

THE RELATIONSHIP BETWEEN KINETIC DATA OF THE LOW-TEMPERATURE THERMOLYSIS AND THE HEATS OF EXPLOSION OF ORGANIC POLYINITRO COMPOUNDS

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(Received 2 March 1984)

ABSTRACT

A linear relationship between the activation energies of the initial stage of non-autocatalysed, low-temperature thermolysis and the heats of explosion of organic polynitro compounds is presented. This was derived from discussions on a set of problems concerning the identity of primary chemical processes of the thermal decomposition and detonation of organic explosives. The necessary kinetic data of thermal decomposition for the studied compounds were taken from the results obtained by the Soviet manometric method (SMM) and the Rogers method of differential scanning calorimetry (DSC). The data obtained from differential thermal analysis (DTA), i.e., Piloyan activation energies of the initial exothermal decomposition of some of the above mentioned compounds, were used as a supplement. It is also shown that the kinetic data obtained by DTA according to Kissinger are not applicable to the study of the micromechanism of the initiation of detonation.

INTRODUCTION

Recently, the systematic specification of mutual relationships existing between the data of low-temperature thermolysis and the detonation characteristics of metastable and non-stable compounds has been studied [1-4]. These relationships are important not only from a purely practical point of view [1] but they are also of consequence for the interpretation of some problems concerning the chemism of the detonation change and the thermal decomposition of the said compounds [3,4]. In the present paper (closely related to ref. 3) the derivation and some application possibilities of the relationship (given in the title) are suggested.

DATA SOURCES

Substances

A survey of the studied organic polynitro compounds, their numeration, or the numeration of the corresponding data, and their code designation are given in Table 1.

Heats of explosion

The heats of explosion, Q , of most substances studied were calculated using the semi empirical relationship of Pepekina et al. [33]; the resulting Q values for maximum densities are collected in Table 1. For substance 10, the Q value was obtained from the value of its detonation velocity (7.99 km s^{-1}) by applying previously described methods [34,35]. For substances 38, 39 and 44 containing a sulfur heteroatom within their molecules, Q values were determined by means of spectroscopic method [35]. In the case of substance 54, the Q value is applied; it was determined by DTA [4]. In the case of substance 65, the Q value was taken from monography [36].

Kinetic data of thermolysis

The basic source data on the kinetics of thermolysis of the studied substances in the present paper are taken from Soviet authors at the Institute of Chemical Physics of the Soviet Academy of Sciences as well as from authors at Moscow Mendeleev University of Chemical Technology; these papers deal with the application of the Soviet manometric method (SMM) [37,38] of determining the kinetics of polynitro compound thermolysis. Another important source of data is the papers by Rogers and co-workers [6,7,19,22,23,39] from the Los Alamos National Laboratory dealing with the study of thermolysis kinetics of polynitro compounds using DSC. The SMM and DSC data are presented in Table 1.

Recent results have been obtained by the application of the Piloyan method of determining activation energies [40] to the thermolysis of organic polynitro [2,4,41–44,80,81] and polynitroso compounds [4] with an evaluation of the corresponding measurements in the sense of refs. 44, 45. These activation energies for some of the substances in Table 1 are also considered in the next paragraphs.

In some of the polynitro compounds studied, the activation energies of decomposition were determined by means of DTA and derivatograph apparatus Q-1500-D (MOM, Budapest) [46], using Kissinger's method [47]; the said activation energies are also considered in the present paper (see Fig. 1).

TABLE 1
Survey of polynitro compounds and the corresponding data

Substance (data) No.	Substance	Code designation	Heat of explosion ^a Q (kJ g^{-1})	Arrhenius parameters			
				State of thermal decomposition.	E (kJ mol^{-1})	$\log A$ (s^{-1})	Ref.
1	1,3,5-Trinitrobenzene	TNB	4.754	liquid	180.03	10.9	5
1.1							
2	2,4,6-Trinitrotoluene	TNT	4.277	liquid	144.44	9.3	5
2.1				liquid	143.90 ^d	11.4 ^d	6, 7
2.2				soln. ^c	194.55	12.9	8, 9
2.3							
3	1,3-Dimethyl-2,4,6-trinitrobenzene	TNX	4.074	liquid	146.95	9.1	5
3.1							
4	1,3,5-Trimethyl-2,4,6-trinitrobenzene	TNMs	3.801	liquid	185.05	12.3	5
4.1							
5	1-Chloro-2,4,6-trinitrobenzene	CTB	—	liquid	118.07	5.7	10
5.1							
6	1,3-Dichloro-2,4,6-trinitrobenzene	DCTB	—	liquid	177.09	10.5	10
6.1							
7	1,3,5-Trichloro-2,4,6-trinitrobenzene	TCTB	—	liquid	185.77	11.4	10
7.1							
8	1-Hydroxy-2,4,6-trinitrobenzene	PA	4.372	liquid	161.18	11.7	11
8.1							
9	1,3-Dihydroxy-2,4,6-trinitrobenzene	TNR	4.130	liquid	144.86	11.2	11
9.1							
10	1,3,5-Trihydroxy-2,4,6-trinitrobenzene	TNPg	3.959 ^b	liquid	226.77	22.0	12
10.1							
11	1-Hydroxy-3-methyl-2,4,6-trinitrobenzene	TNCr	4.072	liquid	192.46	15.6	13
11.1							
12	1-Methoxy-2,4,6-trinitrobenzene	TNA	4.309	liquid	113.80	6.9	13
12.1							

TABLE 1 (continued)

Substance (data) No.	Substance	Code design- ation	Heat of explos- ion $^a Q$ (kJ g^{-1})	Arrhenius parameters			
				State of thermal decompr.	E (kJ mol^{-1})	$\log A$ (s^{-1})	Ref.
13	1-Amino-2,4,6-trinitrobenzene	PAM	4.263				
13.1				liquid soln. ^c	129.79	7.1	11
13.2					174.89	11.0	8, 9
14	1,3-Diamino-2,4,6-trinitrobenzene	DATB	4.138				
14.1				solid	196.77	13.2	12
14.2				solid	193.72 ^d	15.1 ^d	6
14.3				soln. ^c	184.93	11.6	8, 9
15	1,3,5-Triamino-2,4,6-trinitrobenzene	TATB	3.990				
15.1				solid	175.00	11.6	12
15.2				solid	250.62 ^d	19.5 ^d	6
15.3				soln. ^c	177.82	12.3	9
16	1-Methylnitramino-2,4,6-trinitrobenzene	TETRYL	4.830				
16.1				liquid	156.91	14.5	14
17	3-(2,4,6-Trinitrophenylamino)-1,2,4-triazole	PATO	4.182				
17.1				solid	134.72 ^d	10.2 ^d	6
18	2,2',4,4',6,6'-Hexanitrooxanilide	HNO	4.189				
18.1				solid	215.62	16.0	12
19	2,2'-4,4'-6,6'-Hexanitrodiphenylamine	DPA	4.438				
19.1				solid	177.76 ^e	11.0 ^e	3, 43
20	Potassium 2,2',4,4',6,6'-hexanitrodiphenylaminatate	KDPA	-				
20.1				solid	107.57 ^e	5.2 ^e	3, 43
21	3,3'-Diamono-2,2',4,4',6,6'-hexanitrobiphenyl	DIPAM	4.420				
21.1				solid	190.23	12.8	3
22	2,2',4,4',6,6'-Hexanitroazobenzene	HNAB	4.835				

TABLE 1 (continued)

Substance (data) No.	Substance	Code designation	Heat of explosion ^a Q (kJ g ⁻¹)	Arrhenius parameters			
				State of thermal decompn.	E (kJ mol ⁻¹)	log A (s ⁻¹)	Ref.
33.1				solid	269.45	18.2	16
33.2				solid	225.82 ^r	15.2 ^r	3, 44
33.3				soln. ^c	209.61	14.8	9
34	2,4,6-Tris(2,4,6-trinitrophenylamino)-1,3,5-triazine	TPM	4.064	solid	257.06	19.0	12
34.1							
35	2,4,6-Tris(3-methyl-2,4,6-trinitrophenylamino)-1,3,5-triazine	TMPM	3.761	solid	116.18 ^e	7.2 ^e	3, 43
35.1							
36	2,6-Bis(2,4,6-trinitrophenylamino)-3,5-dinitropyridine	PYX	4.341				
37	Azo-bis(2,2',4,4',6,6'-hexanitrobiphenyle)	ABH	4.859				
38	2,2',4,4',6,6'-Hexanitrodiphenylsulfide	DIPS	4.185 ⁱ				
38.1				liquid	131.80	7.4	17
38.2				solid	178.77	12.0	11
38.3				soln. ^c	212.96	14.7	8, 9
39	2,2',4,4',6,6'-Hexanitrodiphenylsulfone	DIPSO	3.773 ⁱ	solid	106.76	5.6	18
39.1				soln. ^e	188.28	13.7	9
39.2							
40	5,7-Dinitro-1-(2,4,6-trinitrophenyl)-benzotrazole	BTX	4.364				
41	1,4,5,8-Tetranitronaphthalene	TENN	4.422				
41.1							
42	1,3,7,9-Tetranitrodi(2,4,6-trinitrophenyl)tetraazapentalene	TACOT-1	4.372	solid	223.05 ^e	15.0 ^e	3, 44
42.1				solid	234.30	15.4	12
42.2				soln. ^c	164.01	10.2	9

43	1,3,8,10-Tetranitrodibenzo-1,3a,6,6a-tetraazapentalene	TACOT-2	4.310					
43.1				solid	189.95	11.7	12	
43.2				soln. ^c	191.21	12.3	9	
44	1,3,7,9-Tetranitrophenothiazine-5,5-dioxide	TNPTD	3.765 ⁱ					
44.1				solid	200.96	11.7	12	
44.2				soln. ^c	259.82	17.4	9	
45	1,3,7,9-Tetranitrophinoxazine	TNPO	3.869					
45.1				solid	158.55 ^e	10.0 ^e	2, 3	
46	1,3,6,8-Tetranitrocarbazole	TENC	3.815					
46.1				soln. ^c	238.06	15.3	8	
47	1,3,5-Trinitro-1,3,5-triazacyclohexane	RDX	5.477					
47.1				solid	211.84 ^d	19.6 ^d	19	
47.2				solid	217.57	19.1	20	
47.3				liquid	198.87	18.5	21	
47.4				liquid	197.10 ^d	18.3 ^d	7	
48	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane	HMX	5.527					
48.1				solid	217.57 ^d	19.5 ^d	23	
48.2				liquid	214.77 ^d	18.8 ^d	22	
49	4-Nitrazavaleric acid	NVA	2.549					
49.1				liquid	176.06	14.7	14, 24	
50	1,3-Dinitro-1,3-diazacyclopentane	PENTOGEN	—					
50.1				liquid	149.46	13.5	25	
51	1,4-Dinitro-1,4-diazacyclohexane	DNDC	5.184					
51.1				liquid	198.45	17.3	25	
52	Composition B (59.5% RDX, 39.5% TNT, and 1% wax)	Comp. B	4.700					
52.1				liquid	180.2 ^d	16.6 ^d	7	
53	1,5-Methylene-3,7-dinitro-1,3,5,7-tetraazacyclooctane	DPT	3.756					
54	1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane	DADN	3.523 ^j					

TABLE 1 (continued)

Substance (data) No.	Substance	Code designation	Heat of explosion ^a Q (kJ g ⁻¹)	Arrhenius parameters			
				State of thermal decompn.	E (kJ mol ⁻¹)	$\log A$ (s ⁻¹)	Ref.
55	trans-1,4,5,8-Tetranitro-1,4,5,8-tetraazadecaline	TNAD	5.639		—	—	
56	N,N-Diethanolnitramine dinitrate	DINA	5.169	liquid	173.75	16.5	26
56.1							
57	Ethyl nitrate	EN	4.349	liquid	167.36	14.7	27
57.1							
58	Ethylene glycol dinitrate	EGDN	6.229	liquid	163.28	14.5	28
58.1							
59	Glycerol trinitrate	NG	6.264	liquid	163.30	15.4	29
59.1							
60	Manitol hexanitrate	HNM	6.533	solid	159.10	15.9	28
60.1							
61	Nitrocellulose (13.35% N)	NC-13.35	4.489	solid	164.12	15.0	30
61.1							
62	Pentaerythritol tetranitrate	PETN	5.729	solid	163.17	15.6	31
62.1							
63	1,1,1-Trimethylolpropane trinitrate	ETRYNIT	4.730	liquid	—	—	—
64	Dipentaerythritol hexanitrate	DPHN	5.048		—	—	—

65	Tetramitromethane	TENM	2.259 ^k				
65.1				liquid	156.48	15.5	32
66	1,1,1-Trinitroethane	TNE	6.559				
66.1				liquid	178.24	16.2	32
67	2-Methyl-1,1,1,3-tetranitropropane	METNP	5.487				
67.1				liquid	175.73	17.7	32
68	1,1,1,3-Tetranitropropane	TENP	-				
68.1				liquid	205.43	17.6	32
69	1,1,1,2,2-Pentanitropropane	PNP	7.312 ^m				
69.1				liquid	166.10	19.2	32
70	2,2,3,3-Tetranitrobutane	TENBU	5.434				

^a Calculated according to ref. 33.

^b Derived from value of detonation velocity (7.99 km s^{-1}) by means of the methods given in refs. 34 and 35.

^c Solution in hexachlorobenzene.

^d Determined by means of DSC.

^e Calculated from DTA results.

^f Calculated from DTA results for the "quasi-liquid" state (see text).

^g Thermolysis in the "quasi-solid" state [43].

^h Determined by means of DSC [6] in the temperature region of the start of fusion.

ⁱ Determined according to ref. 35.

^j Value taken from ref. 4.

^k Value taken from ref. 36.

^m Unreal (high) value.

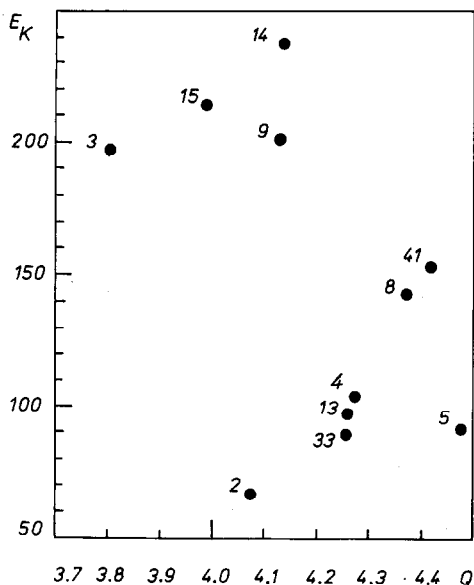


Fig. 1. Graphic representation of eqn. (3) for the Kissinger activation energies, E_K , of the polynitroarenes thermolysis [46]; it is evident that logical correlations do not exist here.

RESULTS AND DISCUSSION

Relationship of micromechanisms of the initiation of detonation and of thermolysis

Kinetic data of the low-temperature thermolysis of organic polynitro compounds was previously applied to the study of the initiation mechanism of their detonation [3]. The conclusion arrived at was that the mechanisms of primary chemical processes of thermal decomposition occurring in the said compounds are identical with the mechanisms of primary chemical processes of their detonation change [3]; this was extended to polynitrosamines [4].

This conclusion [3] is also confirmed by the previous publications of Delpuech and Cherville; it is also supported by the results obtained from the application of theoretical chemistry to the study of the criterion of shock sensitivity in polynitroarenes [48,49], nitramines [48,49], nitric esters [48,50], tetrazoles [48,51] and picryltetrazoles [51]. The authors of these communications have shown that, within the molecule of the given organic explosive, there is an intramolecular bond which, on shock, is liable to be broken immediately (C-NO₂, N-NO₂, O-NO₂, i.e., explosophore bond with the remainder of the molecule), thereby influencing the degree of sensitivity of the explosive in question. This finding was experimentally verified by Delpuech and co-workers on substrate 47 exposed to a shock wave [52].

Depluech and Cherville also stressed the importance of the electron structure of the basic state of the molecule and the distribution of the absorbed energy within the molecule (both factors influence the structure of the excited state) for the beginning of the explosive change within the given explosive [48]. In this context it is suitable to quote Capellos and Iyer [53] who claimed the importance of the identification and characterization of the chemical reactivity of energy transition stages in order to elucidate the initiation mechanism; the said stages are (the authors inferred) due to electron or thermal excitation of the molecules of the given polynitro compound.

The results arrived at in the study of the relationships between the DTA data, and the detonation characteristics of polynitroarenes [2,3] and aliphatic polynitro and polynitroso compounds [4], are in agreement with the results of Delpuech and Cherville; it may, therefore, be assumed that this phenomenon extends to detonation conditions. This, along with the conclusions arrived at in the literature [3,4,48–52] also agree with the findings of Bernard within the field of application of the kinetic theory of detonation to the study of activated states of explosive molecules [55,54]: only explosophore groups are compressed ahead of the shock front, as a result of the activation of explosive molecules.

Partial results obtained by Owens and co-workers from their experimental study of the micromechanism of the initiation of detonation [56–59] in substances 2, 15 and 47 give convincing evidence to the conclusions arrived at in refs. 3 and 4; comparing these results with those obtained by Soviet authors on the micromechanism of thermolysis of substances 15 and 17 (see discussion and quotation in ref. 3, and the present paper for all three substances), and in the case of polynitroarene (15) with the results in ref. 60 provides clear evidence of the identity of thermolysis initiation mechanisms and the detonation initiation of the mentioned polynitro compounds. Owens himself, demonstrating solid copper tetramine nitrate, showed experimentally the identity of primary thermolysis products with the primary decomposition products due to the shock wave [61].

Considering the information contained in the literature [2–4,48–61], the micromechanism of initiation of detonation in organic polynitro and polynitroso compounds can be formulated as follows [62]: the origination of detonation is the result of the primary homolytic monomolecular decomposition of excited molecules in organic explosives; first, the intramolecular bonds are liable to homolysis which eliminates them almost completely, even at low-temperature thermolysis. Primary fragmentation in this sense can occur at an early stage, even during the compression of the molecules by the shock wave. The order of the duration of processes considered are: time of the orbiting electron $\sim 10^{-16}$ to 10^{-15} s [63]; excitation time of molecules by electrons $\sim 10^{-16}$ s [64]; excitation time of molecules by photons $\sim 10^{-18}$ s [64]; expectancy of higher excited states of molecules $\sim 10^{-14}$ s [64,65]; and the rate of detonation wave propagation 5–9 Å per 1×10^{-13} s [66].

The given micromechanism of initiation [62] resembles Walker's radical model of initiation of detonation [66]. Walker, however, assumes fragmentation of the molecules of a given explosive down to its atoms and free radicals via a purely mechanical process without considering the preference of any intramolecular bond [66].

If homolysis is the primary fragmentation within the detonation change of organic explosives, homolysis should, according to the conclusions of refs. 3 and 4, also act as a primary chemical process of thermolysis in polynitro and polynitroso compounds. From the vast amount of data published on kinetics and the mechanism of thermolysis of organic polynitro compounds (especially refs. 3,4,9,12,14,60,67-74) this assumption is verified with convincing facts.

Existing literature on this problem as a whole, however, lacks an unambiguous attitude towards the problems linked with the primary process of thermal decomposition in polynitro compounds in the condensed state: in the case of nitric esters, the beginning of thermolysis has been proved and acknowledged to be the homolytic destruction of O-NO₂ [4,71,74]; in nitramines it is the homolysis of the N-NO₂ bond [3,4,14]; and in polynitroaliphatics there is clear evidence of homolysis of the C-NO₂ bond [3]. In the polynitroarene series, primary destruction of the C-NO₂ bond occurs only if the molecule in the *ortho* position with respect to the nitro group does not contain a substituent liable to oxidation (e.g., methyl, hydroxy, or amino group; i.e., a hydrogen atom in the γ -position towards the nitro group, as well as the sulfur atom [8]); conversely, molecular mechanism is considered to operate as primary fission (the so-called "trinitrotoluene mechanism" [8,42,75,76]) involving simultaneous participation of bimolecular reactions in this process [5,8,75,77]. In the case of substance 8 (with hydrogen in the γ -position towards the nitro group), however, the organic radical has been shown to be the primary product of thermolysis, resulting from fission of the N-OH bond in the *aci*-form of the *ortho* nitro group [78]. This indicates that, in compounds possessing the so-called trinitrotoluene mechanism of thermolysis, hydrogen from the γ -position towards the nitro group migrates to the nitro-group oxygen [53,73,82,83] during the transition of the molecule to the excited state, monomolecular homolysis of the resulting N-OH bond being the primary fragmentation [73].

The homolytic course of the initial stage of thermal polynitroarenes decomposition was also shown by the thermostable characteristics and thermolysis kinetic data influenced by the construction material in contact with the substance under thermolysis [2,41-45,62,79-81]. The concentration dependence of the kinetic data of thermal decomposition in solutions of "inert" solvents [8], indicating the participation of bimolecular reactions in the initial stage of the decomposition [5,8,75,77], may be linked with the termination effect of polynitroarenes in radical reactions (see discussion in ref. 3).

Correlation relationship

The application of quantum-mechanical parameters is advantageous in the elucidation of the physical sense of the reaction capability of molecules and radicals [84]. From the resulting correlations the most widely used equation in the kinetics of radical reactions is that of Polanyi [84,85]

$$\Delta E = -\alpha\Delta\Delta H \quad (1)$$

where ΔE is the difference of activation energies, $\Delta\Delta H$ is the difference of heat effects of one-type reactions, α being a non-dimensional proportionality coefficient. Semenov [86] showed that, in the first approach, relationship (1) holds for the substitution reactions of free radicals and can therefore be written in the following form [84,86]

$$E = B \pm \alpha'\Delta H \quad (2)$$

called the Polanyi–Semenov equation [84], where B is the constant for the given homological series, E is the activation energy, and ΔH is the thermal colouration of the reaction; the minus sign holds for exothermal reactions, and the plus sign for the endothermal ones.

Equation (2) should also be valid for the relationship between the activation energy of the primary homolysis of the thermal decomposition of polynitro compounds, and the thermal colouration of this process. From the attempt to prove the identity of primary chemical mechanisms of thermolysis and of detonation change (see refs. 3 and 4 as well as the present paper), it follows that the values of the thermal effects of the corresponding primary processes of the two decompositions are also identical. According to refs. 3 and 62, under conditions of stable detonation, the colouration of the primary chemical process is, logically, related to the overall reaction heat of the detonation change, i.e., to the heat of explosion, Q . This meditation leads us to suppose that there is a logical relationship between the activation energy of the thermal decomposition, and heat of explosion of organic polynitro and polynitroso compounds.

A detailed analysis of the mutual relationship of the activation energy values, E , and heat of explosion values, Q , (kJ mol^{-1} and kJ g^{-1} , respectively) in classes of compounds possessing similar features of molecular structure from Table 1 revealed the most suitable relationship as the following general form

$$E = C + aQ \quad (3)$$

where E and A are in kJ mol^{-1} , the gradient, a (the difference between eqn. (3) and eqns. (1) and (2)) is in g mol^{-1} , and Q is in kJ g^{-1} . As will be seen from the following this relationship also holds for Piloyan activation energies; Fig. 1 gives the graphical representation for Kissinger activation energies of thermolysis.

Analogous to relationship (3), a dependence was found for the logarithm of the pre-exponential function, $\log A$, in the form

$$\log A = D + bQ \quad (4)$$

The mutual similarity of eqns. (3) and (4) is logical in view of the existence of the kinetic compensation effect [87] existing between E and $\log A$ as presented by the equation [10,12,44,69]

$$\log A = m + dE \quad (5)$$

This compensation effect results from the application of the Arrhenius law to non-homogeneous kinetics both in isothermal and non-isothermal conditions if there is only one factor determining the rate of the reaction [87]. For the thermolysis of polynitroarenes, both in liquid and solid states, only relation (5) has only the one form [44].

Considering the applicability of eqn. (3), or possibly eqn. (4), to the polynitro compounds, the apparent set of substances in Table 1 is broken up into a number of groups; many of these groups consist only of three polynitrocompounds. This grouping is mainly governed by the similarity of molecular structure and, to some extent, also by the state of thermolysis of the given substance.

Polynitroarenes

The division of SMM and DSC kinetic data of polynitroarene thermolysis in the condensed state on the basis of their applicability to the separate forms of the equation (eqns. 3 and 4) is presented in Table 2. The table also contains coefficients of the two relationships.

Group I of the polynitroarenes is made up of mononuclear derivatives of substance 1 whose kinetic SMM data along with the corresponding form of eqn. (3) or eqn. (4), respectively, do not correlate. Also SMM data (data No. 15.1) of the thermolysis of substance 15 in the solid state are members of the group: from the value of the activation entropy which was calculated from these data [3], the trinitrotoluene mechanism of primary thermolysis can be presumed. However, convincing evidence has been reported [60,70] that the primary homolysis of the C-NO₂ bond is the beginning of thermal decomposition in substance 15 (also in the form of a solution [70]); this fission agrees with the DSC kinetic data of thermal decomposition [3,6] (data No. 15.2), thus classifying substance 15 unambiguously into group III of the polynitroarenes.

With neither form of the equation (eqns. 3 or 4) are the kinetic data of thermolysis of the monohydroxy (substance No. 8) and the trihydroxy derivative (substance No. 10) of substance 1 correlated. Everything points to (see, e.g., ref. 42) the fact that polyhydroxy derivatives of substance 1 (also

TABLE 2

Coefficients and standard errors of estimate ($S_{x,y}$) of the individual forms of eqns. (3) and (4) for thermolysis of polynitroarenes in condensed state

Group No.	Structure of group ^a	Equation 3				Equation 4			
		C	a	r	$S_{x,y}$	D	b	r	$S_{x,y}$
I	2.1, 3.1, 4.1, 9.1, 12.1, 13.1, 15.1, 17.1;	664.07	-125.29	0.9212	9.78	49.33	-9.59	0.8213	1.23
II	2.1, 2.2, 11.1, 23.1, 25.1;	1144.04	-233.70	0.9998	0.71	120.94	-25.91	0.9636	1.28
III	13.1, 14.1, 14.2, 15.2;	2008.79	-439.48	0.9927	7.31	199.67	-44.99	0.9765	1.35
IV	13.1, 18.1, 34.1	2734.05	-607.20	0.9408	31.10	247.83	-56.04	0.9107	3.61
V	13.1, 19.1, 21.0; 18.1, 19.1, 21.1,	-1223.26	317.62	0.9581	12.91	-111.24	27.79	0.9180	1.63
VI	22.1, 25.2, 26.2, 34.1;	924.52	-166.14	0.9784	9.35	82.21	-15.67	0.9679	1.08
VII	19.1, 26.2, 28.1, 30.1, 35.1, 39.1;	-277.18	103.05	0.9967	4.11	-26.51	8.69	0.9592	1.26
VIII	22.1, 25.1, 26.1, 38.1;	185.02	-13.19	0.8387	2.87	9.21	-0.40	0.0862 ^b	1.54
IX	29.1, 41.1, 42.1, 43.1;	-1339.29	356.13	0.9445	15.25	-119.47	30.56	0.9612	1.08
X	4.1, 10.1, 15.2;	-1032.33	319.95	0.9772	9.97	-160.97	45.68	0.9193	2.80
XI	1.1, 28.1, 29.1, 30.1	2200.45	-422.40	0.9446	17.34	174.11	-33.92	0.9078	1.85

^a Data numbered as in Table 1.

^b Coefficient of correlation for eqn. (5) is only $r = 0.3718$.

28) will have a separate form of the equation (3 or 4). This means that substance 9, nor the triamine derivative (15), should belong to group I.

On the other hand, the forms of the equation (3 and 4) for group I are correlated to kinetic data 23.1, 25.1, and 38.1, classified as belonging to group VIII, even better than data 2.1 and 2.2. By excluding derivatives 9 and 15 from group I of the polynitroarenes, and by their extension with the data of the given dipicryl derivatives, a group of substances results with the interaction of the *ortho* nitro group with the hydrogen in the γ -position or with the sulfur atom (substance 38) during the transition of the corresponding molecules into the excited state. The coefficients of eqn. (3) for this modified group I are as follows: $C = 630.84$, $a = -117.47$ and $r = 0.9136$; analogously coefficients of eqn. (4) are as follows: $D = 48.01$, $b = -9.35$ and $r = 0.7548$. Deterioration of the correlation in either case is due to data 2.1 and 2.2.

Group II of substances is made up of polynitroarenes which were generated by imaginary substitution from substance 2. As data 2.1, 2.2, 11.1 and 25.1 correspond to thermolysis in the liquid state, values of E and $\log A$ for substance 23 should also correspond to thermal decomposition in the liquid state (they were derived from DTA measurement results [43]). The excellent agreement between E values obtained from DSC measurement (data No. 2.2) and those from SMM application (data 2.1) should be noted.

Structures of groups III, IV and V of the polynitroarenes are logical. Attention should also be paid here to the good agreement between DSC and SMM data for substance 14 (data Nos. 14.1 and 14.2).

Group VI consists of di- and tripicryl derivatives, which were thermolysed in the solid state (except data No. 22.1); these contain a hydrogen atom within their molecules in the γ -position towards the nitro group (again except data No. 22.1). Well correlated with eqns. (3) or (4) for this group are data 33.2. According to the derivation methods from DTA results [44], these data correspond rather to the decomposition of substance 33 in liquid state, their membership to group VI being probably accidental (which follows from the comparison with breaking up polynitroarenes in groups on the basis of DTA measurements; see Tables 4 and 5 as well as the corresponding text). SMM data 33.1 for the thermolysis of substance 33 in the solid state do not correlate with eqns. (3) or (4) for group VI.

Group VII is made up of dipicryl derivatives possessing kinetic data of thermal decomposition in the solid state (except data No. 28.1). Data 38.1 are badly correlated with eqns. (3) or (4); data 38.2 do not correlate. The data for substance 38, which should belong to group VII, could be elucidated by a study of the kinetics of their thermolysis using DSC.

Dipicryl derivatives with the kinetic data of thermolysis in the liquid state were placed in group VIII. In the sense of eqn. (3), these data are unambiguously correlated; correlation, in the sense of eqn. (4), however, does not exist. This is due to a low correlation coefficient of relationship 5 for these data:

kinetic parameters are determined by more than one degree of the reaction (however, effects like crystal melting, change of decomposition rate in the temperature region of the melting point, etc., may also participate).

Group IX includes substances with dinitrophenylene building units within the molecule. However, data 44.1 and 45.1, i.e., the data of polynitroarenes with an angular basic molecular skeleton do not belong to it. Structures of this type will probably form a separate group of substances.

Group X of the polynitroarenes is formed on the basis of the kinetic data of thermal decomposition of 1,3,5-trisubstituted 2,4,6-trinitrobenzenes. Analogous groupings of 1,3-disubstituted or monosubstituted derivatives of substance 1 within the framework of the studied set do not exist.

The structure of group XI of the polynitroarenes is logical. Membership of substance 1 on the basis of DTA data (see Tables 4 and 5) differs, however, from this group.

A discussion on the membership of polynitroarenes to the separate groups (series) of substances from the point of view of electron configuration and steric conditions in the reaction centre of the molecule (see a similar discussion in ref. 2) leads to the following conclusion: in the series of substances with the negative gradient line of eqn. (3) or (4) the dominant influence is exercised by the electron structure while in the series of polynitroarenes with the positive gradient line of the given eqns. the influence of the steric conditions is prevalent within the reaction centre of the molecule upon the kinetics of primary thermolytic processes.

An analysis to verify the validity of eqn. (3) or (4) for a relatively small set of data obtained from polynitroarenes thermolysis in hexachlorobenzene solution (see Table 1) reveals a number of groups of substances; three of them are presented in Table 3. In the coordinate system $Q - E$, also the groups of data 2.3, 14.3, 15.3 and 29.2 can be identified; data 13.2, however, do not correlate with it. Next, in the above-mentioned system, the shape of eqn. (3) is indicated for data 44.2 and 46.1, and also an independent form of the same equation for data 42.2 and 43.2.

The structure of the groups obtained from thermolysis in hexachlorobenzene solution is different from that of data groups obtained from polynitroarene thermolysis in the condensed state. For this reason, if we consider the kinetic data obtained from thermal decomposition in this solution to be a manifestation of the proper molecular structure of a given polynitroarene, then relationship (3) cannot be taken for a mere mathematical relationship of two molecular-structural characteristics of E and Q .

As mentioned above, eqn. (3) is also valid for Piloyan activation energies, E_p ; this is supported by Tables 4 and 5. The data given in Table 4 are based on DTA measurements; during these measurements the substance being thermolysed was in contact with stainless steel (DTA method A [2,41-44]). The data in Table 5 correspond to DTA measurements in which the polynitroarene being examined was in contact with glass (DTA method B

Table 1. Structure of group^a and regression coefficients for Equation 3 and Equation 4. The regression coefficients are given in the columns labeled a, b, c, d, e, f, g, h, i, j, k, l, m, n, o, p, q, r, s, t, u, v, w, x, y, z.

Group No.	Structure of group ^a	Equation 3					Equation 4				
		C	a	r	S _{x,y}	D	b	r	S _{x,y}		
S1	22.2, 26.3, 33.3, 38.3	583.47	-88.14	0.9986	1.65	45.94	-7.35	0.9714	0.64		
S2	25.3, 26.3, 28.2	-867.19	234.44	0.9910	7.46	-72.70	19.06	0.9630	1.26		
S3	28.2, 38.3, 39.2	12.49	47.09	0.9910	4.16	2.11	3.05	0.9949	0.20		

^a Data numbered as in Table 1.

TABLE 4

Coefficients and standard errors of estimate ($S_{x,y}$) of the individual forms of eqn. (3) for thermolysis of polynitroarenes according to DTA method A [2]

Group No.	Structure of substance group ^a	Value of coefficient			$S_{x,y}$
		C	a	r	
A1	1, 2, 3, 4, 13, 15	-1661.70	466.89	0.9927	20.60
A2 ₁	22, 25, 26, 34, 38,	1458.50	-255.55	0.9813	17.22
A2 ₂	18, 22, 23	-282.61	103.27	0.9994	1.57
A3	2, 23, 25	3762.47	-791.34	0.8669	70.76

^a Substances numbered as in Table 1.

[2,41-44]). In order to calculate the coefficients of relationship (3) in Tables 4 and 5, E_p values taken from ref. 2 were applied.

The mutual difference in the structure of the first two groups in Tables 4 and 5 as well as the division of group A2 into two parts is due to the construction material in question with which the substance under thermolysis was in contact (see, e.g., ref. 2).

The factor of importance is the good agreement emerging between the structure of the groups in Table 5 and that of the corresponding groups in Table 2; it should also be noted that during SMM application the substance under thermolysis was in contact with glass. There is an obvious difference in the membership of substance 1; this membership is logical according to both Table 5 and Table 2. Correlation of E_p values obtained from DTA measurements using method B for substances 1, 28 and 30 in the sense of eqn. (3) is not good ($r = 0.5531$). There is, however, a group of substances here, i.e., 28, 30, 33 and 41, exhibiting good correlations of the corresponding data (coefficients of eqn. 3: $C = -266.50$, $a = 123.81$ and $r = 0.9880$). This group exhibits no analogy with SMM data, and from the point of view of the chemical mechanism of the primary fragmentation of thermal decomposition its structure is logical.

TABLE 5

Coefficients and standard errors estimate ($S_{x,y}$) of the individual forms of eqn. (3) for thermolysis of polynitroarenes according to DTA method B [2]

Group No.	Structure of substance group ^a	Value of coefficient			$S_{x,y}$
		C	a	r	
B1	1, 2, 3, 4, 13	-1261.35	348.22	0.9945	14.77
B2	18, 19, 22, 26, 34, 38	859.10	-132.55	0.9108	18.84
B3	19, 26, 28, 39	-427.01	158.17	0.9898	11.13
B4	8, 13, 14, 15	446.28	-52.23	0.9786	2.11
B5	13, 18, 34	2304.19	-485.93	0.9813	13.53

^a Substances numbered as in Table 1.

A study of the initial stage of thermal decomposition of polymethyl and polychloro derivatives of substance 1 using DTA [41] confirmed basically the influence of steric conditions within the reaction centre of the molecule upon thermal reactivity of the said polynitroarenes [41]. This explains why eqn. (3) for group B1 in Table 5 has a positive gradient line. SMM application to the study of thermolysis of the above-mentioned derivatives of substance 1 provided somewhat different information on their thermal reactivities [5,11]. This difference has been previously discussed [41,79], and brings about mutual difference of gradient line marks in eqn. (3) for group I and for group B1 substances.

As mentioned before, for some of the substances in Table 1, Kissinger activation energies, E_K , of decomposition were determined [46]. The relationship of E_K values and the corresponding Q values is represented in Fig. 1: it is evident that logical correlations of E_K values in the sense of eqn. (3) are slightly possible.

Polynitroaliphatic compounds

As compared with polynitroarenes, kinetic data of the thermal decomposition of polynitroaliphatic compounds in the condensed state are less well represented in the existing literature. From the point of view of the number of examined substances, nitric esters have relatively the best situation. Very few data have been published on the thermolysis of condensed polynitroparaffines. There are relatively few data on the thermal reactivity of various nitramines in the condensed state [14]: there have been a considerable number of publications in this field aiming at the technically interesting nitramines 47 and 48 (see, e.g., refs. 14 and 88). For this very reason, the validity of eqns. (3) or (4) for polynitroaliphates is proved in a small number of substances given in Table 6.

TABLE 6

Coefficients and standard errors of estimate ($S_{x,y}$) of the individual forms of eqns. (3) and (4) for thermolysis of polynitroaliphatic compounds in the condensed state

Group No.	Structure of group ^a	Equation 3				Equation 4			
		C	a	r	$S_{x,y}$	D	b	r	$S_{x,y}$
XII	47.1, 47.2, 48.1, 49.1	141.72	13.46	0.9917	3.13	10.63	1.59	0.9961	0.25
XIII	57.1, 58.1, 59.1, 60.1, 61.1, 62.1	175.69	-2.20	0.7922	1.80	13.64	0.27	0.4828 ^b	0.53
XIV	65.1, 66.1, 67.1	145.02	5.27	0.9907	2.29	15.11	0.28	0.5633 ^c	1.37

^a Data numbered as in Table 1.

^b Coefficient of correlation for eqn. (5) is $r = 0.7226$.

^c Coefficient of correlation for eqn. (5) is $r = 0.6703$.

Group XII in Table 6 concentrates the data of nitramine thermolysis possessing $-\text{CH}_2-\text{NNO}_2-\text{CH}_2-$ grouping within the molecule. A selection of these data from the literature was carried out on the basis of a partial knowledge contained in papers [3,4,89] considering the molecular-structural aspect of nitramines' thermal stability (e.g., refs. 91-93) as well as the latest opinions on the thermolysis of substances 47 and 48 in the solid state [93,94]. Data 47.1, 47.2 and 48.1 correspond with thermal decomposition in the solid state, and for nitraminoacid 49 (data No. 49.1) in the liquid state. Substances 48 and 49 exhibit the same conformation of the near neighbourhood of the molecule reaction centre (this is planarity of $\begin{matrix} \text{C} \\ > \\ \text{C} \end{matrix} \text{N}-\text{NO}_2$ grouping, see refs. 92 and 95). The rate of the thermal decomposition of nitramine 48 in the solid state is supposed to be controlled rather by the extinction of intermolecular forces than by the extinction of the covalent bond [93]. In substance 49, on the other hand, in view of its low melting point (52.5-53.5°C) no logical influence can be reckoned with to explain the phenomenon. It follows from this that the decrease of the stabilizing influence of the crystal lattice on the thermal reactivity of nitramines corresponds to the decreasing E , or Q values, within the set of the data in group XII.

Also nitramine 51, which, on basis of DTA [4,89], exhibits a higher thermal stability than substance 47 [4,89], should belong to group XII. Conformation of the surrounding neighbourhood of the reaction centre within the nitramine 51 molecule is the same as in substance 48 [92]. The stabilizing influence of the crystal lattice in substance 51 is responsible for the fact that Arrhenius parameters of its thermal decomposition in the liquid state badly correlate with eqns. (3) or (4) for group XII of the nitramines; the calculated values of E and $\log A$ for the thermolysis of nitramine 51 in the solid state are presented in Table 8.

A problem arises for the specification of eqns. (3) and (4) for the thermolysis of nitramines in the liquid state. Treatment of data 47.3, 47.4 and 48.2, i.e., of data of only two substances, using the least-squares method, results in the form of eqn. (3) with coefficients: $C = -1640.64$, $a = 345.70$ and $r = 0.9958$. Application of eqn. (3) to calculate Q value for nitramine 50 gives a very realistic value of the heat of explosion (5.332 kJ g^{-1}). From the point of view of conformation of the near surroundings of the molecule reaction centre, which is the same for nitramines 47 and 50 (pyramidal arrangement of $\begin{matrix} \text{C} \\ > \\ \text{C} \end{matrix} \text{N}-\text{NO}_2$ grouping, see ref. 92), the correlation in the given sense is logical. Conformation of the near surroundings of the molecule reaction centre in substance 51 (see above) is also responsible for data 47.3, 47.4, 48.2, 50.1 and 51.1 not correlating to each other in the sense of eqns. (3) or (4).

On the basis of the forms belonging to eqns. (3) and (4) for group XII of the nitramines and for the set of data 47.3, 47.4 and 48.2 obtained from

thermolysis in the liquid state, it is possible to "average" Arrhenius parameters of substances 47 and 48. In this way for the thermal decomposition of nitramine 47 in the liquid state, $E = 197.98 \text{ kJ mol}^{-1}$ and $\log A = 18.4$ results, and, in the solid state, $E = 215.44 \text{ kJ mol}^{-1}$ and $\log A = 19.4$. Analogously for substance 48, thermolysis in the liquid state is characterized by values $E = 214.77 \text{ kJ mol}^{-1}$ and $\log A = 18.8$, and, in the solid state, by values $E = 216.11 \text{ kJ mol}^{-1}$ and $\log A = 19.5$. It follows from the given values that the stabilizing influence of the crystal lattice is greater for nitramine 47 than that given in ref. 94; the stabilizing influence for nitramine 48 is, in turn, smaller than could be judged from the results contained in ref. 93. An explanation of this phenomenon can be offered on the basis of the conformation of the near surroundings of the molecule reaction centre and its influence upon the reactivity of the nitramine group (higher reactivity of the pyramidal $\text{N}-\text{NO}_2$ in substance 47 as compared with the lower reactivity in planar $\text{N}-\text{NO}_2$ in nitramine 48), i.e., on the basis of ref. 92. This, of course, means that intermolecular forces control, above all, the rate of thermolysis in the solid state of nitramines possessing pyramidal $\text{N}-\text{NO}_2$ groups within the molecule.

Nitramine 56 data do not correlate with eqns. (3) or (4) for thermolysis of nitramines both in the solid and the liquid state. The mentioned data exhibit a tendency towards the form of eqn. (3) or (4) for group XIII of nitric esters, which can be understood from a molecular-structural point of view. Similarly, data for composition 52 lie in the coordinate system $Q - E$ outside the set of data pertaining to thermolysis of pure nitramines; an account of this fact can be found already in ref. 3 dealing with the influence of polynitroarenes exercised upon polynitroaliphate thermolysis. Neither do data of aliphatic-aromatic nitramine 16 correlate with data sets of aliphatic nitramines. This is again due to the molecular structure (nitramine 16, due to the position of the corresponding data in the $Q - E$ coordinate system, is associated with group XI of the polynitroarenes, which, however, can be an accidental phenomenon).

Arrhenius parameters of thermolysis of nitric esters (group XIII) do not exhibit, in the sense of eqn. (3), a very good correlation; this may be due to a less pronounced dependence of their values upon molecular structure than in the preceding groups of substances. In the case of a bad correlation of these parameters, in the sense of eqn. (4), the reason for this is the same as in group VIII of the polynitroarenes.

Group XIV includes Arrhenius parameters of polynitroparaffin thermolysis. The E value of substance 69 does not correlate with eqn. (3) for this group; inclusion of the value of $\log A$ of this substance, however, into the data set of eqn. (4) improves the correlation ($r = 0.7320$). Steric compression within the molecule of substance 69 may cause a lower activation energy value than that corresponding to its (calculated) heat of explosion. Dependent on the positive oxygen balance of this substance, a lower Q value can

TABLE 7

Coefficients and standard errors of estimate ($S_{x,y}$) of the forms of eqn. (3) for DTA of aliphatic nitramines and of nitric esters according to ref. 4

Structure of group ^a	Value of coefficient			$S_{x,y}$
	C	a	r	
47, 48, 51, 53, 54;	-27.82	66.31	0.9869	12.18
62, 63, 64;	-167.62	79.67	0.9980	3.65

^a Substances numbered as in Table 1.

result; this is the case, e.g., for substance 65 (the calculated Q value = 8.2 kJ g⁻¹). The bad correlation of data in group XIV in the sense of eqn. (4) can, in principle, be thought of in the same way as in the case of data for groups VIII and XIII.

Similar to the polynitroarenes, in this case eqn. (3) is valid for Piloyan activation energies of decomposition E_p . This is supported by the survey in Table 7 (E_p values are taken from ref. 4).

Some application possibilities of the found relationships

The importance and possibilities of applying the found relationships, particularly eqn. (3), for the study and interpretation of the micromechanism of detonation initiation as well as for solving some problems concerning the thermal reactivity of organic explosives, follow from the above discussion.

Application of eqns. (3) and (4) to calculate the heat of explosion is presented in Table 8, addition of data of substances 5, 6, 7, 20, 24, 27 and 68 to the separate groups of data was suggested by their molecular-structural similarity and supported by the preceding discussion of the results obtained. For substance 27, the data 27.3 badly correlate with group VI of the polynitroarenes.

An example of the application of eqns. (3) and (4) to calculate Arrhenius parameters is presented by the survey in Table 9.

CONCLUSION

A considerable amount of knowledge is obtained from the data on the mechanism of thermal decomposition of organic polynitro and polynitroso compounds [3,4,9,12,14,60,67-74,78] and the dependence is shown of the kinetic data values obtained from the study of the thermal decomposition upon the construction material with which the substance being examined is in contact [2,41-45,62,79-81], which proves the homolytic course of the primary thermolytic fragmentation of the above compounds in the con-

TABLE 8
Survey of Q values obtained by means of eqns. (3) and (4)

Sub- stance No. ^a	Substance	Data No. ^a	Group of data	Table No.	Calculated Q values (kJ g^{-1})		average
					according to eqn. (3)	eqn. (4)	
5	CTB	5.1	I	2	4.323	4.410	
		^b	A1	4	4.488	—	
		^b	B1	5	4.695	—	4.479
6	DCTB	6.1	I	2	3.923	4.073	
		^b	A1	4	4.121	—	4.039
7	TCTB	7.1	I	2	3.865	4.009	
		7.1	X	2	3.812	3.779	3.866
20	KDPA	20.1	VII	2	3.733	3.649	
		^b	B3	5	3.871	—	3.751
24	HNBP	24.1	S2	3	4.446	4.428	4.437
27	DMHNB	27.1	II	2	4.441	4.445	
		27.2	I	2	4.451	4.588	
68	TENP	^b	A3	4	4.417	—	4.468
		68.1	XIV	6	11.463 ^c	8.893 ^c	—

^a Numbered as in Table 1.

^b Value of Piloyan activation energy was taken from ref. 2.

^c Unreal (high) value.

TABLE 9

Survey of Arrhenius parameters obtained by means of eqns. (3) and (4)

Sub- stance No. ^a	Substance	Data group	Table No.	State of thermal decompn.	Calculated Arrhenius parameters values	
					E (kJ mol ⁻¹)	log A (s ⁻¹)
23	DPM	VI	2	solid	177.55	11.8
24	HNBP ^b	VIII	2	liquid	126.50	7.4
		VII	2	solid	180.07	12.1
31	DODECA	VII	2	solid	217.48	15.2
32	TPB	I	2	solid	195.47	13.4
36	PYX	VI	2	solid	203.30	14.2
37	ABH	VIII	2	liquid	120.93	7.3
		VII	2	solid	223.56	15.7
40	BTX	IX	2	solid	214.85	13.9
51	DNDC	XII	6	solid	211.50	18.9
53	DPT	XII	6	solid	192.28	16.6
54	DADN	XII	6	solid	189.14	16.2
55	TNAD	XII	6	solid	217.62	19.6
63	ETRYNIT	XIII	6	liquid	165.29	14.9
64	DPHN	XIII	6	liquid	164.59	15.0
70	TENBU	XIV	6	liquid	173.65	16.6

^a Numbered as in Table 1.^b Q value taken from Table 8.

densed state. This is also true for the thermolysis of polynitroarenes having hydrogen in the γ -position towards the nitro group within their molecule (the so-called trinitrotoluene mechanism of thermolysis).

Previous results of analysis of the relationship between kinetic data of low-temperature thermolysis and detonation characteristics of organic polynitro and polynitroso compounds [2-4], as well as the results obtained from the study of the shock sensitivity criterion in organic explosives [48-51] and facts obtained from an experimental research of the micromechanism of initiation of detonation [52,56-59], confirm the identity of the primary chemical processes of thermolysis and detonation change of the above-mentioned nitrogen compounds [62]. The corresponding micromechanism of detonation initiation at the front of the detonation wave [62] is reminiscent of Walker's radical initiation model [66], from which it differs, however, by primary extinction of the preferred intramolecular bond of the excited molecule and by the homolysis beginning as early as in the compression of the molecules of the explosive by the shock wave.

The above is in agreement with the existence of the linear relationship found between the activation energies of the initial non-autocatalytic stage of low-temperature thermolysis, and the heats of explosion of organic polynitro compounds. This relationship cannot be taken for a mere mathe-

mathematical relationship of two molecular-structural characteristics. In order to give a full elucidation of the physical importance of the mentioned relationship of activation energies, which is reminiscent of the Polanyi-Semenov equation we ought to have the necessary kinetic data of thermal decomposition in the condensed state in the homological, or telomeric series, particularly of nitramines, polynitroparaffines and organic polynitroso compounds.

For the purpose of investigating primary chemical processes of detonation change in explosives, the dominant source of serious kinetic data on thermolysis is the Soviet manometric method (see ref. 3). Also very important in this field is the application of the data obtained from differential scanning calorimetry, i.e., of the results obtained by Rogers' methods (see, e.g., refs. 6, 7, 19, 22). Of supplementary importance are also Piloyan activation energies obtained by means of non-isothermal DTA in the sense of refs. 41 and 42. Inapplicable for the study of the micromechanism of detonation initiation are kinetic data resulting from the application of the Kissinger method [47] in DTA measurements along with organic explosives.

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