a condensed state are rare in the literature (see for example, Refs. [4, 8–10]).

Some of the kinetic data concerning thermolysis of polynitroparaffins obtained by Nazin et al. [4, 5] were applied by Kamlet in the interpretation of his relationship [11, 12] between the impact sensitivity and the molecular structure of polynitroaliphatic compounds. This relationship has the form [11, 12]

$$\log h_{50\%} = 1.372 - 0.1681\,(\mathrm{OB}_{100}) \qquad (1)$$

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where $h_{50\%}$ is the height at which 50% of all fall-hammer (weight 2.5 kg) tests were positive, and (OB_{100}) is the oxygen balance of the given polynitrocompound (the balance is defined [11, 12] by the relation $(\mathrm{OB}_{100}) = 100(2n_\mathrm{O} - n_\mathrm{H} - 2n_\mathrm{C})(\mathrm{Mw})^{-1}$, where n_O is the number of oxygen atoms, n_H the hydrogen atoms, n_C the carbon atoms, and (Mw) is the molecular weight).

Kamlet [11, 12] states that a correlation of this type must unconditionally include the chemical reactivity of the nitrocompounds as determined by classical methods. This was confirmed in our previous communications [13, 14] in which we presented and interpreted a new relationship for nitramines, nitrosamines and nitroesters of general form

$$\ln E_\mathrm{a} = a + b(\mathrm{OB}_{100}) \tag{2}$$

where E_a is the activation energy of low-temperature non-autocatalyzed thermolysis. It was pointed out in Ref. [13] that Eq. (2) is indirect evidence of the identity of the primary fragmentation in the detonation conversion of the polynitrocompounds with the primary fragmentation in their thermolysis (for more detail, see Refs. [15, 16]). Ref. [14], in particular, also presents relationship (2) as a quantitative dependence of E_a values upon molecular structure.

Considering the facts presented in Refs. [8–16], relationship (2) should also hold for nitroparaffins. In order to confirm this hypothesis, results are applied to the study of kinetics thermolysis of the above-mentioned group of nitrocompounds using the Soviet manometric method (SMM) [1–5, 7, 9], modified differential thermal analysis (DTA) [10], and also, in one case, infrared spectroscopy (IR) [8]. At the same time, increased attention has been paid to molecular–structural dependences of the kinetic parameters of the thermolysis of nitroparaffins.

Analogously, as in previous communications [13, 14], marginally attention has been paid to the compensation effect of the Arrhenius parameters, the effect being presented by the isokinetic relationship [17–19]

$$E_\mathrm{a} = e_\mathrm{O} + 2.303 R\beta \log A \tag{3}$$

where β is the isokinetic temperature.

2. Results

Table 1 lists the studied nitroparaffins, the corresponding Arrhenius parameters E and $\log A$ of non-autocatalyzed thermolysis, and calculated values of oxygen balance OB_{100} given in Refs. [11, 12]: E_a values are here given with the same number of decimal points as in the original papers.

Analysis of the mutual relationship between E_a and OB_{100} revealed that, in the sense of Eq. (2), the data from Table 1 could be broken down into a number of sub-sets as presented in Figs. 1 and 2 where individual results for Eq. (2) are plotted.

Considering the existence of the isokinetic relationship (3), an equation of the following general shape was found

$$\ln(\ln A) = a_1 + b_1(\mathrm{OB}_{100}) \tag{4}$$

The competency of the compounds under study to the individual forms of this equation is similar to their competency to the individual forms of Eq. (2) and is obvious from Figs. 3 and 4.

Specification of the individual forms of Eqs. (2) and (4) for thermolysis of nitromethanes 1.2 and 4.2 in the liquid state was carried out by simple interpolation of the straight line by two points. This procedure is justified from the results presented so far (see lines in Figs. 1 and 2). From the individual forms of these equations which were formalized in this way (see lines V and VII in Figs. 1 and 2) as well as from the forms confirmed for the remaining sub-groups of nitroparaffins being studied, Arrhenius parameters were calculated a posteriori (also presented in Table 1).

Verification of the results obtained in this way for methane nitrodervatives was carried out by comparing them with the results of quantum–chemical Schlyapochnikov–Gagarin calculations [21] which were carried out using the Hoffmann method [22]: it was shown [23] that charges on the carbon atoms of nitromethanes are in linear correlation with activation energies of thermolysis E_a of these nitrocompounds obtained experimentally in a gaseous state using the equation

$$E_a = a_2 + b_2 q_C \qquad (5)$$

where q_C is the charge on the carbon atom. Values of q_C are presented in Table 2 which also includes values of the dissociation energies of the C–N bond in nitromethanes determined by thermochemical calculation [24]. Fig. 5 is a graphic representation of Eq. (5).

In the sense of Eq. (3), the set of studied nitroparaffins from Table 1 is broken down into three sub-groups, none of which is correlated with the data for 2.1, 2.2, 8.1, 11.2 or 15.1. Fig. 6 presents the structures of the sub-groups.

3. Discussion

The results obtained testify the validity of Eq. (2) for nitroparaffins thermolysis in the gaseous state. Lines I–IV in Fig. 1 confirm that increasing E_a values corresponds to increasing length of the *n*-alkyl group. These lines, together with lines VI–IX in Fig. 2, also confirm the well-known cumulative negative influence exercised by the nitrogroups within a nitroparaffin molecule (here on the α-carbon) upon its thermal stability [24, 25]. The relationships in Fig. 4 (lines VI–VIII) reveal that the increase in the activation entropy of thermolysis in the gaseous state corresponds to the cumulative effect of the nitro groups. Line VIII in Fig. 2 confirms the well-known fact [2] that the length of the *n*-alkyl chain has a negligible influence upon the value of the activation energy of gem-trinitroparaffin thermolysis in the gaseous state: the activation entropy of thermolysis in this group is quite distinct in this sense (see line VIII in Fig. 4).

The validity of Eq. (2) for polynitroparaffin thermolysis in a condensed state confirms the existence of a direct relationship between their impact sensitivity and the activation energy of their non-autocatalyzed thermolysis. The significance of this knowledge for the study of the micromechanism of detonation initiation for polynitroaliphates need not be discussed in greater detail (see Refs. [13, 14]).

Table 1
Survey of the OB_{100} values and Arrhenius parameters of the studied nitroparaffin thermolyses

Sub-stance (data) No.	Substance	Oxygen balance OB_{100}	Method of thermolysis	Arrhenius parameters					
				State of thermal decompn.	Temperature range/K	E_a/ (kJ mol^{-1})	log A/(s^{-1})	Ref.	Calculated according to relationships in Figs. 1 and 2, line no.
1	Nitromethane	−1.298							
(1.1)			SMM	Gas	633–663	227.19	14.3^{a}	[7]	
(1.2)			DTA	Liquid	443–524	173.63	12.8^{b}	[10]	
(1.3)			Calc.	Gas		228	14.3	This paper	I
2	Dinitromethane	3.772							
(2.1)			Calc.	Gas		189	15.7	This paper	VII
(2.2)			Calc.	Liquid		163	14.4	This paper	V
3	Trinitromethane	5.956							
(3.1)			SMM	Gas	453–473	177.40	15.9	[7]	
(3.2)			Calc.	Liquid		159	15.1	This paper	V
4	Tetranitromethane	7.141							
(4.1)			SMM	Gas	359–450	159.83	16.3	[7]	
(4.2)			SMM	Liquid	353–413	156.48	15.5	[4]	
5	Nitroethane	−6.661							
(5.1)			SMM	Gas	763–808	253.55	17.5	[2]	
6	1,1-Dinitroethane								
(6.1)			SMM	Gas	470–539	197.15	16.7	[7]	
7	1,1,1-Trinitroethane	3.029							
(7.1)			SMM	Gas	453–483	180.75	17.2	[5]	
(7.2)			SMM	Liquid	353–413	178.24	16.2	[4]	
8	Hexanitroethane	6.665							
(8.1)			SMM	Gas	363–408	149.79	17.3	[5]	
(8.2)			SMM	Solid	c	149.80	16.4	[20]	
(8.3)			IR	Solid	333–373	162.75	16.3	[8]	

9	1-Nitropropane	−10.101							
(9.1)			Calc.	Gas		259	16.9	This paper	V1
(9.2)			SMM	Liquid	c	205.9	13.9	[9]	
10	1,1-Dinitropropane	−2.983							
(10.1)			SMM	Gas	488–538	200.83	16.9	[7]	
(10.2)			SMM	Liquid	c	182	14.8	[9]	
11	2,2-Dinitropropane	−2.983							
(11.1)			SMM	Gas	488–538	198.74	17.1	[5]	
(11.2)			SMM	Liquid	c	140.16	11.9	[9]	
12	1,1,1-Trinitropropane	0.558							
(12.1)			SMM	Gas	433–473	176.98	16.8	[7]	
(12.2)			SMM	Liquid	c	174.91	16.9	[9]	
13	1,1,1,3-Tetranitropropane	2.677							
(13.1)			SMM	Liquid	c	205.43	17.6	[9]	
14	2-Methyl-1,1,1,3-tetranitropropane	0.840							
(14.1)			SMM	Liquid	c	175.73	17.7	[9]	
15	1,1,1,2,2-Pentanitropropane	4.831							
(15.1)			SMM	Liquid	c	166.10	19.2	[9]	
16	1-Nitrobutane	−11.099							
(16.1)			Calc.	Gas		262	17.1	This paper	d
17	1,1-Dinitrobutane	−5.401							
(17.1)			SMM	Gas	493–538	201.50	17.0	[5]	
18	1,1,1-Trinitrobutane	−1.553							
(18.1)			SMM	Gas	433–473	182.42	17.7	[2, 5]	
(18.2)			SMM	Gas	433–473	177.82	17.2	[5]	

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[a] Entropy of activation, $\Delta S^0 = 13.96\ \mathrm{J\ mol^{-1}\ K^{-1}}$.

[b] Entropy of activation $\Delta S^0 = -12.29\ \mathrm{J\ mol^{-1}\ K^{-1}}$.

[c] Not presented in original paper.

[d] Calculated by means of Eq. (2) for data 17.1, 18.1 and 18.2.

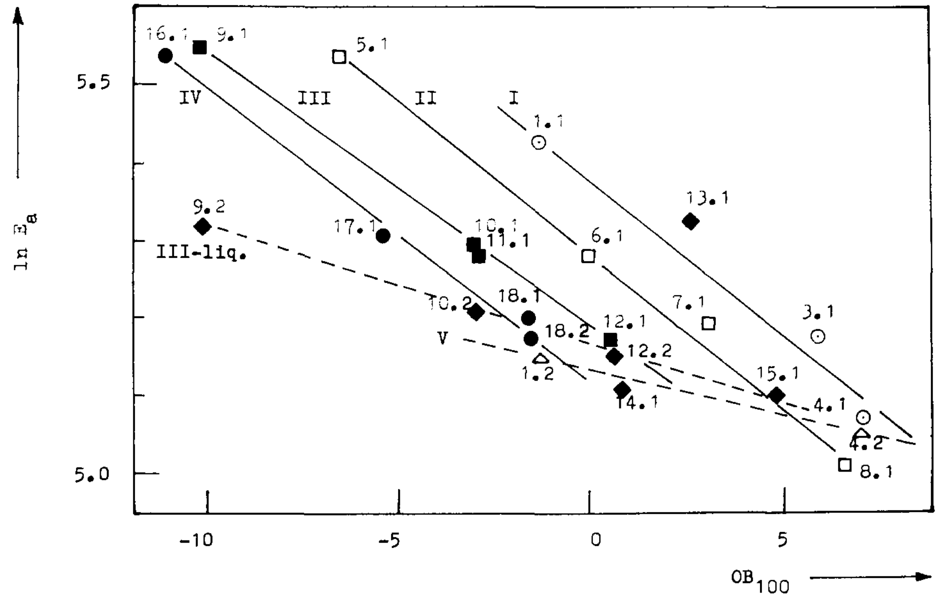


Fig. 1. Activation energies E of polynitroparaffin thermolysis as a function of their oxygen balance OB_{100}: ○, line I for methane derivatives; □, line II for ethane derivatives; ■, line III for propane derivatives; ◆, line III-liq. for thermolysis of nitropropanes in the liquid state (data 13.1 do not correlate); ●, line IV for butane derivatives; Δ, line V for thermolysis of nitromethanes in the liquid state.

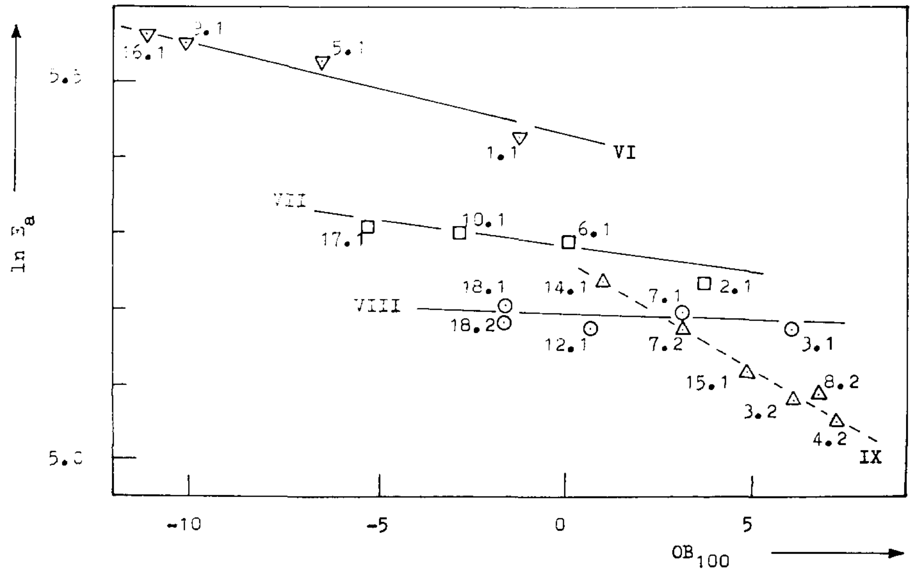


Fig. 2. Activation energies E of polynitroparaffin thermolysis as a function of their oxygen balance OB_{100}: ∇, line VI for mononitromethyl derivatives; □, line VII for dinitromethyl derivatives; ○, line VIII for trinitromethyl derivatives; Δ, line IX for trinitromethyl derivatives which were thermolyzed in the liquid state.

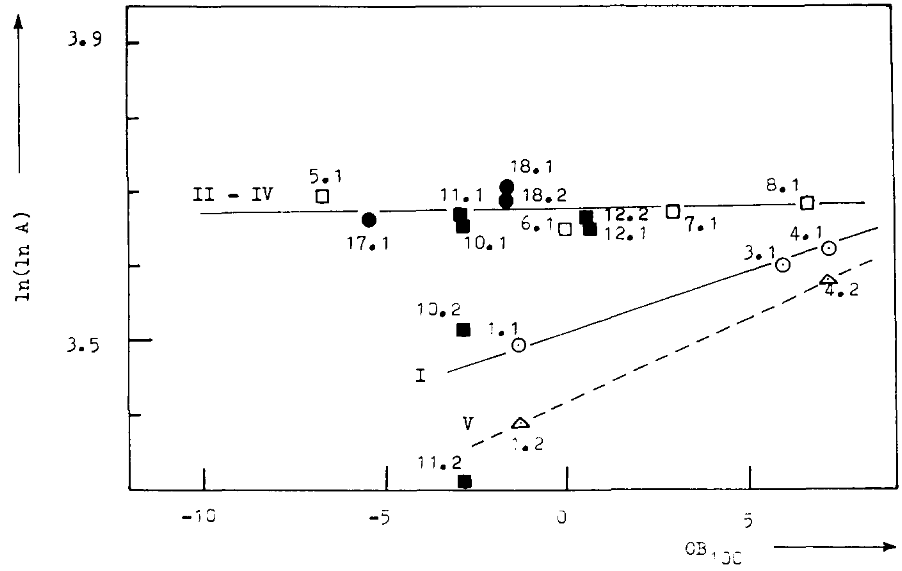


Fig. 3. Pre-exponents A of polynitroparaffin thermolysis as a function of their oxygen balance OB_{100}: ○, line I for methane derivatives; □, ■, ●, lines II–IV for ethane, propane and butane derivatives (data 10.2 and 11.2 are from thermolysis in the liquid state); Δ, line V for methane derivatives which were thermolyzed in the liquid state.

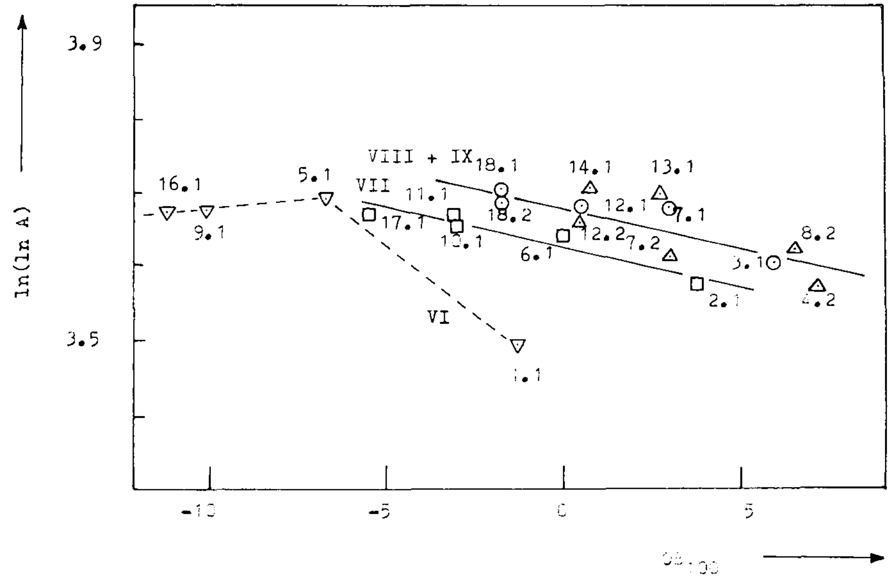


Fig. 4. Pre-exponents A of polynitroparaffin thermolysis as a function of their oxygen balance OB_{100}: ▽, line VI for mononitromethane derivatives; □, line VII for dinitromethane derivatives; ○, Δ, line VIII (points ○) for thermolysis of trinitromethyl derivatives in the gaseous state and line IX (points Δ) for their thermolysis in the liquid state.

Table 2
Survey of the charges on the carbon atoms of nitromethanes and their C–N bond dissociation energies

Substance	Charge on carbon atom [21]	Dissociation energy of C–N bond/(kJ mol^{-1}) [24]
Nitromethane	0.085	252.3
Dinitromethane	0.385	225.5
Trinitromethane	0.743	191.2
Tetranitromethane	0.994	164.4

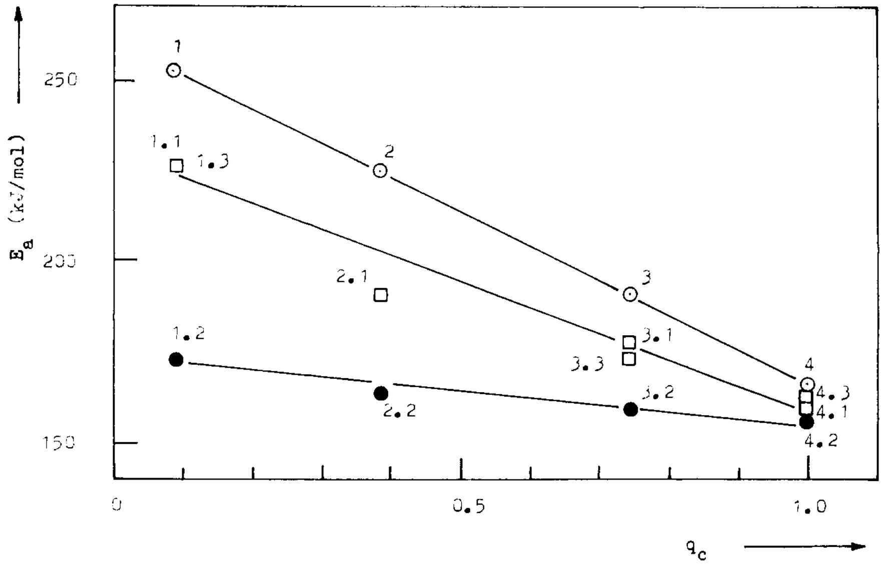


Fig. 5. Graphic representation of Eq. (5): ○, dependence for dissociation energies of C–N bonds (by thermochemical calculation [21]); □, dependence for experimental and calculated values of activation energies of nitromethane thermolysis in the gaseous state; ●, dependence for experimental and calculated values of activation energies of nitromethane thermolysis in the liquid state.

Some polynitroparaffins, e.g. tetranitromethane, 1,1,1-trinitroethane and 1,1,1-trinitropropane, see Table 1, have close values for the kinetic parameters of thermolysis in gaseous and liquid states (see also lines VIII and IX in Fig. 4). Although this has no general validity, the hypothesis was confirmed by this homolytic primary fragmentation during thermal decomposition of the above-mentioned polynitrocompounds in the liquid state [4].

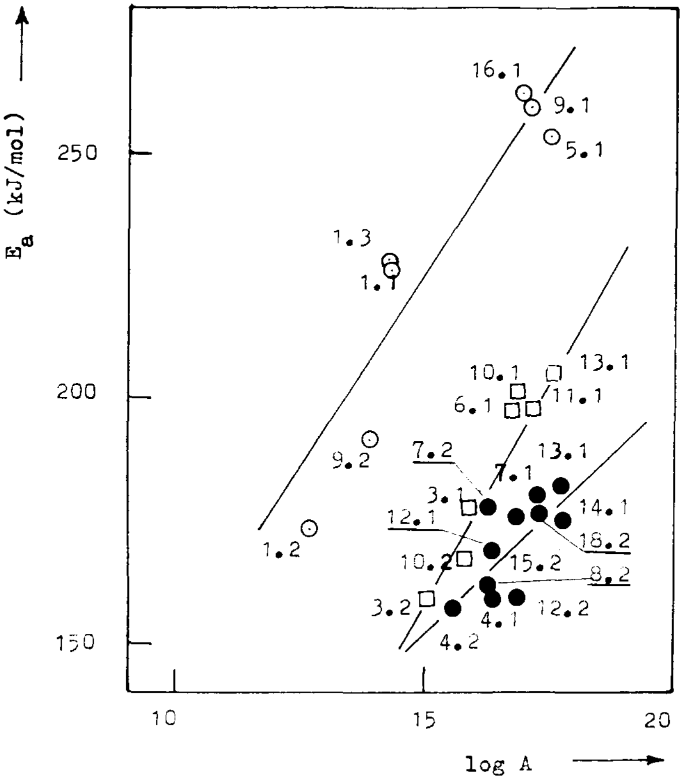


Fig. 6. Graphic representation of the isokinetic relationship (3): ○, dependence for group A (α-mononitroparaffins); □, dependence for group B (derivatives with the "acid" hydrogen on the α-carbon atom); ●, dependence for group C (trinitromethyl derivatives).

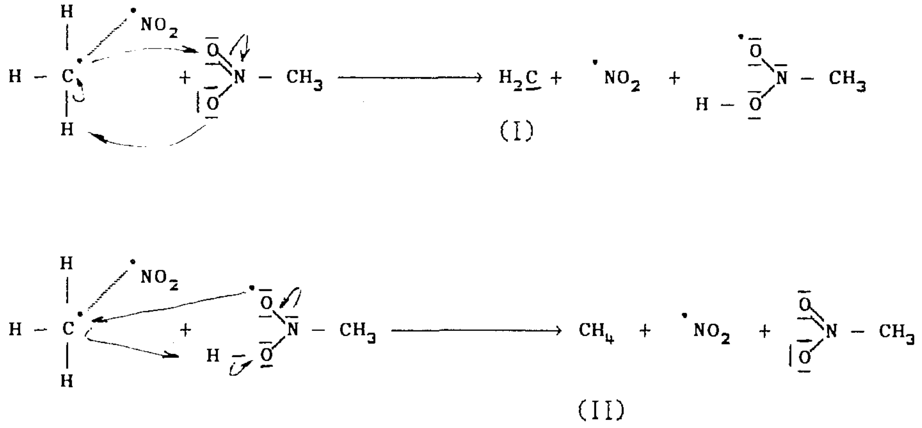
In methane nitroderivatives, an increase in the difference of the E_a values of thermolysis of individual derivatives in gaseous and liquid states corresponds to a decreasing number of nitrogroups within their molecules (see lines I and V in Fig. 1). The same is valid for nitroderivatives of propane (see lines III and III-liq. in Fig. 1). In this connection, it is, however, necessary to draw attention to the good correlation of the E_a values of nitromethane thermolysis, in the sense of Eq. (5), for the separate decomposition in gaseous and liquid states: the facts as presented in Fig. 5 indicate the identity of the primary fragmentation on thermolysis of all nitromethanes in gaseous and liquid states.

Also, the activation entropies of thermolysis of methane nitroderivatives in the liquid state, like the corresponding activation energies E_a, have unambiguously lower values than during thermal fission in the gaseous state (compare lines I and V in Fig. 3 and also footnotes a and b to Table 1). This is ascribed [10] to association of the corresponding molecules in the condensed state. Because the IR spectra of gaseous, liquid or solid mononitromethane are mutually identical [26], it is necessary to see this association, above all, as direct electrostatic intermolecular interaction of its molecules (orientation interaction).

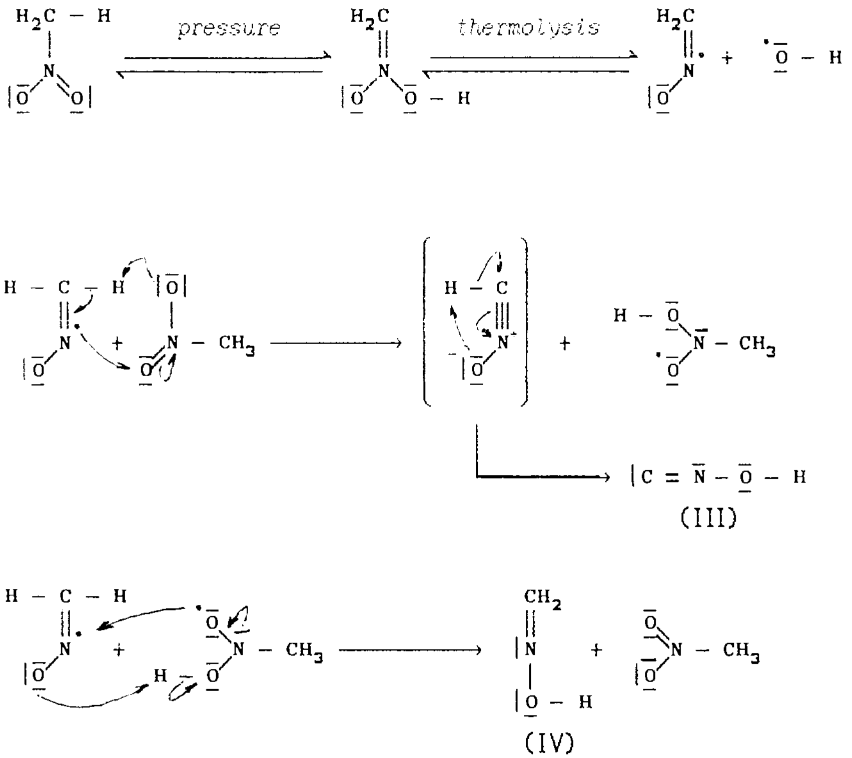
In connection with this molecular association, the initial stage of mononitromethane thermal fission in a condensed state is interpreted [10, 27–30] as a heterolytic biomlecular reaction. This interpretation is also supported by quantum–chemical calculations [10, 28] of the kinetic parameters. Considering the correlations in sense of Eq. (5) (see also Fig. 5), the hypothesis of pseudo-monomolecular homolytic fragmentation should be considered, as presented by Zeman [16] demonstrating nitramine thermolysis in dinitrobenzene solution. This hypothesis [16] is based upon knowledge gained by Urbanski and Buzniak [31–33] on the retarding effect of nitrocompounds on radical polymerization. In order to apply this hypothesis to the case of mononitromethane, the following facts should be taken into consideration:

1. Depending upon pressure, mononitromethane thermolysis in the condensed state can follow two reaction mechanisms [26] which have not yet been specified, one mechanism changing to the other [27] at 5 GPa pressure or at 4 GPa pressure at a temperature higher than 130°C (the latter mechanism has a negative activation volume [29, 30]);
2. Among the thermolysis products of mononitromethane in the gaseous state [32] are methane, hydrogen cyanide, methyl cyanide, ethylene, nitrogen and carbon oxides, water and other products; during thermolysis in the condensed state [27], ammonium formate, oxalate salts, water and a dark brown solid appear;
3. Due to the pressure effect, the enol- (aci-) form [35] is formed in mononitromethane; this form, e.g. in detonation change, exhibits higher reactivity [31].

From the above, primary pseudo-monomolecular homolytic fragmentation in mononitromethane thermolysis, under pressures lower than 4 GPa, could be represented by Scheme 1.



Scheme 1. Primary pseudo-monomolecular homolytic fragmentation of mononitromethane in its thermolysis in the liquid state under pressures lower than 4 GPa: carbonaceous products of this process are carbene (I) and methane (II).



Scheme 2. Primary pseudo-monomolecular homolytic fragmentation of mononitromethane in its thermolysis in the liquid state under pressures above 5 GPa: carbonaceous products of this process are fulminic acid (III) and "nitroso methane" (IV).

Reactive carbene (I) dimers forming ethylene, with hydrogen cyanide yields methyl cyanide, but carbene can also attack nitromethane molecules. This carbene could also be the reason for the formation of the enol- (aci-) form in thermolysed nitromethane and, at the same time, it could cause the mechanism participation in the overall fission according to Scheme 2.

The thermolysis of mononitromethane under pressures above 5 GPa or in the presence of agents causing the formation of its enol- (aci-) form, pseudo-monomolecular fragmentation could be represented by Scheme 2.

Through further decomposition and hydrolysis, "nitrosomethane" (IV) and highly unstable fulminic acid (III) yield ammonium formate, ammonia, oxalates and amorphous polymer products.

It is well known that induction and steric effects are primarily reflected in the thermal reactivity of polynitroparaffins (see, for example, Ref. [36]). This may be connected with the division of the nitroparaffins under study into three groups in the sense of Eq. (3) (see Fig. 6): here group A includes, almost exculsively, α-mononitroparaffins;

group B includes, nearly exclusively, polynitroparaffins with the "acid" hydrogen on the α-carbon atom; and group C includes trinitromethyl derivatives.

4. Conclusion

The relationship found between the activation energies E_a of low-temperature non-autocatalyzed nitroparaffin thermolysis and their oxygen balance confirms the existence of a direct relationship between E_a values and impact sensitivity of the above-mentioned nitrocompounds in the condensed state. This relationship, along with the analogous relationship for pre-exponents, i.e. $\log A$, quantitatively describes, to a certain extent, the thermal reactivity of aliphatic polynitrocompounds from the point of view of their molecular structure.

This quantitative description could also be one of the starting points for the interpretation of the primary process of nitroaliphatic compound thermolysis in the liquid state, e.g. during nitromethane thermolysis in the liquid state its nitrogroup might exercise an analogous influence on the homolysis of the interacting molecule in the same way as on the termination of radical polymerization (for the case of polynitroarenes, see Ref. [16]).

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