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POSSIBILITIES OF APPLYING PILOYAN METHOD OF DETERMINATION OF DECOMPOSITION ACTIVATION ENERGIES IN DIFFERENTIAL THERMAL ANALYSIS OF POLYNITROAROMATIC COMPOUNDS AND THEIR DERIVATIVES

PART IV. 1,3,5-TRINITROBENZENE, 2,2',4,4',6,6'-HEXANITROBIPHENYL, 2,2',2'',4,4',4'',6,6',6''-NONANITRO-*m*-TERPHENYL, 1,4,5,8-TETRANITRONAPHTHALENE AND 2,4,6-TRIPICRYL-1,3,5-TRIAZINE

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The Piloyan activation energies E of decomposition and the initial temperatures T_D of the exotherms of hexanitrobiphenyl (HNB), nonanitro-*m*-terphenyl (NONA), tripicryl-*s*-triazine (TPT) and 1,4,5,8-tetranitronaphthalene (TENN) have been determined by means of non-isothermal DTA. Due to its volatility in the zone of the beginning of thermal decomposition only T_D values are specified for *s*-trinitrobenzene (TNB). From the values of $E \cdot T_D^{-1}$ for HNB and from the derived values of $E \cdot T_D^{-1}$ for TNB on the one hand, and from the published values of the Arrhenius parameters obtained by means of the manometric method on the other, relationships have been derived. The relationship between $E \cdot T_D^{-1}$ and the standard activation enthropy is considered relevant.

This section of the paper deals with 1,3,5-trinitrobenzene (TNB), 2,2',4,4',6,6'-hexanitrobiphenyl (HNB), 2,2',2'',4,4'4'',6,6',6''-nonanitro-*m*-terphenyl (NONA) and 1,4,5,8-tetranitronaphthalene (TENN) as "unsubstituted" polynitroaromatic compounds. 2,4,6-Tripicryl-1,3,5-triazine (TPT) has also been included in this category, its supporting skeleton being of a heteroaromatic character.

With the use of the isothermal manometric method, kinetic data have been determined for the thermal decompositions of liquid TNB [1–4] and liquid HNB [1, 3]. Analogous data on NONA, TENN and TPT have not been found in the literature so far. Determination of the Piloyan activation energies of HNB, NONA and TENN forms a part of papers [5, 6] and determination of these energies of TNB and TPT is presented in paper [6]. Application of the Piloyan method in the thermolysis of HNB and other substance with two picryl groups in the molecule forms a part of paper [7] too.

Experimental

Materials

TNB was obtained from the technical product by means of multiple crystallization from acetone and, in the last stage, from an acetone – methanol mixture. Its m.p. was 395.1–396.1 K.

The HNB used was of the same quality as in paper [7].

NONA was synthesized by the earlier described method [8]; it was purified by multiple crystallization from a large volume of a methyl ethyl ketone – ethanol mixture. No traces of melting were found up to 643.1 K.

TENN was prepared by nitrating 1,4,5-trinitronaphthalene using a H_2SO_4–HNO_3 mixture. The product, which was crystallized several times from nitrobenzene and finally from a dimethylsulfoxide – acetone mixture, exhibited a polymorphic transition at 542.9 (initial [9]) – 549.7 K peak of polymorphic transition; the beginning of sublimation with decomposition was recorded at 581.1 K (by means of DSC) [5].

TPT was prepared by the previously described method [10]. It was purified by double crystallization from an acetone – ethanol mixture. From the TPT adduct with acetone (about 8 per cent acetone) obtained in this way, acetone was removed by vacuum drying at 70 to 80°. The initial temperature of fusion (by means of DTA) was 621.5 K [6, 9], with decomposition.

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

Methods

The DTA apparatus and conditions of measurements were described in the first part [11] of this paper. Measurements using thermocouples in a stainless injection needle [5, 6, 9, 11] are denoted as Method *A*, and measurements by means of thermocouples in a glass capillary [6, 9, 11] as Method *B*. Simax or Rasotherm glass was employed to make test tubes for samples and capillaries for thermocouples.

Results and discussion

A survey of the obtained Piloyan activation energies E and initial temperatures T_D of exothermic decomposition is given in Table 1, together with the Arrhenius parameters E_M and $\log A$, which were derived for TNB and HNB by Andreev [1] and Maksimov and co-workers [2–4].

The influence of the weight of the sample upon the E and T_D values is ambiguous in this category of compounds. In the application of DTA measurements by method *A* there is a slight decrease of the T_D and E values for HNB with decreasing weight; measurements by method *B*, however, exhibit an opposite trend of the values for HNB.

With the decrease in the weighed amounts of NONA and of TENN there is a slight increase in the T_D values, regardless of the type of measurement method employed; moreover, for TENN there is a marked increase of the E values. A decrease of the T_D values and an increase of the E values with decreasing sample weight can be observed for TPT.

When DTA method *B* is applied TNB and HNB exhibit higher thermal stabilities than those found by method *A*. In these two compounds there is thermal decomposition in the liquid state during measurement. For NONA and TENN, whose thermal decompositions occur in the solid state, the opposite is the case;

Table I

Survey of results

Sub-stance	DTA data								Manometric method data	
	Method A [5,6]				Method B[6]					
	Sample weight, mg	Initial temperature of exo-therm, T_D, K	Temperature range, K	E, kJ · mol^{-1}	Sample weight, mg	Initial temperature of exo-therm, T_D, K	Temperature range, K	E, kJ · mol^{-1}	E_M, kJ · mol^{-1}	log A, s^{-1}
TNB	100.8	578.1	—	—	138.2	588.5	—	—	180.03 [1—4]	10.9 [1—4]
	99.1	580.1	—	—	114.0	587.4	—	—		
					109.9	584.4	—	—		
					107.2	588.5	—	—		
HNB	107.9	534.9	541—553	403.93	97.6	546.6	549—557	331.28	207.24 [1,3]	16.1 [1,3]
	103.3	534.4	541—550	362.65	92.2	546.6	549—559	326.01		
	95.2	533.6	538—550	323.17	81.2	548.8	550—560	300.80		
					32.9	549.9	553—565	323.12		
NONA	106.6	576.4	586—596	345.02	97.0	568.7	569—579	305.08	—	—
	97.8	579.1	586—596	355.91	89.1	571.5	572—579	333.95		
					69.2	571.7	573—581	309.88		
TENN	103.5	578.2	583—603	277.83	102.7	570.9	571—595	251.85	—	—
	102.1	579.4	588—605	284.19	118.5	571.1	572—585	318.08		
	95.9	578.9	586—599	307.13	84.7	573.1	574—585	280.01		
					72.2	570.2	571—579	283.01		
TPT	—	—	—	—	148.4	592.9	595—605	217.01	—	—
					96.2	593.1	597—607	266.98		
					91.3	593.7	595—605	278.84		
					69.9	591.8	593—603	271.04		

this is true of compounds that possess a stabilizing influence on the crystal lattice [9] (in this case the glass surface is the destabilizer).

TPT was measured only by method *B*, as the compound was not available when the results of method *A* were finally evaluated [5].

In the region of TNB decomposition, its boiling also occurs. Therefore, a corresponding Piloyan activation energy can not be determined. Consequently, the value of $E \cdot T_D^{-1}$ was subtracted using the equation describing the relationship of the values of this term for TNB derivatives towards the corresponding characteristics of detonation [6, 12]; from DTA measurements by method *A* $E \cdot T_D^{-1} = 0.9770\ \mathrm{kJ \cdot mol^{-1} \cdot K^{-1}}$, and by method *B* $E \cdot T_D^{-1} = 0.6875\ \mathrm{kJ \cdot mol^{-1} \cdot K^{-1}}$ was calculated.

By means of the analogous dependence for compounds containing two and three picryl groups in the molecule, the value of the term for TPT was calculated [6, 12] as $E \cdot T_D^{-1} = 0.4798\ \mathrm{kJ \cdot mol^{-1} \cdot K^{-1}}$ for measurements by method *A*.

The values of $E \cdot T_D^{-1}$ thus obtained for TNB do not correlate with any one of the equations describing the relationship of $E \cdot T_D^{-1}$ and the Arrhenius parameters E_M and $\log A$, which were derived from the results of the manometric method (these relationships are to be seen in papers [6, 7, 11, 13]).

In the compounds examined within the limits of the present paper, there is a real possibility of the identity or considerable affinity between the mechanisms of the primary step of thermal fission. In the case of TPT, all that has been said relates to the decomposition in the solid phase only; the thermal decomposition of TPT in solution is discussed in paper [9]. In NONA and TENN, more pronounced intermolecular non-bonding interactions can be assumed to exist at the same time; this is confirmed by the relatively high physical stabilities.

On the basis of the results given in the preceding parts of the present paper [7, 11, 13], the relationships of $E \cdot T_D^{-1}$ towards the Arrhenius parameters E_M and $\log A$ should be defined by the equations

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

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

For the determination of the coefficients of Eqs (1) and (2), data are available from the application of the manometric method only in the cases of TNB [1–4] and HNB [1, 3]. The coefficients of the two equations estimated in this way are presented in Table 2. The values of E_M and $\log A$ for NONA, TENN and TPT in Table 3 were calculated by means of Eqs (1) and (2).

To assess the feasibility of the given procedure, use was made of the knowledge contained in the paper of Maksimov and Shipitsin [3]. The authors applied E_M and $\log A$ values to estimate the maximum temperature limit T_{max} for exploitation of aromatic polynitro compounds as thermostable explosives (see also ref. [9]).

Table 2

Coefficients of Equations (1) and (2)

Eq.	Coefficient	DTA method	
		A	*B*
1	b	-0.0109	-0.0038
	a	2.9382	1.3747
2	b_1	-0.0570	-0.0200
	a_1	1.5991	0.9055

For the limiting temperature $T_{\max}$, Maksimov and Shipitsin derived the relationship [3]:

$$T_{\max} = \frac{E_M}{19.133\,(\log A + 6)} \tag{3}$$

where E_M is given in $\mathrm{J \cdot mol^{-1}}$.

Data on $T_{\max}$ from the published E_M and $\log A$ values for TNB and HNB and from E_M and $\log A$ values derived here, are contained in Table 3. This Table also presents $T_{\max}$ values obtained by the DTA method according to paper [9].

The criterion, which was derived in paper [9], is in this case the relationship:

$$T_D = 180.28 \exp\left(\frac{T_{\max}}{469.87}\right) \tag{4}$$

It is impossible for the $T_{\max}$ value of the given compound to be higher than the beginning of its exothermal decomposition T_D. Considering this comparison, the data obtained by means of method *A* are possible.

Table 3

Survey of published E_M and $\log A$ values for TNB and HNB, and values of E_M, $\log A$ and $T_{\max}$ calculated by means of relationships (1), (2), and (3), respectively

Substance	DTA measurement				$T_{\max}$, K		
	Method *A*		Method *B*		Method *A*	Method *B*	Method according to paper[9]
	E_M, $\mathrm{kJ \cdot mol^{-1}}$	$\log A$, $\mathrm{s^{-1}}$	E_M, $\mathrm{kJ \cdot mol^{-1}}$	$\log A$, $\mathrm{s^{-1}}$			
TNB[1]	180.03	10.9	180.03	10.9	556.1	556.1	551.6
HNB[1]	207.24	16.1	207.24	16.1	490.1	490.1	516.4
NONA	214.11	14.1	214.77	17.6	556.7	475.6	544.3
TENN	223.85	15.0	230.16	20.5	555.8	453.9	545.0
TPT	225.82	15.2	239.66	22.3	556.7	442.6	559.3

Using method B, E_M values were obtained which are essentially identical with the E_M values from method A. The former method, however, gave unreal log A values, particularly for TPT and TENN. This is due to the fact that the coefficients of Eqs (1) and (2) were determined by means of data for thermolysis in the liquid state. When thermocouples in a stainless injection needle are used (method A), there is probably no appreciable influence of primary thermolytic processes due to the contact of the compounds with the surface of the needle. In DTA measurements by method B, however, the contact of the measured compound with the glass surface of the capillary does influence its activation entropy; the intensity of the interaction with this surface of the glass is, of course, more pronounced in the liquid state.

The activation entropy involves relationships of the Eq. (2) type: considering the theory of activated complexes [14, 15], it should therefore hold that

$$\frac{E}{T_D} \approx \frac{\Delta S^{0\neq}}{R} \tag{5}$$

where $\Delta S^{0\neq}$ is a standard activation entropy. The term $E \cdot T_D^{-1}$, however, cannot be considered as entropy.

There is a compensating dependence between the Arrhenius parameters E_M on the one hand, and log A on the other (see for example [2, 16, 17]):

$$\log A = b_2 \cdot E_M + a_2 \tag{6}$$

As stated in paper [16], the existence of dependence [6] cannot be accounted for from the point of view of the mechanism of the elementary action. Its essence has not explained so far.

Considering the published values of E_M and log A for the thermolysis of polynitroaromatic compounds in the gaseous [17], liquid [1, 2, 3, 18–21] and solid [1, 2, 16, 21] states, the coefficients of Eq. (6) were obtained by linear regression analysis. These coefficients, together with the corresponding correlation coefficients r, are presented in Table 4. The found values of b_2 and a_2 indicate that relationship (6) exhibits an identical slope for the thermolysis of the polynitroaromatic compounds in both the liquid and the solid states.

Table 4

Coefficients of relationship (6)

Phase of thermal decomposition	b_2	a_2	r
gaseous	0.0734	−2.5479	0.9868
liquid	0.1009	−5.8084	0.9066
solid	0.0986	−5.7939	0.9097

By means of relationship (6) it is possible in turn to demonstrate the feasibility of E_M and log A values derived from DTA measurements by method A for NONA, TPT and TENN, $b_2 = 0.0945$ and $a_2 = -6.1197$ being calculated; from calculations for method B, $b_2 = 0.1905$ and $a_2 = -23.3510$.

The results of this part of the paper, too, reveal that the combination of non-isothermal DTA with a method suitable for the study of reaction kinetics permits the derivation of satisfactory results from the point of view of reaction kinetics.

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Résumé — On a déterminé par ATD les températures initiales T_D des phénomènes exothermiques de l'hexanitrobiphényle (HNB), du nonanitro-*m*-terphényle (NONA), du tripicryle-*s*-triazine (TPT) et du 1,4,5,8-tétranitronaphtalène (TENN) et les énergies d'activation E de la composition d'après la méthode de Piloyan. En raison de la volatilité du *s*-trinitrobenzène (TNB) dans la zone de la décomposition thermique initiale, on n'a déterminé pour celui-ci, que les valeurs T_D. On a dégagé des corrélations d'une part, à partir des valeurs. $E \, . \, T_D^{-1}$ pour HNB et des valeurs dérivées de $E \, . \, T_D^{-1}$ pour TNB et d'autre part, à partir des valeurs publiées des paramètres d'Arrhenius obtenues par la méthode manométrique. On a souligné l'importance de la corrélation qui existe entre le terme $E \, . \, T_D^{-1}$ et l'entropie d'activation standard.

ZUSAMMENFASSUNG — Die Aktivierungsenergien E nach Piloyan der Zersetzung sowie die Anfangstemperatur T_D der exothermen Vorgänge von Hexanitrobiphenyl (HNB), Nonanitro-*m*-terphenyl (NONA), Tripicryl-*s*-triazin (TPT) und 1,4,5,8-Tetranitronaphthalin (TENN) wurden durch nicht-isotherme DTA bestimmt. Wegen seiner Flüchtigkeit im Bereich der beginnenden thermischen Zersetzung wurden für *s*-Trinitrobenzol (TNB) nur die T_D-Werte angegeben. Von den Werten von $E.T_D^{-1}$ für HNB und von den abgeleiteten Werten von $E.T_D^{-1}$ für TNB einerseits und von den durch manometrische Methoden erhaltenen veröffentlichten Angaben der Arrhenius-Parameter andererseits wurden die Zusammenhänge ermittelt. Der zwischen dem Ausdruck $E.\ T_D^{-1}$ und der standarden Aktivierungsenthropie bestehende Zusammenhang wird als wesentlich hervorgehoben.

Резюме — С помощью неизотермического ДТА определены энергии активации Е разложения по Пилояну и температурные начала T_D экзотерм для гексанитробифенила (ГНБ). нонанитро-м-терфенила (НОНА), трипикрил-*s*-триазина (ТПТ) б 1,4,5,8-тетранитронафталина (ТЕНН). Для *s*-тринитробензола (ТНБ), вследствии его летучести в зоне начала термического разложения, только значения T_D точно определены. Исходя из значений $E.T_D^{-1}$ для ГНБ и ТНБ, а также из опубликованных значений аррениусовских параметров, полученных манометрическим методом, точно определена взаимосвязь между ними. Отмечено, что уместной является взаимосвязь между выражением $E.\ T_D^{-1}$ и стандартной энтропией активации.