

KINETIC DATA FROM LOW-TEMPERATURE THERMOLYSIS IN THE STUDY OF THE MICROSCOPIC INITIATION MECHANISM OF THE DETONATION OF ORGANIC POLYNITRO COMPOUNDS

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ABSTRACT

Seventy-three organic polynitro compounds and one nitroso compound were subjected to thermal decomposition; the process was followed using the Soviet manometric method (SMM) or DSC. From the kinetic data of the initial stage of the decomposition, corresponding values were calculated of the natural logarithm of equilibrium constants of the activated complex ($\ln K^\ddagger$). A relationship was found and discussed between the values $\ln K^\ddagger$ and $\ln D$, where D is a detonation velocity at maximum theoretical density of the above-mentioned compounds. Taking into account the previously published relationships, i.e. the relationships existing between thermochemical kinetic characteristics from DTA and detonation characteristics of polynitroaromates, it is concluded that the chemical mechanisms of primary thermolytical processes and initial detonation reactions of organic polynitro compounds are identical. Attention was also paid to the influence exercised by the solvent upon kinetic parameters of thermolysis in the above-mentioned compounds; it is proved that polynitroaromates can in no way be classified as inert solvents.

INTRODUCTION

Explosion and detonation have so far been considered as a thermohydrodynamic phenomenon. This idea is found fully satisfactory for solving problems occurring in routine technological practice though mechanisms of initiation are not included therein [1,2]. It must be stated that initiating mechanisms of detonation, have always been responsible for frequent injuries and crashes; therefore, safety engineering requires that they should be understood and paid attention to [1,2].

So far only a few papers (see refs. 3–9), have been published dealing with the study of the microscopic mechanism of detonation initiation and of other explosive changes during initiation in general. All are basically reduced to experiments aiming at specifying primary fragmentation molecule reactions in thermodynamically unstable compounds by shock wave using spectroscopic [3,4,7–9] and kinetic [6] methods; other papers aim at interpreting the said reactions by modelling procedures (e.g. ref. 5).

However, the primary fragmentation processes within molecules of thermodynamically unstable substances due to shock wave have not been, described in a satisfactory manner. The question arises as to whether their

specification should or could be based upon both extensive experimental and theoretical description of the thermal reactivity of organic polynitro compounds. The opinion of specialists which prevails at present is that, due to shock wave upon the molecule of an explosive, other intramolecular bonds become primarily extinct, which is not the case in low-temperature thermolysis (see for example ref. 9), or that logical relationships existing between low-temperature and detonation reaction parameters are less probable.

The present paper is based directly on Zeman's study [10] from whose results a logical relationship can be deduced between low-temperature thermolysis of primary mechanisms and primary fragmentation explosives at the head of the shock wave. In Zeman's study [10], the relationship between the data obtained from nonisothermal DTA, on the one hand and detonation characteristics of polynitroaromatic compounds, on the other was studied. The said relationship is represented by the general equation [10]

$$\ln \frac{E}{T_D} = bX + a \quad (1)$$

where X can be the $P\rho^{-1}$ term (P being the Chapman—Jouguet pressure, and ρ the maximum crystal density), or the square of the detonation velocity, D^2 , or detonation energy, Q ; in terms of the thermochemical kinetic characteristic, ET_D^{-1} is the Piloyan activation energy of decomposition, E [11–15] within the temperature range immediately after the initial T_D of the exotherm. It should also be added that the ET_D^{-1} term is closely linked to the molecular structure [11,13,14,16,17].

Analysis of the allocation of the studied polynitroaromates to separate forms of one relation (1) type revealed [10] that, in addition to thermochemical factors, the decisive role is played by electron configuration and steric conditions within the reaction centre of the molecule. The reaction centre of the molecule is, the author infers, that part of the molecule within a given compound where primary fission processes occur at low-temperature thermolysis [10].

Equation (1) best represents the relationship between the data obtained from non-isothermal DTA, and detonation characteristics. Somewhat worse correlations are obtained if solely Piloyan activation energy is taken for the datum of DTA; in which case the most suitable equation is [18,43]

$$\ln(\ln D) = c \ln E + d \quad (2)$$

The correspondence of the studied polynitroaromates to the separate shapes of relation (2) is based roughly upon identical conclusions [18,43] as was in the case of eqn. (1).

As eqns. (1) and (2) were derived from the results of measurements carried out only by DTA, doubts may arise as to whether they represent the logical relationship of mutually linked phenomena. It is therefore necessary to analyze, in addition, data obtained from another method, independent of DTA methods, of the kinetics of the thermolysis study, to characterize the detonation of thermodynamically unstable substances.

The most reliable and, at the same time, extensive data obtained from the study of thermal reactivity in thermodynamically unstable compounds are

supplied by the Soviet manometric method (SMM), which uses a glass compensating manometer of the Bourdon type in isothermal measurements [19–21]. The resulting Arrhenius parameters (i.e. activation energy, E_M , and logarithm of the pre-exponent, $\log A$) were originally considered to be characteristics of a monomolecular thermolysis course; the methods used for calculating these parameters from experimental data in the given sense continue to be applicable in practice today.

During the past 8 years, some Soviet authors abandoned the idea of a purely monomolecular character of the initial stage in thermolysis of organic polynitro compounds in the condensed state. Starting from the study of the Trouton relationship in the melts of polynitroaromatic compounds [25,26] and taking into account the concentration dependence of the reaction rate in thermolysis of some polynitroaromates in a solution [27], it was proposed that bimolecular reactions also participate in the initial stage of thermal decomposition in the said compounds [28–30]. According to Maksimov and Kogut [30], bimolecular reactions are absent in the primary fragmentation of polynitroaromates due to heat, if oxidizable substituents (methyl-, hydroxy-, or amino groups) are not contained within the molecules of the compounds, or in the case of homologues of 2,4,6-trinitrotoluene with a branched side-chain. The problems of participation of bimolecular reactions in the measured data are also linked with the detection method of secondary phenomena occurring in the initial stage of thermolysis (see, for example, refs. 11,12,31,32 and 43).

Though there is a basic difference, not only as far as the principles and apparatus equipment are concerned, between the DTA and SMM methods, Zeman managed to discover a relationship between the kinetic data resulting from the application of each of the two above-mentioned methods to the study of the thermal reactivity of polynitroaromates. These relationships are, in general, represented by the expressions [12–14, 22–24]

$$\frac{E}{T_D} = b_1 E_M + a_1 \quad (3)$$

$$\frac{E}{T_D} = b_2 \log A + a_2 \quad (4)$$

Taking relationships of the equations, type 1 and 2, into consideration, the existence of dependence in eqns. (3) and (4), within the framework of the present paper, is the very reason for search of the mutual dependence between the data from SMM and characteristics of stable detonation of the organic polynitro compounds. This set of problems is the subject matter of refs. 18 and 43; in the present paper it is supplemented by a number of aspects dealing with the thermal decomposition of organic polynitro compounds. Some attention is also paid to the possibility of applying the kinetic data obtained from following the thermolysis of the above-mentioned compounds by means of differential scanning calorimetry (DSC), in the study of micro-mechanisms of the initiation of detonation.

SOURCES OF THE DATA

Substances

A survey of the studied compounds, their numbering and code designation is given in Table 1.

Detonation parameters

Detonation parameters, i.e. detonation velocities of the stable detonation at maximum theoretical density as well as values of the crystal density, are summarized in Table 1. The detonation velocities, D , were mostly calculated by means of the semi-empirical Kamlet and Jacobs relationships [33] using values of heat of formation, either tabulated [34–36] or published [10,37,38] (for substances 21, 26, 27, 37, 41, 45, and 47) as well as unpublished values [39] (for substances 50, 51 and 52: 21.21 kJ mole⁻¹, -509.74 kJ mole⁻¹, and -517.77 kJ mole⁻¹, respectively). For substances containing further heteroatoms within the molecule (substances 11, 13, and 29) D values were considered which were obtained experimentally or were calculated using eqn. (1) (see ref. 10 — substances 30, 37, and 40).

The calculation of D values according to Kamlet and Jacobs [33] gave unreal, i.e. too high values (8.1 km s⁻¹, 7.66 km s⁻¹, 9.22 km s⁻¹, 9.71 km s⁻¹, and 9.26 km s⁻¹) for compounds 55, 57, 64, 67, and 72. Therefore, in the case of compounds 56 and 62, maximum values were used in the present work which were obtained from experimentally determined detonation velocities; for substance 57 the calculation was carried out with compression density per 1.3 g cm⁻³.

The maximum theoretical crystal densities were taken from the existing literature; for other substances these values were estimated [10] on the basis of the work of Tarver [40] or calculated [43] according to ref. [41]. The data characterizing crystal densities and detonations of some polynitroaromates were taken from the work of Rouse [42].

Kinetic data of thermolysis

The main source of data on the kinetics of the thermolysis of the studied organic polynitro compounds is papers by Soviet authors dealing with the application of SMM. Within the framework of the present work, it must be added, however, that E_M and $\log A$ values of substances were also applied which have not yet been studied by means of SMM (compounds 23, 24, 26, 32, 33, 34, 35, 37, and 41); the values of these Arrhenius parameters were obtained from the results of the corresponding DTA measurements [22–24, 32] by means of eqns. (3) and (4).

Thermolysis of compound 23 was followed by means of SMM, but only at one temperature [21,44], i.e. without E_M and $\log A$ values being specified. This is also the case for substance 22 [44]; the Arrhenius parameters for this polynitroaromate were obtained from its detonation characteristics [42] using eqn. (1), with subsequent application of eqns. (3) and (4) for poly-

TABLE 1

Survey of the studied compounds, their numbering, code designation, crystal density and detonation velocity

Compound No.	Compound	Code designation	Crystal density ρ (g cm ⁻³)	Detonation velocity ^a D (km s ⁻¹)
1	1,2-Dinitrobenzene	1,2-DNB	1.565	6.43
2	1,3-Dinitrobenzene	1,3-DNB	1.575	6.38
3	1,4-Dinitrobenzene	1,4-DNB	1.625	6.50
4	2,4-Dinitrotoluene	2,4-DNT	1.495	5.99
5	2,6-Dinitrotoluene	2,6-DNT	1.560	6.10
6	3,5-Dinitrotoluene	3,5-DNT	1.53	6.04
7	1,3,5-Trinitrobenzene	TNB	1.688	7.42
8	2,4,6-Trinitrotoluene	TNT	1.654	7.02
9	1,3-Dimethyl-2,4,6-trinitrobenzene	TNX	1.615	6.71
10	1,3,5-Trimethyl-2,4,6-trinitrobenzene	TNMs	1.480	6.20
11	1-Chloro-2,4,6-trinitrobenzene	CTB	1.797	7.20 ^b
12	1,3-Dichloro-2,4,6-trinitrobenzene	DCTB	1.860	6.74 ^c
13	1,3,5-Trichloro-2,4,6-trinitrobenzene	TCTB	1.87	6.55 ^b
14	1-Hydroxy-2,4,6-trinitrobenzene	PA	1.760	7.57
15	1,3-Dihydroxy-2,4,6-trinitrobenzene	TNR	1.830	7.71
16	1,3,5-Trihydroxy-2,4,6-trinitrobenzene	TNPg	1.91	7.99
17	1-Amino-2,4,6-trinitrobenzene	PAM	1.770	7.50
18	1,3-Diamino-2,4,6-trinitrobenzene	DATB	1.837	7.71
19	1,3,5-Triamino-2,4,6-trinitrobenzene	TATB	1.938	7.95
20	3-(2,4,6-Trinitrophenyl-amino)-1,2,4-triazole	PATO	1.940	7.78
21	2,2',4,4',6,6'-Hexanitroxanilide	HNO	1.74	7.34
22	3,3'-Diamino-2,2',4,4',6,6'-hexanitrobiphenyl	DIPAM	1.790	7.62
23	2,2',4,4',6,6'-Hexanitrodiphenylamine	DPA	1.640	7.20
24	Potassium 2,2',4,4',6,6'-hexanitrodiphenyl-aminat	KDPA	1.850	6.92 ^b
25	2,2',4,4',6,6'-Hexanitroazobenzene	HNAB	1.775	7.73
26	2,2',4,4',6,6'-Hexanitrodiphenylmethane	DPM	1.66	7.29
27	α,β -bis(2,4,6-trinitrophenyl)-ethane	DPE	1.69	7.13
28	2,2',4,4',6,6'-Hexanitrostilbene	HNS	1.740	7.27

TABLE 1 (continued)

Compound No.	Compound	Code designation	Crystal density ρ (g cm ⁻³)	Detonation velocity ^a D (km s ⁻¹)
29	2,2',4,4',6,6'-Hexanitrodiphenylsulfide	DIPS	1.660	7.15 ^b
30	2,2',4,4',6,6'-Hexanitrodiphenylsulfone	DIPSO	1.840	6.72 ^c
31	2,2',4,4',6,6'-Hexanitrobiphenyl	HNB	1.740	7.50
32	3,3'-Dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl	DMHNB	1.68	6.83 ^c
33	2,2',2'',4,4',4'',6,6',6''-Nonanitro- <i>m</i> -terphenyl	NONA	1.780	7.61
34	1,4,5,8-Tetranitronaphthalene	TENN	1.800	7.30
35	2,4,6-Tris(2,4,6-trinitrophenyl)-1,3,5-triazine	TPT	1.670	7.08
36	2,4,6-Tris(2,4,6-trinitrophenylamino)-1,3,5-triazine	TPM	1.750	7.29
37	2,4,6-Tris(3-methyl-2,4,6-trinitrophenylamino)-1,3,5-triazine	TPMP	1.67	6.87 ^c
38	1,3,7,9-Tetranitrobenzo-1,3a,4,6a-tetraazapentalene	TACOT-1	1.850	7.44
39	1,3,8,10-Tetranitrodibenzo-1,3a,6,6a-tetraazapentalene	TACOT-2	1.810	7.32
40	1,3,7,9-Tetranitrophenothiazine-5,5-dioxide	TNPTD	1.70	6.50 ^c
41	1,3,7,9-Tetranitrophenoxazine	TNPO	1.70	6.80
42	1-Methylnitramino-2,4,6-trinitrobenzene	TETRYL	1.730	7.77
43	1,3,5-Trinitro-1,3,5-triazacyclohexane	RDX	1.830	8.89
44	1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane	HMX	1.903	9.13
45	1,4-Dinitro-1,4-diazacyclohexane	DNDC	1.80	8.16
46	1,3-Dinitro-1,3-diazacyclopentane	DNDP		
47	<i>N,N</i> -Bis(2,2-dinitropropyl)nitramine	BDNA	1.65	8.20
48	<i>N,N</i> -Dimethylnitramine	NDMA	1.109	6.29
49	<i>N,N</i> -Diethylnitramine	NDEA	1.057	5.34
50	4-Nitrazavaleronitrile	NVN	1.43	6.07
51	4-Nitrazavaleric acid	NVA	1.45	5.77
52	Methyl-4-nitrazavalerate	MNV	1.34	5.42
53	Pentaerythritol tetranitrate	PETN	1.780	8.73
54	Mannitol hexanitrate	MHN	1.730	8.26
55	Glycerol trinitrate	NG	1.600	7.70 ^b
56	Ethylene glycol dinitrate	EGDN	1.506	7.32

TABLE 1 (continued)

Compound No.	Compound	Code designation	Crystal density ρ (g cm ⁻³)	Detonation velocity ^a D (km s ⁻¹)
57	Nitrocellulose (13,35% N)	NC-13, 35	1.659	6.53 ^d
58	<i>N,N</i> -Diethanolnitramine dinitrate	DINA	1.660	8.17
59	1,2-Propyleneglycol dinitrate	1,2-PGDN	1.36	6.71
60	1,3-Propyleneglycol dinitrate	1,3-PGDN	1.30	6.95
61	Nitromethane	MNM	1.138	6.38
62	Nitroethane	MNE	1.058	5.48
63	Trinitromethane	TNM	1.597	8.86
64	Tetranitromethane	TENM	1.650	6.55 ^b
65	1,1-Dinitroethane	1,1-DNE	1.364	7.19
66	1,1,1-Trinitroethane	1,1,1-TNE	1.640	8.55
67	Hexanitroethane	HNE	1.810	9.71 ^e
68	1,1-Dinitropropane	1,1-DNP	1.261	6.48
69	2,2-Dinitropropane	2,2-DNP	1.300	6.56
70	1,1,1-Trinitropropane	1,1,1-TNP	1.53	7.86
71	1,1,1,3-Tetranitropropane	1,1,1,3-TENP	1.60	
72	1,1,1,2,2-Pentanitropropane	PNP	1.80	9.26 ^e
73	2-Methyl-1,1,1,3-Tetranitropropane	MTENP	1.41	7.41
74	<i>N,N</i> -Dimethylnitrosamine	DMNSA	1.006	5.23

^a Calculated according to Kamlet and Jacobs [33].

^b Experimental value.

^c Value from ref. [10].

^d The calculation according to ref. [33] was carried out with compression density per 1.3 g cm⁻³.

^e Unreal, value too high.

nitroaromates of the polyamino-2, 4, 6-trinitrobenzene type [22].

For substance 27, the Arrhenius parameters, E_M and $\log A$, were calculated [23] from DTA measurements [eqns. (3) and (4)]; however, these values, correspond to the thermolysis of substance 27 in the solid state [23]. Within the given temperature range [23], however, the solid state of compound 27 is not stable. In view of the fact that the kinetics of the thermolysis of polynitroaromate 27, using SMM, was studied in hexachlorobenzene medium [30], the corresponding E_M and $\log A$ values for decomposition within the smelt were estimated graphically by plotting the E_M , or $\log A$ values which resulted from the thermolysis of substances 8, 17, 29, and 31 in hexachlorobenzene against the E_M or $\log A$ values of the same substances thermolysed in the smelt.

In the case of substances 43 and 53, within the framework of the present work, E_M and $\log A$ values were also applied which had been obtained using the Robertson isothermal manometric method [45,46]. To demonstrate and compare application possibilities in relation to SMM, kinetic data are pre-

TABLE 2

Survey of the Arrhenius parameters and the thermodynamic data from the initial stage of the thermolysis of the studied compounds

Com- pound No.	Compound	State of thermal decompn.	Arrhenius parameters				Ave. temp. (K) T_m	Thermodynamic data			
			Temp. range (K)	E_M (kJ mole ⁻¹)	log A (s ⁻¹)	Ref.		ΔH^\ddagger (kJ mole ⁻¹)	ΔS^\ddagger (J mole ⁻¹ K ⁻¹)	ΔG^\ddagger (kJ mole ⁻¹)	ln K^\ddagger
1	1,2-DNB	Gas	573-623	230.54	14.6	96	598.0	-225.57	20.49	-237.82	-7.83
2	1,3-DNB	Gas	568-683	221.33	13.0	96	625.5	-216.13	19.34	-228.22	43.90
3	1,4-DNB	Gas	573-623	224.68	13.5	96	598.0	-219.71	-0.56	-219.37	44.12
4	2,4-DNT	Gas	543-603	205.43	13.3	96	573.0	-200.67	-3.08	-198.90	41.75
5	2,6-DNT	Liquid	a	139.56	9.0	25	522.5 ^b	-135.22	-85.59	-90.50	20.83
6	3,5-DNT	Liquid	a	198.87	14.3	25	504.5 ^b	-194.68	16.16	-202.83	48.35
7	TNB	Gas	573-623	201.66	12.4	96	598.0	-196.69	-21.62	-183.76	36.96
8	TNT	Liquid	a	186.08	12.4	25	530.0 ^b	-181.66	-20.62	-170.73	38.74
9	TNX	Gas	543-628	217.15	13.6	96	585.5	-212.28	1.52	-211.39	43.42
10	TNMs	Liquid	523-583	180.03	10.9	28	553.0	-175.43	-49.69	-147.95	32.18
11	CTB	Gas	553-593	144.35	8.4	96	573.0	-139.59	-96.89	-84.07	17.65
12	DCTB	Liquid	463-523	144.44	9.3	28	493.0	-140.34	-79.37	-101.21	24.69
13	TCTB	Liquid	493-533	146.95	9.1	28	513.0	-142.69	-83.53	-99.84	23.41
14	PA	Liquid	514-545	185.05	12.3	28	529.5	-180.65	-22.53	-168.72	38.32
15	TNR	Gas	563-603	154.81	8.4	96	583.0	-149.96	-97.03	-93.39	19.27
16	TNPg	Liquid	a	118.07	5.7	25	540.0 ^b	-113.58	-149.05	-33.09	7.37
17	PAM	Liquid	a	177.09	10.5	25	525.0 ^b	-172.73	-56.92	-142.85	32.72
18	DATB	Liquid	a	185.77	11.4	25	515.0 ^b	-181.49	-39.53	-161.13	37.63
19	TATB	Liquid	456-543	161.18	11.7	21	499.5	-157.03	-33.53	-140.28	33.78
20	PATO	Liquid	453-473	144.86	11.2	21	463.0	-141.01	-42.47	-121.34	31.52
21	HNO	Gas	418-438	226.77	22.0	44	428.0	-223.21	164.94	-293.80	82.56
22	DIPAM	Liquid	574-616	161.08	8.8	96	595.0	-156.13	-90.50	-102.28	20.67
		Liquid	523-573	129.79	7.1	21	548.0	-125.24	-122.36	-58.18	12.77
		Solid	a	193.72	15.1	47	597.0 ^d	-188.75	29.50	-206.36	41.57
		Solid	493-543	196.77	13.2	44	518.0	-192.46	-5.11	-189.81	44.07
		Solid	a	250.62	19.5	47	608.0 ^d	-245.56	114.16	-314.97	62.30
		Solid	557-593	175.00	11.6	44	575.0	-170.22	-40.08	-147.17	30.78
		Solid	a	134.72	10.2	47	562.0 ^d	-130.04	-63.61	-94.29	20.18
		Solid	503-568	215.62	16.0	44	535.5	-211.17	48.21	-236.98	53.23
		Solid	a	190.23	12.8	e	543.0 ^b	-185.71	-12.59	-178.87	39.62

23	DPA	Solid	506-515	177.76	11.0	23,32	510.5	-173.52	-47.11	-149.47	35.21
24	KDPA	Solid	498-509	107.57	5.2	23,32	503.5	-103.39	-158.03	-23.82	5.69
25	HNAB	Liquid	463-493	121.83	6.8	44	478.0	-117.86	-126.97	-57.17	14.38
26	DPM	Solid	462-473	92.95	5.2	23,32	467.5	-89.07	-157.42	-15.47	4.00
27	DPE	Liquid		124.00	6.3	f	528.0 ^b	-119.61	-137.37	-47.08	10.72
28	HNS	Solid ^g	518-528	209.03	15.3	23,32	523.0	-204.68	35.01	-222.99	51.28
				126.77	9.2	47	590.0 ^d	-121.86	-83.16	-72.80	14.84
29	DIPS	Solid	533-573	183.80	12.0	44	563.0	-187.20	-28.63	-171.37	37.27
		Liquid	508-528	131.80	7.4	97	618.0	-127.49	-116.15	-67.32	15.63
30	DIPSO	Solid	473-493	178.77	12.0	21	483.0	-174.76	-27.51	-161.47	40.21
		Solid	473-563	106.76	5.6	92	518.0	-103.45	-150.61	-25.43	5.90
31	HNB	Liquid	513-573	207.24	16.1	21	543.0	-202.73	50.01	-229.88	50.92
32	DMHNB	Solid	491-496	148.18	10.0	23,32	493.5	-144.08	-65.97	-111.52	27.18
33	NONA	Solid	572-596	214.11	14.1	24,32	584.0	-209.26	11.11	-215.75	44.43
34	TENN	Solid	572-605	223.05	15.0	24,32	588.5	-218.16	28.28	-234.80	47.99
35	TPT	Solid	595-607	225.82	15.2	24,32	601.0	-220.82	31.94	-240.01	48.03
36	TPM	Solid	523-563	257.06	19.0	44	543.0	-252.55	105.53	-309.85	68.63
37	TPMP	Solid	507-515	116.18	7.2	23,32	511.0	-111.93	-119.87	-50.68	11.93
38	TACOT-1	Solid	583-623	234.30	15.4	44	603.0	-229.29	35.74	-250.84	50.03
39	TACOT-2	Solid	583-623	189.95	11.7	44	603.0	-184.94	-35.10	-163.77	32.67
40	TNPTD	Solid	573-623	200.96	11.7	44	598.0	-195.99	-35.02	-175.05	35.21
41	TNPO	Solid	509-517	158.55	10.0	32	513.0	-154.29	-66.30	-120.28	28.20
42	TETRYL	Liquid	413-438	167.36	16.0	99	425.5	-163.83	50.12	-185.15	52.33
43	RDX	Liquid ^h	487-513	211.84	19.6	48	500.0	-207.69	117.70	-266.54	64.11
		Liquid	486-572	198.87	18.5	45	529.0	-194.47	96.17	-245.34	55.78
		Solid	423-470	213.52	18.6	21	446.5	-209.31	99.50	-254.23	68.48
		Solid	423-470	217.57	19.1	77	446.5	-213.86	109.07	-262.56	70.72
		Soln. ⁱ	433-473	166.10	14.3	83	453.0	-162.34	17.06	-170.07	45.15
		Gas ^j	443-463	125.60 ^j	11.7 ^j	89	453.0	-121.84	-32.91	-106.93	28.39
44	HMX	Liquid ^k	544-558	214.77	18.8	49	551.0	-210.18	101.58	-266.15	58.10
		Solid	449-503	158.67	11.2	77	476.0	-154.71	-42.70	-134.38	33.96
		Solid	449-503	152.81	10.7	21	476.0	-148.85	-52.27	-123.97	31.32
		Soln. ⁱ	444-488	187.86	15.0	83	466.0	-183.99	30.22	-198.07	51.12
		Gas ^j	503-523	133.97 ^j	13.5 ^j	89	513.0	-129.71	0.13	-129.77	30.42
		Gas ⁱ		193.42	16.4	79	ca. 550.0	-188.85	55.65	-219.46	47.99
45	DNDC	Liquid	489-507	198.45	17.3	78	498.0	-194.30	73.70	-231.00	55.79
		Soln. ⁱ	498-518	155.74	12.0	78	508.0	-151.52	-27.92	-137.33	32.51
46	DNDP	Liquid	423-473	149.46	13.5	78	448.0	-145.74	1.83	-146.56	39.34
		Soln. ⁱ	443-483	155.74	13.6	78	463.0	-151.88	3.47	-153.49	39.87

TABLE 2 (continued)

Compound No.	Compound	State of thermal decompn.	Arrhenius parameters				Ave. temp. (K)	Thermodynamic data			
			Temp. range (K)	E_M (kJ mole ⁻¹)	log A (s ⁻¹)	Ref.		ΔH^\ddagger (kJ mole ⁻¹)	ΔS^\ddagger (J mole ⁻¹ K ⁻¹)	ΔG^\ddagger (kJ mole ⁻¹)	ln K^\ddagger
47	BDNA	Soln. ⁱ	418-443	166.21	15.7	100	430.5	-162.63	44.28	-181.70	50.76
48	NDMA	Gas	453-533	170.82	14.1	101	498.0	-166.72	12.52	-172.90	42.18
49	NDEA	Gas	453-478	174.17	15.1	102	498.0	-170.30	32.15	-185.26	47.87
50	NVN	Soln. ^m	463-503	175.42	14.4	70	488.0	-171.41	19.01	-180.59	44.97
51	NVA	Soln. ^m	473-503	170.82	14.0	70	488.0	-166.76	11.27	-172.26	42.45
52	MNV	Soln. ^m	473-503	169.14	13.7	70	488.0	-165.08	6.29	-168.15	41.44
53	PETN	Liquid	434-506	196.65	19.8	46	470.0	-192.75	122.05	-251.21	64.00
		Soln. ⁿ	343-413	167.47	15.8	84	378.0	-164.33	47.28	-182.20	57.97
54	MHN	Solid	343-413	159.10	15.9	103	378.0	-155.96	49.19	-174.55	55.54
55	NG	Liquid	343-413	163.30	15.4	104	378.0	-160.14	39.62	-175.11	55.70
56	EGDN	Liquid	343-413	163.28	14.5	103	378.0	-160.14	22.39	-168.60	53.64
57	NC-13,35	Solid	408-433	164.12	15.0	105	420.5	-160.62	31.08	-173.67	49.68
58	DINA	Liquid	373-433	173.75	16.5	106	403.0	-170.40	60.15	-194.64	58.10
59	1,2-PGDN	Liquid	345-413	168.72	15.8	107	379.0	-165.57	47.26	-183.53	58.22
60	1,3-PGDN	Liquid	345-413	163.70	14.9	107	379.0	-160.55	30.03	-171.93	54.56
61	MNM	Gas	633-663	227.19	14.3	108	648.0	-221.80	14.85	-231.42	42.95
62	MNE	Gas	763-808	253.55	17.5	109	785.5	-247.02	73.74	-304.95	46.69
63	TNM	Gas	453-473	177.40	15.9	108	463.0	-173.55	47.08	-195.55	50.79
64	TENM	Gas	359-450	159.83	16.3	108	404.5	-156.47	56.30	-179.23	53.29
		Liquid	353-413	156.48	15.5	110	383.0	-153.30	41.43	-169.04	53.08

65	1,1-DNE	Gas	470-539	197.15	16.7	108	504.5	-192.95	62.11	-224.28	53.47
66	1,1,1-TNE	Gas	433-483	180.75	17.2	111	458.0	-176.94	72.47	-210.14	55.18
		Liquid	353-413	178.24	16.2	110	383.0	-175.06	54.83	-196.06	61.56
67	HNE	Gas	363-408	149.79	17.3	111	385.5	-146.81	75.83	-176.04	54.92
68	1,1-DNP	Gas	488-538	200.83	16.9	108	513.0	-196.56	65.80	-230.31	54.00
69	2,2-DNP	Gas	448-483	198.74	17.1	111	465.5	-194.87	70.44	-227.66	58.82
70	1,1,1-TNP	Gas	433-473	176.98	16.8	108	453.0	-173.21	64.92	-202.62	53.80
71	1,1,1,3-TENP	Liquid	^a	205.43	17.6	112	445.0 ^b	-201.73	80.38	-237.50	64.19
72	PNP	Liquid	^a	166.10	19.2	112	430.0 ^b	-162.52	111.30	-210.38	58.84
73	MTENP	Liquid	^a	175.73	17.7	112	440.0 ^b	-172.07	82.39	-208.32	56.94
74	DMNSA	Gas	523-553	210.04	15.3	113	538.0	-205.57	34.77	-224.28	50.14

^a Not presented in original paper.

^b The value assumed on the basis of results of DTA [10] (for polynitroaromatics) and/or on the basis of molecular structure analogy.

^c The temperature region of the start of fusion (DSC measurements); for substance 19 thermolysis in the solid state.

^d The lowest temperature (critical temperature) at which any specific size and shape of explosive can self heat to explosion [47].

^e Arrhenius parameters assumed on the basis of detonation characteristics [42] using eqn. (1) with subsequent application of relationships (3) and (4) for polyamino-2,4,6-trinitrobenzenes [22].

^f Arrhenius parameters assumed on the basis of data from the study of thermolysis in hexachlorobenzene medium (see text).

^g Thermolysis in the "quasi-solid" state [23] (see text).

^h Determined by means of DSC.

ⁱ Solution in 1,3-dinitrobenzene.

^j Calculated by the authors of the original paper from kinetic data, which were obtained from thermolysis within the temperature range near the melting point.

^k By means of DSC in the temperature region of the phase change "solid phase-liquid".

^l The theoretical calculation for the thermal decomposition in the gas phase [79].

^m Solution in dibutylphthalate.

ⁿ Solution in 2,4,6-trinitrotoluene.

sented for substances 18, 19, 20, 28, 43, and 44 which were obtained by Rogers using DSC [47–49].

A survey of the Arrhenius parameters, together with references to literary sources, is given in Table 2.

RESULTS AND DISCUSSION

In the present paper, the original opinion of SMM is maintained, i.e. that they continue to be considered as characterizations of the monomolecular process of the initial stage of thermolysis. The starting point for seeking the relationships existing between these data and detonation characteristics was the knowledge contained in ref. 10, i.e. relationship (1), next the conclusions of refs. 12–14, 22–24 and 43, i.e. relationships (3) and (4), and last but not least, a thermodynamic formulation of the transient state [50,51].

Taking the detonation velocity in a stable detonation at maximum theoretical density for a given form in which the reaction rate is manifested, then this rate is in agreement with the Gibbs activation energy ΔG^\ddagger . In its calculation for the initial stage of thermolysis of substances which are represented by Tables 1 and 2 the following procedure was adopted:

the activation enthalpy, ΔH^\ddagger , of exothermal decomposition (monomolecular reaction)

$$-\Delta H^\ddagger = E_M - T_m R \quad (5)$$

where T_m is the average temperature, i.e. the medium temperature of the overall temperature range for activation energy, E_M ;

activation entropy, ΔS^\ddagger , was obtained in the usual way from the pre-exponent on the basis of the relationship

$$\Delta S^\ddagger = R(\ln A - \ln T_m) - 205.86 \quad (6)$$

values of the Gibbs activation energy were obtained by means of the relationship

$$\Delta G^\ddagger = \Delta H^\ddagger - T_m \Delta S^\ddagger \quad (7)$$

From the practical point of view, the ΔG^\ddagger values were transferred to the non-dimensional natural logarithm of the equilibrium constant of the activated complex (K^\ddagger) using the relationship

$$\ln K^\ddagger = -\frac{\Delta G^\ddagger}{RT_m} \quad (8)$$

The results of the mathematical treatment in the sense of eqns. (5)–(8) are represented in Table 2.

Analysis of the mutual relationship of the $\ln K^\ddagger$ values and those of detonation velocities, D , in the substances given in Tables 1 and 2 reveals that it can best be described by [18,43]

$$\ln D = b_3 \ln K^\ddagger + a_3 \quad (9)$$

Dependence (9) is graphically represented in Figs. 1–5. It follows from these illustrations and data contained in Table 2 that, in the set of compounds studied, relationship (9) exhibits, depending on the molecular structure, or on the mechanism of primary fission and, last but not least, on the physical condition of the substance during thermolysis, a number of concrete shapes. It is according to the membership of the studied compounds as belonging to the separate shapes that the compounds in question are broken up into individual groups.

Polynitroaromatic compounds

Membership of separate polynitroaromatics as belonging to individual shapes of relationship (9) is, to a considerable extent, similar to their membership of separate shapes of eqn. (1) [10]: differences are due to various principles of detecting secondary phenomena occurring during primary thermolytical processes.

The group of compounds, designated in Fig. 1 as group I, is formed by polynitroaromatics 5, 8, 9, 10, 11, 12, 13, 26, 32; to this group also belong, in the case of liquid state decomposition, compounds 27, 28, and 29. For substances 5, 8, 9, 10, 27, and 32 the initial stage of thermolysis is characterized by hydrogen migration from the methyl group, or α -carbon of *n*-alkyl on to the oxygen of the *ortho*-nitro-group [4,22,52–54]. Membership of compound 5 as belonging to group I confirms that the reaction centre of the molecule is formed here by the substituent in position 1 and by the nitro-group in position 2 or 6. The absence of substance 4 in group I of polynitroaromatics is a logical conclusion in the sense that 2, 6-dinitration exercises a decisive influence upon the spatial arrangement within the activated complex.

The shape of relationship (9), for group I, is in good correlation with the

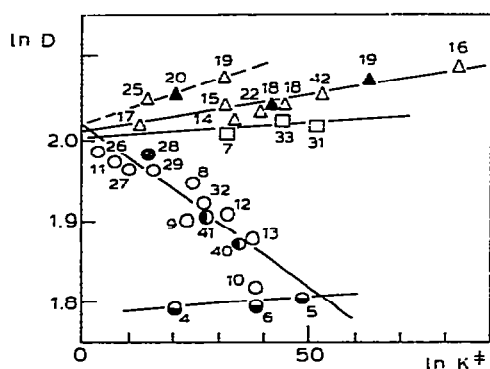


Fig. 1. Graphic representation of eqn. (9) for the thermolysis of polynitroaromatics in the condensed state: \circ , group I; \square , group II; \triangle , group III; \odot , group IV; points \bullet and \blacktriangle correspond to DSC measurements; \bullet , compounds with dinitrophenylene building units.

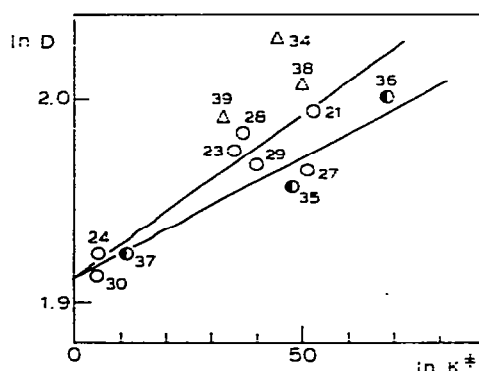


Fig. 2. Graphic representation of eqn. (9) for the thermolysis of polynitroaromatics in the solid state: \odot , group V of 1, 3, 5-triazine derivatives; \circ , group VI of dipicryl compounds; \triangle , compounds with dinitrophenylene building units.

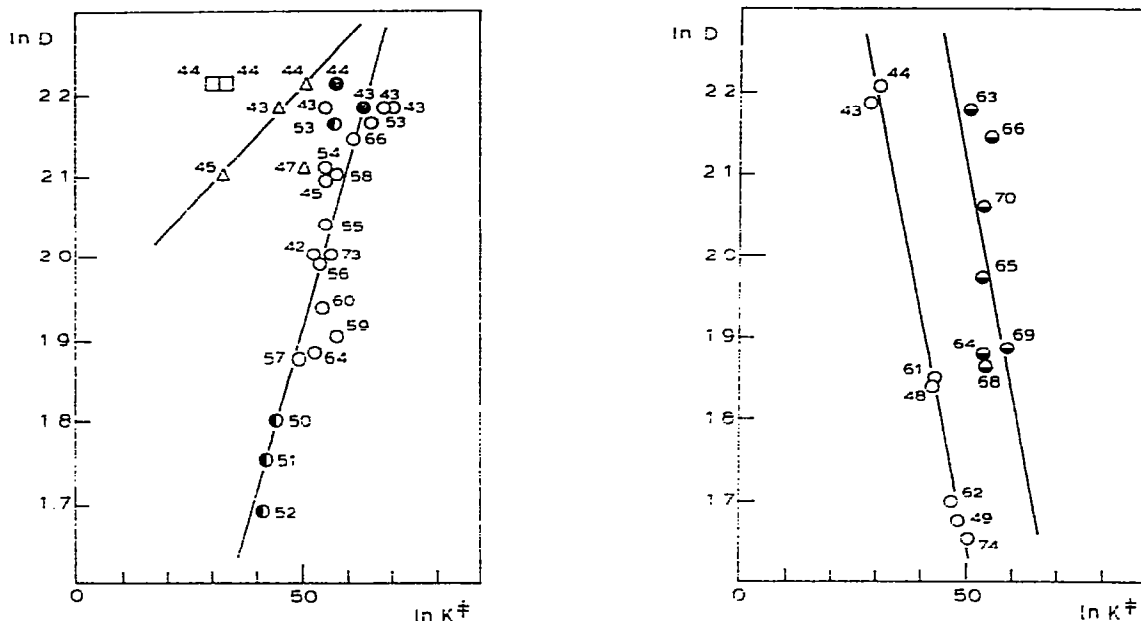


Fig. 3. Graphic representation of eqn. (9) for the thermolysis of aliphatic polynitro compounds: \circ , group VII compounds in the condensed state or \bullet , in solution without the influence exercised by the solvent; points \bullet correspond to DSC measurements. Δ , group VIII compounds thermolysed in 1, 3-dinitrobenzene solution; \square , heterolytic primary fission mechanism.

Fig. 4. Graphic representation of eqn. (9) for the thermolysis of aliphatic polynitro compounds in the gaseous state: \circ , group IX of derivatives and dimethylnitrosamine; \bullet , group X of gem.-polynitroparaffins.

In K^\ddagger value of compound 28, which was calculated from the Arrhenius parameters as obtained by Rogers using DSC [47]. These parameters, correspond to the temperature region where compound 28 melts. Also in the case of this polynitroaromate, the hydrogen migration from the carbon of the vinyl bridge on to the oxygen of the *ortho*-nitrogroup can be taken as the

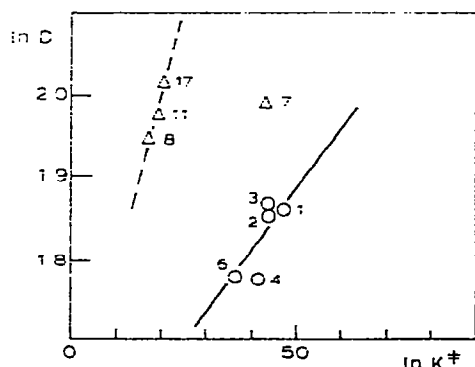


Fig. 5. Graphic representation of eqn. (9) for the thermolysis of polynitroaromates in the gaseous state: \circ , group XI dinitrobenzene derivatives; Δ , group XII trinitrobenzene derivatives.

primary step of thermolysis. (This is a common phenomenon typical of the initial stage of thermolysis of nitroaromates with the hydrogen in the γ -position towards the nitro-group [22,53,54]).

On the basis of the study of the thermolysis in compound 29, Koroban and Maksimov [55] concluded that its thermostability is not restricted by the reactivity of the nitro-group: in the authors' opinion, homolysis of the C—S bond is the primary thermolytic process [55]. From the inclusion of compound 29 in group I, chemical interaction between the *ortho*-nitro-group oxygen and the—S—bridge bond might be considered as being the primary disintegration process of the said polynitroaromate in the liquid state.

However, no attempts have yet been made to carry out a more detailed interpretation of the mechanism of the initial stage of thermolysis in polychloro-2,4,6-trinitrobenzenes. Maksimov et al. [28] suggested, however, that there might be a certain analogy between the thermal decomposition of these derivatives (compounds 11, 12, and 13), on the one hand, and thermolysis of polymethyl-analogues (compounds 8, 9, and 10), on the other. The idea of the said analogy was also suggested by Zeman [12] on the basis of relationships (3) and (4); this idea can further be extended to a given shape of relationship (9) for group I of polynitroaromates.

As can be seen from Fig. 1, there is an apparent correlation between the $\ln K^\ddagger$ values of tetranitrodibenzo derivatives 40 and 41, on the one hand, and the shape of relationship (9) for group I of the compounds, on the other. Thermal decomposition of compound 40 was followed by means of SMM [44]. The authors of the former study [44] are of the opinion that thermolysis of compound 40 starts with homolysis of the C—NO₂ bond. The Arrhenius parameters for compound 41 were obtained from DTA measurement using relationships (3) and (4) [10,32]. On the basis of the inclusion of compounds 40 and 41 in the separate form of relationship (1) [10], as well as considering the molecular structure of the said polynitroaromates, it is possible to suppose the primary mechanism of thermolysis for the two substances which is identical with the ideas of the mechanism at work in the thermal decomposition of nitroaromates with hydrogen in the γ -position towards the nitro-group. To this idea, i.e. to the process of primary fission via a six-member transition state, correspond ΔS^\ddagger values in the two compounds (see Table 2). As will be seen later, compounds of the type tetranitro derivatives 40 and 41 should be corresponded by a separate shape of relationship (9) which cannot be specified because of a small number of points.

Homolysis of the C—NO₂ bonds should characterize as the primary process of thermal decomposition the compounds within group II which is composed of polynitroaromates 7, 31, and 33. This hypothesis may favourably be supposed by ΔS^\ddagger values of compounds 31 and 33. The said value is not in favour of substance 7; as, during its thermolysis in the liquid state, there may be, according to Maksimov [25], a fragmentation due to bimolecular mechanism, where the nitrous acid is a primary product. This hypothesis is, however, in disagreement with a later idea of Maksimov and Kogut [30] who conclude that there should be no participation of bimolecular reactions in primary fragmentation during thermolysis of compounds of group II type.

Group III is made up of polyamino and polyhydroxy derivatives 14, 15,

16, 17, 18, 19, 20, 22, 25 and 42. In the majority of these compounds, migration of hydrogen in the γ -position towards the nitro-group on the oxygen of this nitro-group [22,56] may be the primary step of thermolysis. In the case of nitramine 42, which simultaneously belongs to group VII of the compounds (see Fig. 3), the primary process is the N—NO₂ bond homolysis [57]. From the molecular structure point of view, the $\ln K^\ddagger$ value of compound 20 should be correlated with the shape of relationship (9) for group III; as seen from the Fig. 1 the said value, calculated from DSC measurements data [47], does show a marked tendency towards this shape of the equation.

Considering the results of Zeman [10] as well as the basic features of the molecular structure, polynitroaromates 19 and 25 are also members of group III; however, their $\ln K^\ddagger$ values, calculated from the SMM kinetic data, are not correlated with the shape of eqn. (9) for this category of compounds. In the case of compound 19, we have to do with the planar molecule which is characterized by anomalously prolonged C—C bonds of the benzene nucleus [58], on the one hand, and by anomalously shortened C—NH₂ bonds [58], on the other; six bilateral hydrogen bonds are also present [58]. These inter- and intramolecular hydrogen bonds result from agglomeration of molecules into a planar network in compound 19 [58]. It is in these features that compound 19 differs markedly from the rest of the group III amino derivatives (see refs. 59—62) on their conformation. This difference should, of course, manifest itself in the thermodynamic characteristics during formation of the activated complex in the thermolysis of compound 19. In the case of compound 25, it was proved [63] that homolysis of the C-bridge heteroatom bond, and not reactivity of the nitro-group, is the process limiting thermal stability. This is, however, in disagreement with the ΔS^\ddagger values which was obtained from the SMM kinetic data of the thermolysis of compound 19 (see Table 2).

The position of compounds 19 and 25 in the coordinate system " $\ln K^\ddagger$ — $\ln D$ " can also be interpreted by detecting the primary thermolytic processes, i.e. by influence of the above-mentioned structural, or fragmentation, anomalies on the kinetics of gas products formation. On the basis of the thermal effects of primary thermolytic processes (see ref. [10] — relationship (1)), excellent correlation of data can be obtained for compounds 19 and 25 with those of the remaining polyamino- and polyhydroxy derivatives of 1, 3, 5-trinitrobenzene. What has been said can also be witnessed by an excellent correlation of $\ln K^\ddagger$ values, obtained for compounds 18 and 19 from the corresponding DSC measurements [47], with the shape of eqn. (9) for group III.

However, from the thermodynamic characteristics derived from Rogers's DSC results [47], it follows that the mechanism of primary fragmentation of compounds 18 and 19 differs from the mechanism in the case of other polyamino-polynitroaromates of group III: the corresponding ΔS^\ddagger values are in favour of the primary homolytic fragmentation in some of the intramolecular bonds of the two compounds during their thermolysis. This is in agreement with the idea suggested by Maksimov et al. [64], i.e. that homolysis of some of the C—NO₂ bonds may be a priority monomolecular fission process of compound 19 thermolysis, both in the solid state and solution [64].

Groups I, II, and III of polynitroaromates include, besides most compounds whose $\ln K^\ddagger$ values correspond to thermolysis in the liquid state, these derivatives whose thermodynamic characteristics of thermal decomposition are related to the reaction course in the solid state (compounds 18, 19, 21, 22, 26, 32, and 33). On the basis of the DTA measurements in 1, 3, 5-trinitrobenzene solution [32], only a slightly marked stabilizing influence was confirmed which is exercised by the crystal lattice in compound 26. In compounds 19 and 33, however, this very influence had a most marked character, being, in its turn, hardly observable in compound 18 [32]. Compounds 22 and 32 were not studied from this standpoint. It follows, therefore, that the influence exercised by the solid phase upon thermal reactivity in compounds 18, 19, 26, and 33, and most probably also in 22 and 32, varies, being conditioned by the structure of their molecules. From the inclusion of the said compounds in groups I, II, and III, it may be concluded that, from the standpoint of influence exercised upon the primary formation of the thermolysis gaseous products, their molecular structure is dominant.

It can be easily proved by linear regression analysis that for the value $K^\ddagger = 1$ linear dependences of relationship (9) for groups I, II, and III in practice intersect at one point (see Fig. 1) which is characterized by the detonation velocity value $D = 7.45 \text{ km s}^{-1}$. This can easily be understood as, excepting compound 5, the members of these groups are generated by an ideal substitution within the 1, 3, 5-trinitrobenzene molecule. This point of intersection might correspond to the 2, 4, 6-trinitrophenyl radical. The above-mentioned idea can be verified using the relationships of Kamlet—Jacobs [33] for calculation of detonation characteristics: from the calculated density 1.7 g cm^{-3} of the 2, 4, 6-trinitrophenyl radical (density of compound 7, see Table 1) and from the published value of the heat of formation of the said radical [25,67] $\Delta H_f = 70.75 \text{ kJ mole}^{-1}$, the detonation rate value $D = 7.43 \text{ km s}^{-1}$ is obtained, which is in good agreement with the D value for $K^\ddagger = 1$.

Group IV compounds consist of *m*-dinitro derivatives of toluene. While in compounds 4 and 5 the primary thermolysis step should be linked with the hydrogen transfer from the methyl group onto the oxygen of the *ortho*-nitrogroup, in compound 6 homolysis of the C—NO₂ bond is supposed to occur. The ΔS^\ddagger values, however, in the case of compounds 5 and 6 (see Table 2), do not correspond to these hypotheses. This may be due either to the very method of detecting the primary chemical processes, or it may be caused by bimolecular mechanisms participating in the primary reactions.

The shapes of relationship (9) for groups V and VI polynitroaromates correspond to thermolysis in the solid state (see Fig. 2). Group V is composed of 1, 3, 5-triazine derivatives. These derivatives are a self-contained group even in the sense of relationship (1) [10]. Group VI consists of dipicryl derivatives which, in terms of relation (1), belonged to the group of compounds designated as I in this paper (i.e. derivatives 24, 29 and 30), on the one hand, and also to the group designated here as group III (involving compounds 21, 23, and 28). Contrary to the heat effects of primary thermolytic processes, the kinetics of the formation of the gaseous products in the initial stage of group VI polynitroaromates thermal decomposition, is determined by their respective states. This is clearly visible, particularly in compounds

29 and also 28, whose $\ln K^\ddagger$ values for thermolysis in the liquid state do correlate with the shape of relationship (9) for group I.

From the standpoint of mechanism of thermal decomposition primary reactions, compounds 21, 23 and 28 are comparable with polynitroaromates having hydrogen in the γ -position towards the nitro-group. Compound 29 has already been mentioned, from the standpoint of primary fragmentation, within group I. As far as compound 30 is concerned, homolysis of the C—S bond was proposed by Koroban and Maksimov [55] — SO_2 being released as the primary gaseous product. Thermal fission of ionic compound 24 can be thought of as being an analogy to the thermal fragmentation of picrates [68]. In the case of 1, 3, 5-triazine derivatives, homolysis of the C— NO_2 bond in the *ortho*-positions of picryl is supposed to be primary [24] for compound 35; in the remaining two derivatives (compounds 36 and 37), destruction of the 1, 3, 5-triazine skeleton, or analogy of γ -hydrogen transfer, might be taken into consideration. From the above discussion, it follows that the influence exercised by the solid state in compounds of groups V and VI abolishes the difference within the primary mechanisms thermolysis of these polynitroaromates, it should also be stressed that this holds only for the thermodynamic characteristics of primary production of gaseous products.

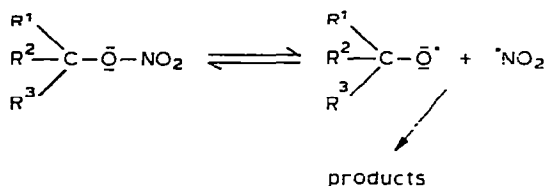
It is evident from Fig. 2 that linear dependences, of the relationship (9) type, for groups V and VI ($K^\ddagger = 1$) intersect one another ($D = 6.77 \text{ km s}^{-1}$). It is a most difficult task, however, to specify the basic fragment corresponding to this point of intersection within the present paper. Also, compounds of the two groups are, to a certain extent, generated by an ideal substitution within the 1, 3, 5-trinitrobenzene molecule.

As seen from Fig. 2, there are apparent correlations between the relationship (9) shape in groups VI, on the one hand, and $\ln K^\ddagger$ values of thermolysis of compounds 34, 38, and 39, in the solid state, on the other. It follows from what has so far been said that a separate shape of relationship (9) will also exist for these derivatives containing dinitrophenylene building units within the molecule. This shape of relationship (9) cannot, however, be specified in a reliable manner because of a small number of points and their scatter. It is, however, possible to assume separate shapes of relationship (9) for derivatives of compounds of type 40 and 41 (angular systems) and for derivatives of compounds of type 34, 38, and 39 (planar systems from the standpoint of the basic skeleton) which will intersect each other at $K^\ddagger = 1$.

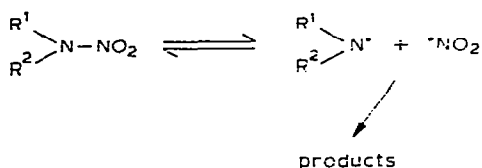
Polynitroaliphatic compounds

Polynitroaliphatic compounds are, within the present paper, represented by aliphatic esters of nitric acid, by aliphatic cyclic and linear nitramines and gem.-polynitroparaffins. For thermolysis in the condensed state as well as in an "inert" solvent, all these compounds are, on basis of eqn. (9), quoted in group VII (see Fig. 3). Compounds belonging to group VII are characterized by primary thermolytic processes which are given in Schemes 1–3.

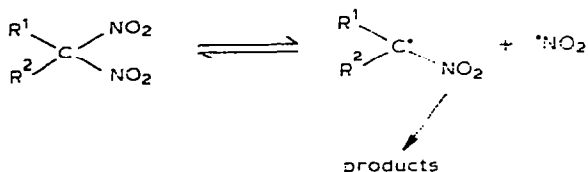
Correspondence of the compounds to the shape of relationship (9) for group VII is, therefore, unambiguously determined by the mechanism of the primary reaction of thermal decomposition. This is why the shape of rela-



Scheme 1. Primary fission of nitric esters in the initial stage of thermolysis [69].



Scheme 2. Primary fission of nitramines in the initial stage of thermolysis [70].



Scheme 3. Primary fission of gem.-poly nitroparaffins in the initial stage of thermolysis [65,66].

tionship (9) for group VII is perfectly correlated, e.g. to the $\ln K^\ddagger$ value of aliphatic—aromatic nitramine 42 thermolysis (see group III of polynitroaromates).

From the graphic representation of relationship (9) shape for group VII (see Fig. 3), the scatter is obvious of the $\ln K^\ddagger$ values of the initial stage of thermolysis of nitramines 43 and 44. The scatter, particularly in the case of compound 43, may be due to the difference in physical conditions under which corresponding experiments are carried out, i.e. it may be caused by the varying degree of bimolecular mechanisms and autocatalytic reactions participating in the results. The possibility of bimolecular mechanisms participating in the thermal decomposition of cyclic nitramines 43 and 44 results from intermolecular non-bonding interactions in the condensed state of these compounds, particularly in the molecular crystal (nitramine 43, see ref. 71 and for nitramine 44 see ref. 72). These bimolecular reactions of nitramines most probably set in very early after the beginning of the monomolecular fragmentation in the sense of Scheme 2.

Products of the thermal decomposition of cyclic nitramines 43 and 44 exhibit a marked autocatalytic influence upon this chemical change [73—76, 93,98]. Participation of bimolecular and autocatalytic reactions in the resulting kinetic data obtained from thermolysis of nitramines 43 and 44 (as well as organic polynitro compounds in general) can be excluded by following a suitable part of this reaction under an appropriate choice of reaction condi-

tions and, above all, by using a suitable method of detecting secondary phenomena of primary processes, i.e. by a suitable choice of physical conditions of the experiment. A great variety of physical conditions applied by various authors as well as a high sensitivity of the thermolysis of nitramines 43 and 44 towards the presence of decomposition products cause divided opinion over primary fragmentation processes of the thermal decomposition in these compounds.

As far as nitramine 43 is concerned, kinetic data were applied in the present paper which were obtained from thermolysis in the liquid state by Robertson [45] as well as by Rogers and Smith's DSC method [48]; for decomposition in the solid state, the $\ln K^\ddagger$ calculations are based upon the results obtained from SMM [21,77]. There is a fairly good correlation between the $\ln K^\ddagger$ values, derived from all the above-mentioned methods for compound 43, on the one hand, and the shape of relationship (9) for group VII (see Fig. 3), on the other. By that means as well as by an excellent correlation of the $\ln K^\ddagger$ values of compounds 42, 45, 50, 51, and 52, to the mentioned shape of eqn. (9), the hypothesis of the Institute of Chemical Physics of the Soviet Academy of Science research officers that the N—NO₂ bond homolysis is the primary fragmentation process of nitramine thermal decomposition in the condensed state [78], was proved beyond all doubt.

It is obvious from Fig. 3 that the kinetic parameters of nitramine 44 thermolysis, in the solid state, do not correspond to the N—NO₂ bond homolysis. An analysis of the possible monomolecular reaction of compound 44 thermal decomposition in the gaseous state revealed [79] that the N—NO₂ bond or C—N bond homolysis might occur here, other explanations being a four- or five-centre nitrous acid elimination, or depolymerization to CH₂=N—NO₂. The N—NO₂ bond homolysis predominates at the reaction temperature above 550 K [79]. Quite recently confirmation has been obtained by means of ESR [80—82] that, during nitramine 44 thermal decomposition within the temperature range below its melting point (i.e. below 550 K), CH₂=N[•] and [•]NO₂ radicals come into existence, with the former prevailing. By thermolysis of compound 44, within the temperature range above 550 K, predominance of [•]NO₂ radicals was proved in the resulting products of the reaction [80—82]. The obtained results from ESR are supposed to be related to the thermal decomposition of compound 44 in the condensed stage [80—82]; arrangement of the experiments and conditions of their realization [80—82], however, suggest a real possibility of detecting the nitramine 44 thermolysis products in both the condensed and gaseous states.

Carrying out thermal fission of nitramine 44 in a solution or in the gaseous state, the above-mentioned Soviet authors unambiguously proved the N—NO₂ bond homolysis to be the primary thermolytic process (see further). The cyclic nitramine 44 is, therefore, an example of a substance whose crystal lattice influence may, under a given set of conditions, bring about a change of the fission mechanism as compared to an "isolated" molecule or its structural analogues. As evidenced from Fig. 3, as well as from the survey of kinetic and thermodynamic data contained in Table 2, application of DSC seems to be a most suitable procedure for the study of the initial stage of thermal decomposition of compound 44.

The influence exercised by the solvent

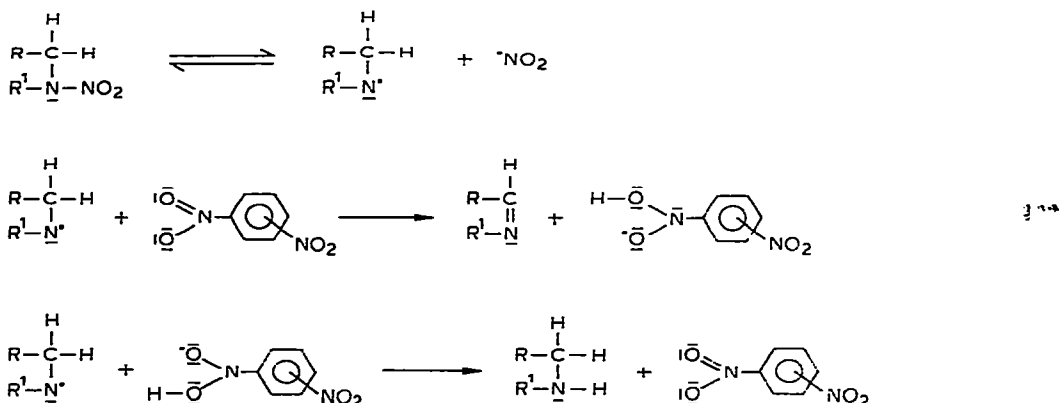
Thermal decomposition of group VIII compounds (see Fig. 3), i.e. nitramines 43, 44, 45, and 46, was kinetically studied in 1,3-dinitrobenzene solution [78,83]. The thermal decomposition of nitramine 47 was studied under the same conditions; the corresponding $\ln K^\ddagger$ value for this compound, however, was well correlated with the shape of relationship (9) for group VII (see Fig. 3).

Another member of group VII is nitroester 53 whose thermal decomposition was studied both in the melt [46] and in 2, 4, 6-trinitrotoluene solution [84]: here also the two resulting $\ln K^\ddagger$ values are well correlated to the shape of relationship (9) for the above-mentioned group of compounds (see Fig. 3).

The facts given above can be accounted for on the basis of Urbański and Buźniak's knowledge [85–87] concerning the study of the retardation influence exercised by nitroaromates upon the radical polymerization. The application of one of the suggested mechanisms [86] of the said influence upon nitramines thermolysis in dinitrobenzenes solution leads to Scheme 4.

For the nitroester (see Scheme 1) similar results would be obtained by the aldehyde and alcohol, and for gem.-dinitroparaffin (homolysis according to Scheme 3) these results would be yielded by the nitro-olefin and nitroparaffin.

The viability of the nitroaromate and the radical interaction, in the sense of Scheme 4, should primarily be determined by steric conditions in the neighbourhood of the α -carbon: in the case of compound 53, the radical of neopentyl type originates according to Scheme 1; therefore termination, according to Scheme 4, should not occur. This is why there is correlation between the $\ln K^\ddagger$ value of nitroester 53 thermolysis in 2, 4, 6-trinitrotoluene, on the one hand, and the shape of relationship (9) for group VII compounds, on the other. Similarly, the thermolysis of compound 47 (see Scheme 2 of homolysis) in 1, 3-dinitrobenzene could be interpreted: here β , β -dinitration makes termination, in the sense of Scheme 4, sterically non-



Scheme 4. The probable mechanism of the polynitroaromate's interaction with the primary products in the thermolysis of nitramines (reproduced from ref. 43).

viable; this is also why the corresponding $\ln K^\ddagger$ value is well correlated to the shape of relationship (9) for group VII compounds.

Interaction in the sense of Scheme 4 reduces the $\ln K^\ddagger$ values. This reduction is greater, the lower the sterical disturbances in the neighbourhood of the α -carbon (see the trend of the $\ln K^\ddagger$ values in relation to the molecular structure of group VIII compounds).

From what has been discussed above, it may be concluded that nitroaromates can in no case be considered as inert solvents in thermolytical reactions. In the case of the 1, 3, 5-trinitrobenzene this fact was stressed by Zeman [32].

It is most tempting to consider an analogous influence, as presented in Scheme 4, to be at work also in the thermolysis of polynitroaromates themselves. Interaction of this type might be the starting-point of participation by bimolecular processes at the start of the thermal decomposition of these polynitro compounds (see the thermal decomposition of compound 7 mentioned above). Conclusions reached by Janzen [88] are, to some extent, in favour of this hypothesis.

Within the realm of the polynitroaliphatic compounds studied here, dibutylphthalate may be considered an "inert" solvent; the former was already applied as a medium in the study of the kinetics of the thermal decomposition of nitramines 50, 51, and 52 [70]. In the case of these nitramines, the mechanism of primary fission in the sense of Scheme 2 was proved again by analyzing the obtained kinetic data from various standpoints [70]. Inclusion of compounds 50, 51, and 52 in the shape of relationship (9) for group VII compounds is stressed by the fact that the radical $\cdot\text{NO}_2$ is the primary joint product of thermolysis of polynitro compounds belonging to this group in the condensed state.

Using the shape of relationship (9) for group VIII nitramines as well as the $\ln K^\ddagger$ value of the thermolysis of compound 46 in 1,3-dinitrobenzene, the corresponding D value was calculated (see Table 3).

TABLE 3
Survey of D values obtained by means of eqn. (9)

Compound	Detonation velocity (km s^{-1})		
	According to eqn. (9)		According to ref. 33
	Shape of eqn. (9) ^a	D	
DNDP	VIII	8.5	
HNE	X	7.2	9.7
1,1,1,3-TENP	VII	8.8	
PNP	VII	8.0	9.2

^a Shape of eqn. (9) numbered as in Figs. 3 and 4.

Thermolysis in the gaseous state

Figure 4 demonstrates dependences of relationship (9) type for polynitroaliphatic compounds; the corresponding kinetic data of thermolysis (see Table 2) were obtained by means of SMM in the gaseous state.

Group IX is composed of compounds 43, 44, 48, 49, 61, 62, and 74. The Arrhenius parameters of compounds 43 and 44 for thermolysis in the gaseous state were derived on the basis of mathematical treatment [89] of kinetic data of their thermal decomposition within the temperature range near the melting points of each separate nitramine given. Here, due to sublimation, thermal decomposition of the two nitramines occurs even in the gaseous state. This is why, perhaps due to a less fortunate choice of calculation model, the value $\Delta S^\ddagger < 0$ results for nitramine 43 (see Table 2).

The group X is made up of gem.-polynitroparaffins 63, 64, 65, 66, 68, 69, and 70. The $\ln K^\ddagger$ values of these compounds do not show a more marked dependence upon the molecule structure. Using the relationship (9) shape for this group of polynitro compounds, the D value of compound 67 was estimated (see Table 3).

Figure 5 demonstrates the shape of relationship (9), above all, for dinitrobenzene derivatives (group XI of polynitro compounds). An analogous dependence for some 1, 3, 5-trinitrobenzene derivatives is also indicated (group XII compounds).

Comparison of dependences presented in Fig. 3 with those in Fig. 4 reveals unambiguously a marked influence exercised by intermolecular interactions of molecules in the condensed state upon the kinetics of the thermolysis of organic polynitro compounds, with the primary fission mechanism being maintained at the same time. In this connection it must be stressed that dependences, presented in Figs. 1–3, are more valuable for the study of mechanisms ruling detonation initiation of thermodynamically unstable materials.

Interpretation of dependences found

In order to interpret relationships (1), (2), and (9) it is necessary, above all, to specify in a more detailed manner the initial region of primary molecule fragmentation occurring during detonation change of organic polynitro compounds. There is a general belief that the chemical reaction does not start until the shock compression of the molecule layer of the explosive [90] has been achieved; another theory being that the explosive does not change chemically at all during the compression process [91]. The temperature of the compressed molecules layer, reaching as high as 1000 or 2000 K [91], is achieved by a pressure ranging from 10 to 35 GPa; the heat stability of the most stable explosives, however, varies from 570 to 620 K [92]. It must logically follow that the primary thermolytic processes must be occurring as early as during the compression process of the original explosive. It cannot be argued that the shock compression is instantaneous as "instantaneous" is generally understood only from the point of view of man's conception of time; it should be understood in terms of the reaction time.

A stable detonation is characterized by constant parameters, i.e. by an unchanging detonation velocity, D , detonation pressure, P , and detonation energy, Q , throughout the whole period of duration of this explosive change. This means that fragments, or possibly radicals produced by the primary fission processes, at shock compression of molecules in a given explosive at the front of the detonation wave are constant throughout the whole detonation process; this must also correspond to the constant character of the chemical mechanism of this process. In the same way, also constant must be the chemical mechanisms and their relative representation during mutual fragments or, possibly, radicals interaction within the chemical reaction zone of the detonation wave. It follows from these conditions of the stable detonation that, e.g., thermal colouration of the primary fission processes at the front of the detonation wave must be in a logical relationship towards the overall reaction heat, i.e. towards the detonation energy. If there is a correlation between the thermochemical kinetic characteristic of the primary fragmentation processes in low-temperature explosives thermolysis (without autocatalysis influence), on the one hand, and detonation energy [relationship (1)], or detonation velocity [relationship (2)], on the other, then there must necessarily be an identity or logical link-up between the primary mechanisms of low-temperature and detonation reaction.

Studies of relatively extensive experimental material available have confirmed that the decomposition reaction of the explosive, on being compressed by a shock wave, does not initiate in a coherent layer of compressed molecules but in the so-called "hot spots" [91,31]. Moreover, it is well known that the detonation rate of a stable detonation does not depend upon the concentration of a given explosive. The chemical change of a one-component explosive at the front of the detonation wave is therefore of zero order.

The reaction rate of the zero order reaction can be presented by the relationship

$$\ln w = \ln K^\ddagger + \ln \left(\kappa \frac{k \cdot T}{h} \right) \quad (10)$$

where κ is the transmission coefficient, k is Boltzman's constant, h is Planck's constant, and T is the average temperature of the reaction. It need not be stressed that eqn. (10) is formally identical with eqn. (9): relationship (9) represents the reaction of zero order, coefficients b_3 and c_3 including the correction in view of the detonation conditions. This is in favour of the identity of the primary fission processes of low-temperature and detonation reactions. What has so far been said is evidenced by the fact that primary fragmentation of the compound 43 molecule by the shock wave results unambiguously in the homolytic extinction of the N—NO₂ bond [7—9].

In contrast to the information contained in the present paper are conclusions arrived at by Owens and Sharma [9]. These authors are not critical enough in exclusively comparing the results obtained from the study of the primary molecules fragmentation in compounds 8 and 43 due to shock with those obtained from their slow and extensive destruction by heat. In extensive thermal decomposition of organic polynitro compounds, an important role is played by autocatalytic processes setting in rather early after the initiation

of decay in a given compound [11,13,14]. The results contained in the present paper testify again to the fact (see also refs. 10, 94 and 95) that only kinetic data of such "low-temperature processes" in which the influence of autocatalysis is excluded can be extrapolated to detonation conditions.

CONCLUSIONS

In organic polynitro compounds there are reciprocal relationships between the kinetic, or thermodynamic characteristics of thermal decomposition, on the one hand, and their detonation parameters, on the other, under the condition that the given kinetic or thermodynamic data are related to that stage of thermolysis of the above-mentioned substances in which autocatalysis has not yet started. The most reliable and extensive kinetic data of this kind available as yet, are presented by the Soviet manometric method (SMM). A most promising source of these data is differential scanning calorimetry (DSC), namely the method of Rogers [49,114], and that of Rogers and Smith [48]; good results can, of course, also be gained by differential thermal analysis (DTA).

The relationships found to exist between the thermochemical kinetic characteristics obtained from DTA, or thermodynamic characteristics which were derived from SMM, or DSC application, on the one hand, and detonation characteristics of organic polynitro compounds, on the other, testify in favour of the identity of primary fragmentation mechanisms of thermolytic and detonation reactions of the above-mentioned compounds.

During the application of benzene or toluene polynitro derivatives as solvents to the study of the kinetics of the thermal decomposition of organic polynitro compounds, the above-mentioned nitroaromates can by no means be considered as inert solvents. In thermolytic studies of aliphatic polynitro derivatives, the said polynitroaromates can exercise influence upon homolytic fragmentation analogous to their termination interactions in the radical polymerization. It is also possible to consider the same or similar influence in thermolysis of the polynitroaromates themselves.

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