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

PART I. POLYMETHYL AND POLYCHLORO DERIVATIVES OF 1,3,5-TRINITROBENZENE

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Conditions are presented for application of the Piloyan method to the DTA of polynitro aromatic compounds. Activation energies (E) of the thermal decomposition and the initial values T_D of the exotherms are determined for trinitrotoluene, trinitro-*m*-xylene, trinitromesitylene, picryl chloride and dichlorotrinitrobenzene. Linear relationships are derived between the terms $E \cdot T_D^{-1}$ and published kinetic data on these compounds, obtained by an isothermal manometric method. The mechanisms of the primary steps in the thermolyses of these polynitro compounds are discussed. A negative influence on their thermal stability has been confirmed, arising from the contact of the measured compounds with the glass surface.

The study of the thermal stabilities of organic polynitro compounds is important from the point of view of technological application. In this realm of knowledge, Soviet science occupies a dominant position. Soviet authors use the isothermal manometric method with a glass compensating manometer of Bourdon type [1–4] to examine the kinetics of thermolysis in these compounds.

The thermal reactivities of organic polynitro compounds, however, can also be studied using thermoanalytical methods [5–8]. The application of differential thermal analysis to this set of problems has lately been dealt with to a considerable extent by a number of Japanese researchers too [7, 9–19].

From the point of view of the reaction kinetics, the interpretation of the DTA results, continues to be complicated [20–22]. In the case of polynitro compounds, this interpretation lay in the application of the Kissinger method [7, 9–14, 19]. Rogers [5] is of the opinion, that the Kissinger method [23, 24] is popular in the DTA of explosives. Wendlandt [25, 26], on the other hand, quotes the conclusions arrived at by Reed and co-workers [27], Melling and co-workers [28] and Piloyan and co-workers [29], who claim that the Kissinger method has not proved very successful in practice.

Recent data are available on application of the Piloyan method of determining activation energies of decomposition [20, 21, 25, 26, 29] in the non-isothermal DTA of polynitroaromatic compounds [30, 31] and polynitrosoamines [32, 33].

The Piloyan method is based on the fact, that the deviation of the DTA decomposition curve from the baseline is, in its initial stage, described by the relationship [21, 25, 26, 29, 34]:

$$\Delta T = S \cdot \frac{d\alpha}{d\tau} \tag{1}$$

where ΔT is the deviation from the baseline, S is the area of the thermal effect, and $d\alpha/d\tau$ is the reaction rate. To describe the reaction rate of the reaction, Piloyan and co-workers [21, 29] consider the general relationship:

$$\frac{d\alpha}{d\tau} = A_0 \cdot f(\alpha) \cdot \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where $f(\alpha)$ is a function of the extent of the reaction: the most general expression for $f(\alpha) = \alpha^m \cdot (1-\alpha)^n$ [21]. After substitution of the expression for the reaction rate in Eq. (1) and after taking logarithms, the resulting relationship is [21, 25, 26, 29]:

$$\ln \Delta T = C + \ln f(\alpha) - \frac{E}{RT} \tag{3}$$

For the initial stage of the decomposition, Piloyan and co-workers suppose the existence of a very low degree of conversion [21, 29]: they neglect the expression in $f(\alpha)$, obtaining thereby the following equation:

$$\ln \Delta T = C' - \frac{E}{RT} \tag{4}$$

The values ΔT for individual temperatures are then directly subtracted from the DTA curve in length units [20, 21, 25, 26, 29]. Šesták and Berggren [20] are of the opinion, that the above method yields good results for decompositions in the solid phase if the external heating of the sample exercises a greater influence upon its decomposition then its self-heating.

In the papers [30–33] the Piloyan method was applied to exothermic decomposition in both solid and liquid phases. In this way, E values relating to the molecular structure were obtained [22, 30, 31]. Analogously, relationships were found to exist between the initial T_D values of exothermic decomposition and characteristics of the molecular structure [22, 30, 31].

Taking into consideration the material in papers [22, 30, 31], $E \cdot T_D^{-1}$ was selected as being the most suitable datum resulting from the application of the Piloyan method to the non-isothermal DTA of polynitroaromatic compounds. Comparison of values of this term with the published kinetic data, obtained by following the thermolysis of polynitroaromates using a manometric method, is a component part of paper [31]. The comparison led to the division of the compounds involved into a number of groups: the first part of the present paper deals with polymethyl and polychloro derivatives of 1,3,5-trinitrobenzene. Individual data resulting from the application of the Piloyan method to the non-isothermal DTA of other polynitroaromate groups are contained in contributions related to the present paper.

Partial results from the study of the thermal reactivities of the polymethyl- and polychloro-2,4,6-trinitrobenzenes are contained publications in [3, 9, 12, 35, 39, 40 – 54]. These papers deal primarily with the study of the kinetics and mechanisms of thermal decomposition of 2,4,6-trinitrotoluene (TNT) in both gaseous [3, 35, 46, 49] and liquid [3, 6, 9, 37, 38, 41 – 48, 50, 54] states or in solution [3, 45, 46] including identification of the decomposition products [41, 43, 46] and study of their influence upon the kinetics of TNT pyrolysis [47].

Less attention has so far been devoted to the study of the thermal decompositions of 1-chloro2,4,6-trinitrobenzene (CTB) [3, 18, 45, 46] and 1,3-dichloro- and 1,3,5-trichloro- 2,4,6-trinitrobenzene (DCTB and TCTB) [3, 45, 46].

Determination of the kinetic data and discussion of the pyrolysis mechanisms of 1,3-dimethyl- and 1,3,5 trimethyl-2,4,6-trinitrobenzene (TNX and TNMs) in the condensed state are topics of paper [38].

Differential thermal analysis of TNT and TNX to study their thermal stabilities has so far been confined only to the initial thermal decomposition [6, 50]. Application of the Kissinger method to the DTA of TNT has been published in [9, 54]. DTA has also been applied to the study of reactions preceding TNT deflagration [55].

From among the thermoanalytical methods, DSC has been used to determine kinetic data on TNT thermolysis [51, 53]. DSC has also been applied to the study of the thermolysis mechanism of TNT [52]. However, no literary data have been published so far on, the application of thermoanalytical methods to the study of thermal reactivities of TNMs and DCTB.

Experimental

Materials

2,4,6-trinitrotoluene (TNT) was prepared from the technical product by means of multiple crystallization from an acetone – methanol mixture; m. p. 354.6 – 355.1 K.

1,3-dimethyl-2,4,6-trinitrobenzene (TNX) was obtained by nitrating *m*-xylene with nitric acid in sulfuric acid. It was purified by threefold-crystallization from acetone; m. p. 455.1 – 455.6 K.

1,3,5-trimethyl-2,4,6-trinitrobenzene (TNMs) was obtained by nitrating mesitylene with nitric acid in sulfuric acid. It was purified by threefold crystallization from acetone; m. p. 504.1 – 505.1 K.

1-Chloro- and 1,3-dichloro-2,4,6-trinitrobenzene (CTB and DCTB) were prepared from picric acid or styphnic acid, respectively, by reaction with $POCl_3$ in pyridine [57]. The two compounds were purified by repeated crystallization from tetrachloromethane. CTB had m. p. 355.1 – 356.1 K and DCTB had m. p. 421.1 – 422.1 K.

The purities of compounds were checked by thin-layer chromatography against Silufol UV 254 with acetone-cyclo-hexane as mobile phase.

Methods

Measurements were carried out with a DTA apparatus [56] whose furnace (an aluminium block) had the shape of a perpendicular cylinder. The height of the cylinder was 150 mm and its diameter 108 mm. In the upper part of the cylinder were openings for placing test-tubes containing samples, or the standard. These openings were situated 10 mm from the perpendicular axid of the cylinder (20 mm altogether), their depth being 63 mm.

Backer tubing was built into the aluminium block of the furnace for heating purposes. To bring about quick cooling after measurements were finished a cooling water coil was also built into the block of the furnace.

For control of the linear temperature increase, a thyristor regulating element was utilized, equipped with a feedback. The rate of temperature increase was 6° min^{-1}.

Some of the measurements were carried out using Fe – Co thermocouples enclosed in a stainless injection needle of 19112e No. 36 – 1 type, produced by Chirana, Stárá Turá, ČSSR; these measurements are lebelled as method *A*. Thermocouples employed for measurement according to method *B* were enclosed in glass capillaries with lengths from 130 to 150 mm. The diameter of that part of the glass capillaries which reached into the sample was from 1.5 to 2.1 mm.

For recording temperature differences, an EZ-11 recorder was used, produced by Laboratorní přistroje Prague. In the processes of measurements the recorder worked within the range of 0.5 mV in the whole scale, i.e. 0° up to 355°, with a paper speed of $20\ \mathrm{mm} \cdot \mathrm{min}^{-1}$.

Measurements were made under atmospheric pressure, with direct contact of the sample and the reference material 95 – 105 mg Al_2O_3 with the atmosphere of the air; open glass test-tubes were used for samples and Al_2O_3. Their outer diameter was 6 mm, the wall was 0.8 mm thick, and the length was from 74 to 76 mm. Used test-tubes were cleaned with organic solvents (dimethylformamide, acetone); after every third measurement the impurities were removed from the test-tubes with CrO_3 solution in sulfuric acid.

Simax, or Rasotherm glass was employed to produce test-tubes for samples and capillaries for the thermocouples (method *B*).

Results and discussion

The application of relationship (4) in the non-isothermal DTA of polynitroaromatic compounds is demonstrated graphically in Figs 1 and 2. The Fig. 2 representation does not fit into this part of the present paper from the point of view of the molecular structure of the thermolysed compound; it is represented here only to enable an overall survey.

Both Figures reveal that semilogarithmic analysis of the initial exothermic decomposition, in the sense of Eq. (4), yields a number of linear sections (two in our case). This corresponds to the known considerable kinetic variability of thermal decomposition of organic polynitro compounds with the temperature of reaction.

A survey of the results obtained from the DTA measurements with pure polymethyl and polychloro derivatives of 1,3,5-trinitrobenzene is contained in Table 1, together with literature values of the Arrhenius parameters E_M, and log A, obtained from results of the manometric method.

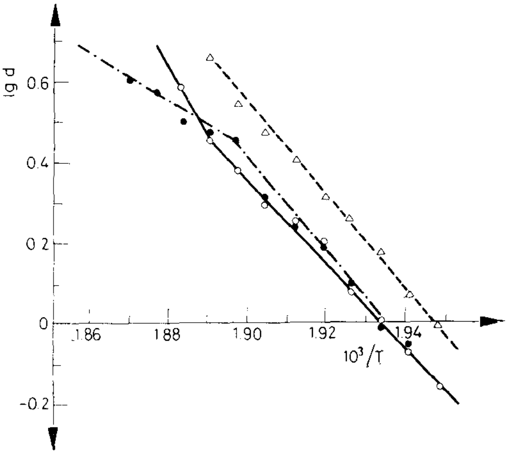

Fig. 1. Application of equation 4 to the initial part of the exotherm of 2,4,6-trinitrotoluene with substraction of the temperature difference in length units (d symbol in mm); reproduced from [31]. DTA method B — weight of sample: —·— ● —·— 67.1 mg; — ○ — 113.2 mg; — — △ — — 123.8 mg

From the results of the DTA measurements it is obvious that the smaller weight of the sample caused a slight shift of the initial exotherm T_D towards higher values, the trend being of an opposite character for TNX and possibly CTB. The low reproducibility of measurements with CTB and DCTB may be due to their volatility in the realm of exothermic decomposition.

With the manometric method Maksimov and co-workers [38] discovered a decrease in the reaction rates of thermal decomposition in the condensed state in the series TNT, TNX, and TNMs. They also found that the decrease of the reaction rates in this sense is correlated with the increase of the activation energy values E_M. An increase of E_M with the increase of the number of chlorine atoms in the molecule in polychlorotrinitrobenzenes was found by Andreev [3, 38]. Taking this into account, Maksimov and co-workers arrived at the conclusion [38] that the thermal stability in the condensed state increases with the number of methyl groups in the polymethyl-2,4,6-trinitrobenzene molecule.

Table 1

Survey of results

Substance	Differential thermal analysis data								Manometric method data		
	Method A [30, 31]				Method B [31]						
	Sample weight, mg	Initial decomposition, K	Temperature region, K	E, kJ · mol^{-1}	Sample weight, mg	Initial decomposition, K	Temperature region, K	E, kJ · mol^{-1}	E_M, kJ · mol^{-1}	log A, s^{-1}	Reference
TNMs	105.6	487.4	491–501	116.93	118.6	464.1	465–476	92.32	185.05	12.3	38.
	98.3	487.9	491–501	114.75	102.6	464.3	465–476	69.85			
					102.1	463.1	465–476	66.52			
					73.5	465.0	465–476	55.97			
TNX	102.1	519.1	523–533	229.80	121.0	493.7	495–505	166.92	146.95	9.1	38.
	98.0	523.5	525–535	275.02	97.3	493.1	495–505	135.19			
					57.6	492.4	495–505	138.51			
TNT	107.4	525.3	529–541	345.98	123.8	512.1	513–527	219.33	144.44	9.3	37.
	98.7	527.2	529–539	343.14	113.2	512.7	513–527	196.64			
					96.4	512.9	513–527	220.58			
					67.1	513.1	515–525	212.30			
CTB	109.1	572.8	577–584	500.18	127.1	564.5	565–573	560.33	118.08	5.7	45.
	107.8	565.9	571–585	374.20	116.1	563.1	565–575	326.11			
					104.6	564.6	565–575	423.37			
DCTB	110.0	567.4	574–591	216.28	—	—	—	—	177.09	10.5	45.
	108.1	573.1	578–590	309.98	—	—	—	—			

The results of the DTA measurements, i.e. the trend of the T_D values and partially also of the E values in the series TNMs, TNX, TNT, DCTB and CTB, however, provide opposite evidence.

The decrease of the thermal stability, with the increase of the number of substituents in the 1,3,5-trinitrobenzene molecule is a generally known phenomenon (see e.g. [58]). Along with the increasing volume of the substituent, or with multiple substitution within the 1,3,5-trinitrobenzene molecule, nitro groups ortho to the substituent undergo increasing deviation from the plane of the benzene ring.

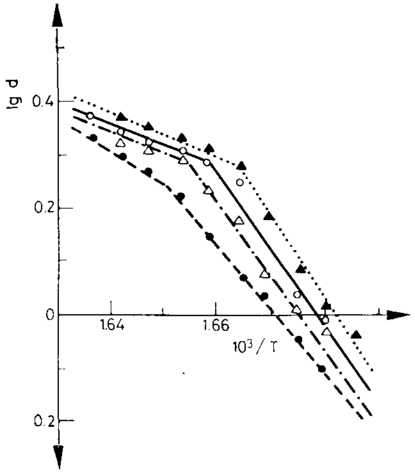

Fig. 2. Application of equation 4 to the initial part of the exotherm of 2,4,6-tripicryl-1,3,5-triazine with substraction of the temperature difference in length units (d symbol in mm); reproduced from [31]. DTA method B — weight of sample: - - - ▲ - - - 69.9 mg; —○— 91.3 mg; —·— △ —·— 96.2 mg; — ● — 148.4 mg

This can be proved by the CTB [59], DCTB [60] and TNX [61] molecular conformations. If an aci tautomer of ortho-quinone type [62] is assumed to act as the primary intermediate of thermolysis in polymethyl 2,4-6-trinitrobenzene, then the decreasing order of the C—N bond of the nitro-groups in the ortho-positions is correlated with the decreasing reaction rate of thermal decomposition.

From the point of view of its course and the structures of its products the thermolysis of organic polynitro compounds can be divided into two limiting types:

(a) fission whose products have low molecular weight; its course does not involve too many intermediate stages (nitramines, polynitroaliphatic compounds);

(b) fission whose intermediates are relatively stable compounds: its induction period need not necessarily be linked with a more pronounced development of gaseous products (polynitroaromatic compounds).

Reaction kinetics of the first type of fission can conveniently be studied by methods based on following the quantity of reaction products in time. Reaction kinetics of the second type of fission can best be studied by methods based on following thermal effects of the reaction.

Induction periods of the two limiting types of thermolysis can, of course, be recorded by DSC and DTA in particular. Application of the two sets of methods therefore can offer a more reliable order of thermal stabilities of the studied compounds than would follow measurements carried out by gasometric methods.

Regardless of the difference in principles and application possibilities of non-isothermal DTA and the isothermal manometric method, by a more detailed analysis of the data given in Table 1 a general relationship was found:

$$\frac{E}{T_D} = b \cdot E_M + a \tag{5}$$

Using all the measured T_D values, as well as the obtained E values, the coefficients of Eq. 5 were calculated by linear regression analysis. These coefficients, along with the correlation coefficient r, are given in Table 2.

Table 2

Coefficients of Equation 5

DTA method	b	a	r
A	−0.0068	1.5774	0.8657
B	−0.0069	1.4044	0.9057

In the same way, a relationship was found between the values of $E \cdot T_D^{-1}$ and the logarithm of the pre-exponent A:

$$\frac{E}{T_D} = b_1 \cdot \log A + a_1 \tag{6}$$

The coefficients of Eq. (6) are listed in Table 3.

Table 3

Coefficients of Equation 6

DTA method	b_1	a_1	r
A	−0.077	1.242	0.8699
B	−0.074	1.054	0.9244

From the similar correlations of both polymethyl and polychloro derivatives of 1,3,5-trinitrobenzene in terms of relationship (5) or relationship (6), a certain analogy can be considered to exist between the mechanisms of the primary step of thermolysis for the two groups of compounds. This hypothesis is confirmed for example, by the same trend of the E_M values and log$A$ with the increase of the number of methyl groups, or chlorine atoms in the molecules, of the above compounds [3, 38].

Comparison of the results of DTA method A with those of DTA method B reveals that the thermal stabilities of the studied compounds are negatively influenced by their contact with the glass surface. This phenomenon is due to the influence of the alkaline component of the glass.

*

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RÉSUMÉ — On présente les conditions de l'application de la méthode Piloyan à l'ATD des composés polynitroaromatiques. On a déterminé les énergies d'activation *(E)* et les valeurs initiales T_D des réactions exothermiques pour le trinitrotoluène, le trinitro-*m*-xylène, le trinitromésitylène, le chlorure picrylique et le dichloro-trinitrobenzène. On a trouvé des corrélations linéaires entre les valeurs $E.T_D^{-1}$ et les données cinétiques publiées des composés mentionnés obtenues par une méthode isotherme manométrique. On discute le mécanisme de l'étape primaire de la thermolyse des composés polynitrés étudiés. On a confirmé l'influence négative, sur la stabilité thermique, provenant du contact de ces composés avec le verre.

ZUSAMMENFASSUNG — Die Bedingungen der Anwendung der Methode von Piloyan bei der DTA polynitroaromatischer Verbindungen werden beschrieben. Die Aktivierungsenergien *(E)* der thermischen Zersetzung und die Anfangswerte T_D der exothermen Vorgänge werden für Trinitrotoluol, Trinitro-*m*-xylol, Trinitromesitylol, Picrylchlorid und Dichlortrinitrobenzol bestimmt. Lineare Zusammenhänge werden zwischen den Werten $E.T_D^{-1}$ und den unter Anwendung der isothermen manometrischen Methode erhaltenen veröffentlichten kinetischen Angaben der besagten Verbindungen, abgeleitet. Der Mechanismus der primären Stufe in der Thermolyse der untersuchten Polynitroverbindungen wird diskutiert. Der sich aus dem Kontakt der gemessenen Verbindungen mit dem Glas ergebende negative Einfluß auf ihre Stabilität wird bestätigt.

Резюме — Представлены условия применения метода Пилояна для ДТА полинитроароматических соединений. Определены энергии активации (E) термического разложения и начала T_D экзотерм для тринитротолуола, тринитро-м-ксилола, тринитромезитила, пикрилхлорида и трихлортринитробензола. Установлена линейная взаимосвязь между величинами $E \cdot T_D^{-1}$ и кинетическими данными, опубликованными и которые были получены изотермическим манометрическим методом. Обсужден механизм первоначальной стадии термолиза исследованных полинитроароматических соединений. Возникающий вследствии контакта изученных соединений с поверхностью стекла эффект оказывает отрицательное влияние на термическую стабильность соединений.