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POSSIBILITIES OF APPLYING THE PILOYAN METHOD OF DETERMINATION OF DECOMPOSITION ACTIVATION ENERGIES

PART III. DERIVATIVES CONTAINING TWO PICRYL GROUPS IN THE MOLECULE, AND MELAMINE DERIVATIVES

S. Zeman

Department of Research, Chemko, 072 22 Stražske, ČSSR

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Via the Piloyan method, activation energies E were determined for polynitroaromatic compounds containing two picryl groups, and for melamine derivatives. At the same time the initial temperatures of exothermic decomposition T_D were determined by means of non-isothermal DTA. Linear relationship were derived between $E \cdot T_D^{-1}$ and published kinetic data obtained from the study of HNB, HNAB, DIPS, DIPSO, HNS and TPM by isothermal manometry. On the basis of the derived relationship, as well as E and T_D values from DTA measurements, kinetic data were calculated for DPA, KDPA, DMHNB, DPM, DPE and TMPM with the manometric method.

From the point of view of the study of the kinetics of thermal decomposition, literature data dealing with the category of compounds in question contain little relevant information. An isothermal manometric method has been used to determinate kinetic data on the thermal decomposition of 2,2',4,4'6,6'-hexanitrobiphenyl (HNB) [1], 2,2', 4,4', 6,6'-hexanitrodiphenyl-sulfide (DIPS) [1–5], 2,2', 4,4', 6,6'-hexanitrodiphenylsulfone (DIPSO) [3–5], 2,2', 4,4', 6,6'-hexanitrostilbene (HNS) [4, 5], and 2,2', 4,4', 6,6'-hexanitroazobenzene (HNAB) [4, 5]. There is only mention of 2,2', 4,4', 6,6'-hexanitrodiphenylamine (DPA) in papers [1, 5], but no data are given on the Arrhenius parameters of its thermal decomposition. As regards N-picrylsubstituted melamine derivatives, the thermal decomposition of N^2, N^4, N^6-tris(2, 4, 6-trinitrophenyl)-melamine (TPM) was studied by the manometric method [5]. From the kinetic standpoint, the thermal decomposition of 2, 2', 4, 4', 6, 6'-hexanitrooxanilide (HNO) was also described [1, 4, 5]; on the basis of the assumed primary step mechanism of its thermal decomposition [6], HNO may be grouped within this category, with polyamino and polyhydroxy derivatives of 1,3,5-trinitrobenzene [6].

By means of the American vacuum test, the rates of thermal decomposition of HNB [7], HNAB [7], HNS [8, 9] and DPE [9] have been determined. The values obtained in this way are absolutely different from analogous data obtained by application of the manometric method. This difference is revealed by the dependence of the kinetic data values (obtained from thermal decomposition of organic polynitro compounds) upon the techniques and physical conditions of thermal measurements (see also [6]).

Application of DTA to the investigation of the thermal stability of DPA is a part of paper [10]. Application of non-isothermal DTA to a determination of the Piloyan activation energies of this group compounds forms part of papers [11, 12]; this has not been published elsewhere so far.

Experimental

Materials

2,2',4,4',6,6'-Hexanitrobiphenyl (HNB) was obtained by the Ullmann condensation of picryl chloride in nitrobenzene, catalyzed by activated powdered copper. It was purified by fourfold crystallization from acetone; m.p.: 515.1 – 516.1 K.

2,2',4,4',6,6'-Hexanitrodiphenylsulfide (DIPS) was prepared by the action of picryl chloride solution in ethyl alcohol upon $Na_2S_2O_3$ aqueous solution [13]. It was purified by threefold crystallization from acetone; m.p.: 507.1 – 508.1 K.

2,2',4,4',6,6'-Hexanitrodiphenylsulfone (DIPSO) was prepared by DIPS oxidation with CrO_3 solution in fuming nitric acid [14]. It was purified by evaporation with crystallization from acetone – toluene solution; m.p.: 614.1 K under decomposition.

2,2',4,4',6,6'-Hexanitrostilbene (HNS) was prepared from the technical product by crystallization from dimethylformamide with subsequent crystallization from cyclohexanone; m.p.: 585.1 – 587.1 K under decomposition.

2,2',4,4',6,6'-Hexanitroazobenzene (HNAB) was prepared from picryl chloride and hydrazine [15], with subsequent oxidation of the resulting hexanitrohydrazobenzene with nitric acid. It was crystallized several times from an acetone methanol mixture; m.p.: 495.1 – 496.1 K.

2,2',4,4',6,6'-Hexanitrodiphenylamine (DPA) was obtained by nitrating 2,4-dinitrodiphenylamine with a H_2SO_4-HNO_3 mixture. It was purified by crystallization from dimethylformamide, with subsequent crystallization from a dimethylformamide – acetone mixture; m.p.: 516.1 – 517.6 K.

The potassium salt of DPA (KDPA) was obtained by the action of potassium acetate on DPA in a dimethylformamide – ethanol mixture [16]; m.p.: above 573 K under decomposition.

3,3'-Dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl (DMHNB) was prepared by the Ullmann condensation of 3-methyl-2,4,6-trinitrochlorobenzene. It was purified by multiple crystallization from acetone; m.p.: 512.6 – 513.6 K.

2,2',4,4',6,6'-Hexanitrodiphenylmethane (DPM) was prepared by condensation of trinitrotoluene with picryl chloride [17]. It was purified by threefold crystallization from acetone; m.p.: 503.1 K under decomposition.

2,2',4,4',6,6'-Hexanitro-α,β-diphenylethane (DPE) was prepared by condensation of trinitrotoluene [18]. After twofold crystallization from acetone, it exhibited a m.p. of 491.1 – 492.6 K.

N^2,N^4,N^6-Tris(2,4,6-trinitrophenyl)-melamine (TPM) was obtained by nitration of triphenylmelamine with a H_2SO_4-HNO_3 mixture [19]. It was purified by threefold crystallization from an acetone – methanol mixture. It does not melt up 573 K, but decomposes above that temperature.

N^2,N^4,N^6-Tris(3-methyl-2,4,6-trinitrophenol)-melamine (TMPM) was prepared by nitration of tris(m-tolyl)-melamine with a H_2SO_4-HNO_3 mixture [20]. It was purified by crystallization from an ethyl acetate – methanol mixture. It does not melt up tu 533 K, but decomposes above that temperature.

The purities of the compounds were checked by thin-layer chromatography against Silufol UV 254, with acetone – cyclohexane in varying ratios as mobile phase.

Methods

The first part of the present series [21] gives a description of the DTA apparatus, methods and conditions of measurements. Simax or Rasotherm glass was employed for production of the test-tubes and capillaries to place the sample and thermoelements in the equipment.

Measurements with Fe-Co thermocouples enclosed in Type 19112e No. 36-1 stainless injection needles (produced by Chirana, Stará Turá, ČSSR) are devoted method A. Method B, on the other hand, involves measurements using Fe-Co thermocouples, enclosed in glass capillaries.

Results and discussion

Table 1 shows values of the Piloyan activation energies E, and also the initial temperatures of the exotherm T_D obtained by DTA measurements. Simultaneously, it includes the published values of activation energies E_M and the logarithm of the preexponent A of the Arrhenius equation, provided the values were determined by manometry on the same compounds which are studied here.

The influence of the weight of the sample upon the value of the initial exothermic decomposition temperature T_D is ambiguous; in a number of measured compounds it is even unspecified, because of the small number of measurements. For example, in DTA measurements by method A on HNB the decrease in weight of the sample leads to a slight drop in the T_D values, while in measurements by method B the trend of these values is the reverse. The T_D shift with the change in weight of HNS is of the same sense as, for example, in TNT [21], and similar for DPA as in 2,4,6-trinitroaniline [6], with the same method of DTA measurements. However, no systematic dependence of the T_D value upon the sample weight was found for DIPS.

In so far as compounds were measured according to methods A and B in the present paper, mutual comparison of the results obtained reveals that contact of the compounds with the glass surface causes an overall decrease of their thermal stability when exposed to heat, though HNB and HNAB exhibit a certain increase in T_D values. As regards the initial temperature of exothermic decomposition of HNS and DIPS, no marked influence was observed when stainless steel (method A) was exchanged for glass (method B).

Table 1

Survey of

Substance	Differential thermal				
	Method A[11,12]				Method
	sample weight mg	initial decomposition K	temperature region K	E kJ · mol^{-1}	sample weight mg
HNB	107.9	534.9	541–553	403.93	97.6
	103.3	534.4	541–550	362.65	92.2
	95.2	533.6	538–550	323.17	81.2
					32.9
DIPS	102.1	525.7	531–541	386.18	102.0
	100.1	525.4	529–539	410.71	101.4
					99.7
					87.5
					80.1
DIPSO	103.1	525.7	537–557	207.91	102.6
	100.0	534.1	538–561	232.19	89.3
	97.7	531.2	538–553	226.04	85.1
HNAB	100.1	514.1	519–527	245.00	102.8
	94.3	516.0	521–539	189.65	100.3
					88.7
HNS	117.0	544.1	550–558	312.24	99.4
	73.7	544.3	550–581	299.97	92.0
					52.5
					38.2
DPE	107.7	514.8	518–528	374.83	–
	106.5	514.3	518–527	350.42	
DPM	115.4	460.9	464–473	182.08	–
	106.0	461.6	462–473	178.77	
DMHNB	104.9	486.1	491–496	237.59	–
	98.4	487.1	491–496	277.53	
DPA	101.3	ca 513	–	–	120.3
					108.4
					86.7
KDPA	–	–	–	–	109.1
					100.1
					87.3
TPM	102.9	549.9	558–568	435.79	124.6
	95.0	550.1	558–568	370.18	120.8
					108.6
					98.3
TMPM	108.6	505.3	507–515	237.38	–
	96.7	505.3	507–515	216.62	

results

analysis data			Manometric method data		
B[12]					
initial decomposition K	temperature range K	E kJ · mol^{-1}	E_M kJ · mol^{-1}	log A s^{-1}	reference
546.6	549—557	331.28	207.24	16.1	1.
546.6	549—559	326.01			
548.8	550—560	300.80			
549.9	553—565	323.12			
525.1	528—537	308.18	180.03	15.5	1.
526.6	531—541	321.87			
526.9	529—539	342.64			
525.1	529—539	278.63			
526.3	529—539	324.63			
525.9	529—549	163.50	106.76	5.6	4., 5.
526.1	532—551	174.87			
528.1	533—551	176.70			
518.1	520—532	190.61	121.83	6.8	4.
517.8	519—532	209.06			
518.6	520—532	227.19			
541.7	547—561	249.60	183.80	12.0	4., 5.
543.7	547—561	299.22			
546.3	549—561	318.60			
549.3	551—563	327.39			
—	—	—	—	—	—
—	—	—	—	—	—
—	—	—	—	—	—
506.5	507—515	296.40	—	—	1., 5.
503.7	506—515	249.27			
501.0	506—515	240.09			
495.1	497—507	204.50	—	—	
497.3	498—509	171.07			
498.5	499—508	176.21			
536.8	537—546	370.11	257.06	19.0	5.
538.1	539—548	272.22			
541.3	539—551	348.32			
539.1	541—551	332.36			
—	—	—	—	—	—

From the point of view of the probable mechanism of the primary step of thermal decomposition, the measured compounds represent a heterogeneous group. On the basis of the knowledge derived from mass-spectral 2,2'-dinitrobiphenyl fragmentation [22], the splitting-off of one of the nitro groups in the 2,2' or 6,6' positions can be taken the primary step of thermal decomposition of HNB.

Just as with polymethyl [21], polyamino [6] and hydroxy derivatives [6] of 1,3,5-trinitrobenzene, the course of thermal decomposition of HNS, DMHNB, DPM, DPE and DPA is *via* the aci tautomer as the primary reaction intermediate [6, 21].

The mechanism of the initial thermal decomposition of KDPA might present a certain analogy to the course of thermal analysis of alkaline metal picrates [23].

HNAB, DIPS and DIPSO are derivatives of polynitroaromatic compounds, whose thermal stability is not restricted by the reactivity of the nitro group. According to investigation [7], HNAB is split to picryl radicals, which subsequently attack the neighbouring HNAB molecules to form macromolecular, non-specified benzene-insoluble products [7]. The presence of 1,3,5-trinitrobenzene inhibits HNAB thermal decomposition [7]. From the experimental data on DIPS [3] and DIPSO [3] decomposition, the theory can be derived [3] that HNB is formed as an intermediate product, with elementary sulfur being liberated in the case of DIPS, and gaseous SO_2 in the case of DIPSO.

Analogously, the thermal stability of melamine picryl derivatives, with only one substituted hydrogen atom in the amino groups, is conditioned by the stability of the s-triazine nucleus (see also paper [24]). As a result of a two-hour isothermal exposure of TPM at 240°, 2,4,6-trinitroaniline formation results [25]; this was proved by TLC on Silufol UV 254. The mechanism of the primary step in TPM thermal analysis (that is, the opening of the s-triazine nucleus) might offer a certain analogy to the mechanism of thermal decomposition of N,N'-diarylureas [26].

Similarly as in the preceding parts of the series [6, 21], linear relationships were found between all the obtained values of $E \cdot T_D^{-1}$ for HNB, HNS, DIPS, DIPSO, HNAB and TPM and the values of the Arrhenius parameters E_M and log A found by manometry [1–5]:

$$\frac{E}{T_D} = b \cdot E_M + a \tag{1}$$

$$\frac{E}{T_D} = b_1 \cdot \log A + a_1 \tag{2}$$

The coefficients of relationship 1, together with the correlation coefficient r, are presented in Table 2, the coefficients of relationship 2 being presented in Table 3.

The relationships 1 and 2 join together compounds having not only different mechanisms for the beginning of thermal decomposition, but also different molecular conformations. Considering the result contained in the previous parts of the present series [6, 21], it can be stated that these compounds follow the derived relationships depending on the character and intensity of the intermolecular force

Table 2

Coefficients of the relationship 1

Method	b	a	r
A	0.0025	0.1587	0.8430
B	0.0021	0.1411	0.9003

Table 3

Coefficients of the relationship 2

Method	b_1	a_1	r
A	0.0285	0.2430	0.9324
B	0.0258	0.2365	0.9230

Table 4

Calculated values of E_M and of log A

Substance	State of thermal decomposition	Method A		Method B	
		E_M kJ · mol^{-1}	log A, s^{-1}	E_M kJ · mol^{-1}	log A, s^{-1}
DPA	solid	—	—	177.76	10.98
KDPA	solid	—	—	107.57	5.18
DMHNB	solid	148.18	10.02	—	—
DPM	solid	92.95	5.18	—	—
DPE	liquid	209.03	15.34	—	—
TMPM	solid	116.18	7.20	—	—

effect and the mechanism of the primary splitting process of thermal decomposition. The mechanism of the primary step of thermal analysis might predominate in compounds exhibiting stronger intra- and intermolecular interactions (for example, by means of a hydrogen-bond), or in relatively small molecules.

Using relationships 1 and 2 and considering the results of DTA measurements of the derived average values of $E \cdot T_D^{-1}$ values of E_M and log A were calculated for DPA, KDPA, DPM, DPE and TMPM.

It may be assumed that DPA follows the relations derived for polyaminotrinitrobenzenes [6], if the existence of a strong intramolecular hydrogen-bond in its molecule is taken into account. From this standpoint, E_M and log A values were calculated for this compound: $E_M = 223.7$ kJ · mole^{-1} and log $A = 16.4$. These values are realistic, as is obvious from a comparison with E_M and log A values for 2,2',4,4' 6,6'-hexanitrooxanilide [1, 4–6].

E_M and log A values for the remaining compounds in Table 4 are entirely within the limits of our expectations. The Arrhenius parameters for DPE most probably correspond to its decomposition in the solid state. This is obvious from a mutual comparison with E_M and log A values for TNT [21, 27], HNS or DPM. Taking into account the knowledge of the relation between the structures and thermal stabilities of 1,3,5-trinitrobenzene derivatives (see, for example [24, 28]), both E_M and log A values are expected to decrease in the series TNT, DPE and DPM.

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RÈSUMÉ — On a déterminé, à l'aide de la méthode de Piloyan, les énergies d'activation E des composés polynitroaromatiques contenant deux groupes picryles et des dérivés de la mélamine. Simultanément on a étudié le début de la décomposition exothermique T_D en utilisant l'ATD non-isotherme. On en a déduit des corrélations linéaires entre les termes $E \cdot T_D^{-1}$ et les données cinétiques publiées, obtenues par l'étude de HNB, HNAB, DIPS, DIPSO, HNS et TPM par la méthode manométrique isotherme. A partir des corrélations dérivées ainsi que des valeurs E et T_D des mesures d'ATD, on a calculé les données cinétiques de DPA, KDPA, DMHNB, DPM, DPE et TMPM par la méthode manométrique.

ZUSAMMENFASSUNG — Unter Einsatz der Methode von Piloyan wurden die Aktivierungsenergien E für zwei Picrylgruppen enthaltende Polynitroaromatische Verbindungen und Melaminderivate bestimmt. Gleichzeitig wurde der Beginn der exothermen Zersetzung T_D durch nicht-isotherme DTA bestimmt. Lineare Zusammenhänge zwischen den Ausdrücken $E \cdot T_D^{-1}$ und den veröffentlichten kinetischen Daten wurden abgeleitet, wobei letztere aus der Untersuchung von HNB, HNAB, DIPS, DIPSO, HNS und TPM unter Einsatz isothermer manometrischer Methoden erhalten wurden. Aufgrund der abgeleiteten Zusammenhänge, sowie der Werte E und T_D aus DTA-Messungen, wurden die kinetischen Angaben von DPA, KDPA, DMHNB, DPM, DPE und TMPM mit der manometrischen Methode berechnet.

Резюме — Используя метод Пилояна, определены энергии активация (E) для полинитроароматических соединений, содержащих две пикрильные группы, а также для производных меламина. Одновременно, с помощью неизотермического ДТА, определено начальное экзотермическое разложение $T_Д$. Установлена линейная зависимость между членами $E . T_Д^{-1}$ и опубликованными кинетическими данными, которые были получены при изучении ГНБ, ГНАБ, ДИПС, ДИПСО, ГНС и ТПМ с помощью изотермического манометрического методы. На основании выведенных соотношений, из данных ДТА были вычислены также и значения E и $T_Д$. С помощью манометрического метода были вычислены кинетические параметры для ДПА, КДПА, ДМГНБ, ДПМ, ДПЭ и ТМПМ.