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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 THEIR DERIVATIVES

PART VII. RELATIONSHIP FOUND BETWEEN CHROMATOGRAPHIC AND THERMAL ANALYSIS DATA ON N-SUBSTITUTED 2,4,6-TRINITROANILINES

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The Piloyan activation energies E, as well as the initial exotherm temperatures T_D, are determined for six *N*-monoalkyl- and five *N*,*N*-dialkyl-2,4,6-trinitroanilines. By comparison with R_f-factors, or R_M-functions of paper chromatography, the molecular-structural dependences of E and T_D are studied for these compounds. Relationships are also found between the term $E \cdot T_D^{-1}$ and the R_M-functions. The effects are discussed of the introduction of the 6-nitro group into the *N*-substituted 2,4-dinitroanilines, and of the introduction of the 4-nitro group into the 2,6-dinitro analogues, upon the thermal stabilities of the resulting 2,4,6-trinitroanilines.

Similarly as for *N*-substituted 2,4- and 2,6-dinitroanilines [1, 2], the relationships between the Piloyan activation energies E of the thermal decompositon, the initial exotherm temperatures T_D, and the structures of the molecules have also been studied for 2,4,6-trinitro analogues [3, 4]. The results obtained in this way are extended in the present paper and discussed from the point of view of new knowledge on the DTA of polynitroaromatic compounds, i.e. as contained particularly in papers [4–8] and [1, 2].

As in preceding parts of the present series [1, 2] molecular-structural dependences of the E and T_D values are formulated by comparison with paper chromatography (PC) data [9] on *N*-substituted 2,4,6-trinitroanilines.

Experimental

Materials

The origins, methods of purification and melting point determination of the compounds, their R_f-factors and the PC R_M-functions, are described in paper [9].

Methods

The method of DTA measurements was detailed earlier [5]. Measurements using thermocouples in a stainless injection needle are designated as method *A*, while method *B* involves measurements using thermocouples in a glass capillary. In contrast to previously [5–8], averaged E and T_D values are given here to denote the weighed samples within the range 90–150 mg.

Results of DTA measurements obtained by method *A* are to be understood as average values of two measurements, whereas in the case of method *B*, they are average values of three measurements.

As previously [1, 2], Sial glass was employed for test tubes to take samples and capillaries to make thermocouples.

PC methods are described in paper [9].

Results and discussion

The average values of E and T_D are listed in Table 1.

The mutual relationship of the T_D values and R_f-factors is similar to that found for 2,4-dinitro- [1] and 2,6-dinitroanilines [2] and is presented in Fig. 1.

Similarly as for the *N*-monosubstituted 2,4- and 2,6-dinitroanilines [1, 2], for the 2,4,6-trinitro analogues too a relationship exists between the E values and R_M-functions; this is graphically presented in Fig. 2. For measurements by method *B*, the division in this dependence (Fig. 2) differentiates derivatives containing the *N*-alkyl substituent, and derivatives in which the substituent displays branching on the α-carbon. This division is much less pronounced than that for the corresponding derivatives of 2,4-dinitroanilines [1].

Similarly as in paper [1, 2] a relationship was discovered for *N*,*N*-di-*n*-alkyl-2,4,6-trinitroanilines, between the E values and the R_M-functions; this is depicted in Fig. 3.

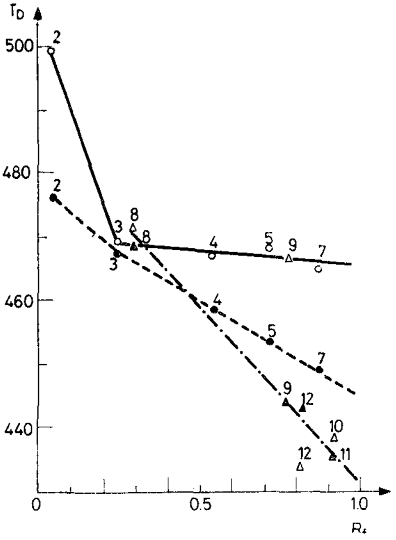

Fig. 1. Relationship between initials of exotherm T_D and R_f-factors: points ○ and △ correspond to DTA-measurements according to method *A*; points ● and ▲ correspond to DTA-measurements according to method *B*

Table 1

Survey of results

Sub-stance No.	Substance	Method *A*			Method *B*		
		Initial of exotherm T_D, K	Temperature range, K	*E*, kJ · mol^{-1}	Initial of exotherm T_D, K	Temperature range K	*E*, kJ · mol^{-1}
1	2,4,6-Trinitroaniline	514.6	516–524	291.4 ±2.4	518.2	522–532	201.0±11.2
2	*N*-Methyl-2,4,6-trinitroaniline	499.2	503–511	553.0 ±28.4	476.1	479–497	153.9±12.0
3	*N*-Ethyl-2,4,6-trinitroaniline	469.2	471–478	343.8 ±14.1	468.1	470–478	136.6±6.6
4	*N*-Propyl-2,4,6-trinitroaniline	467.1	468–475	249.4 ±25.4	458.8	460–478	120.8±9.9
5	*N*-*n*-Butyl-2,4,6-trinitroaniline	467.7	470–491	213.6 ±5.6	453.4	455–471	114.0±2.7
6	*N*-Isopropyl-2,4,6-trinitroaniline	467.7	471–479	189.2 ±1.4	—	—	—
7	*N*-Cyclohexyl-2,4,6-trinitroaniline	437.1	442–452	194.8 ±8.5	448.9	451–463	132.3±10.3
8	*N*,*N*-Dimethyl-2,4,6-trinitroaniline	470.7	473–483	225.8 ±12.4	468.5	470–483	208.7±3.3
9	*N*,*N*-Diethyl-2,4,6-trinitroaniline	466.7	452–473	186.52±2.2	444.8	447–485	140.7±1.4
10	*N*,*N*-Dipropyl-2,4,6-trinitroaniline	439.2	442–452	185.0 ±15.8	439.9	442–467	137.9±6.7
11	*N*,*N*-Di-*n*-butyl-2,4,6-trinitroaniline	439.2	442–459	150.3 ±6.6	436.3	438–462	127.1±2.6
12	*N*-(2,4,6-Trinitrophenyl)-piperidine	434.2	436–457	154.6 ±4.4	443.9	445–473	145.1±14.3

Graphical representations of the probable relationships between the activation entropies of thermal decomposition of the compounds and their molecular structures are given in Figs 4 and 5. From the data in papers [1, 2, 8], this entropy is approximately represented by the term $E \cdot T_D^{-1}$, and the molecular structure by the R_M-function [1, 2, 9].

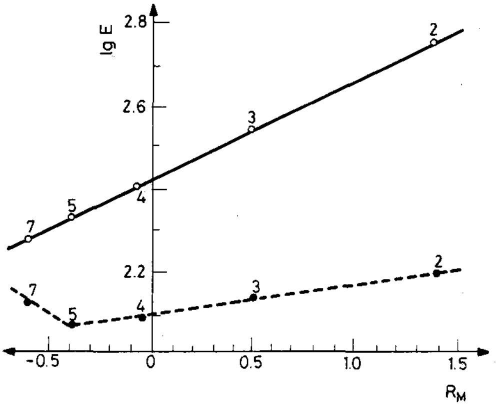

Fig. 2. Relationship between the E-values and R_M-functions for N-monoalkyl 2,4,6-trinitroanilines: ○ measurements according to DTA method A; ● measurements according to DTA method B

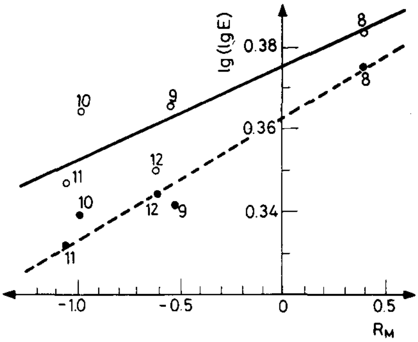

Fig. 3. Relationship between the E-values and R_M-functions for N,N-dialkyl 2,4,6-trinitroanilines: ○ measurements according to DTA method A; ● measurements according to DTA method B

Relationships of the type in Fig. 4 (i.e. for N-monosubstituted derivatives) show an analogous course as the similar dependences in Fig. 2. Interaction of the thermolyzed compounds with the glass surface can therefore be assumed to lead to a decrease in the activation entropy. Due to the absence of amine hydrogen from N,N-disubstituted 2,4,6-trinitroanilines, the activation entropy decrease in these is less pronounced (see Fig. 5) than in N-monosubstituted analogues.

The results of this and earlier work [1, 2, 4, 8] illustrate the influence of the construction materials (and, to some extent, the construction parameters of the

DTA apparatus) upon the kinetics of thermolysis of polynitroaromatic compounds and their derivatives. At the same time they prove the difficulties in the interpretation of the results obtained from DTA measurements as regards the reaction kinetics.

As far as the glass type is concerned, practically no differences were discovered between DTA measurements with capillaries of either Símax or Rasotherm glass.

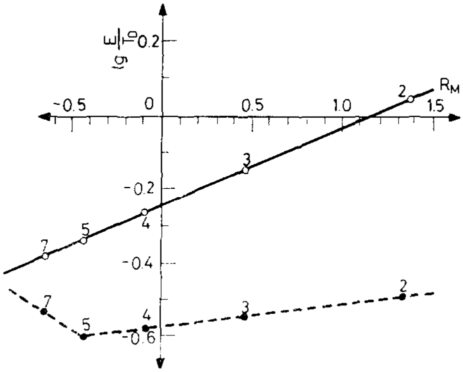

Fig. 4. Relationship between the $E \cdot T_D^{-1}$ terms and R_M-functions for N-monoalkyl 2,4,6-trinitroanilines: ○ measurements according to DTA method A; ● measurements according to DTA method B

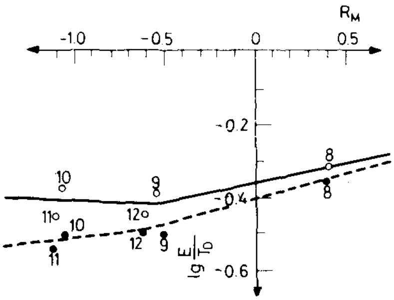

Fig. 5. Relationship between the $E \cdot T_D^{-1}$ terms and R_M-functions for N,N-dialkyl 2,4,6-trinitroanilines: ○ measurements according to DTA method A; ● measurements according to DTA method B

Somewhat different values resulted, however, when Sial was employed: for 2,4,6-trinitroaniline with Rasotherm glass, average values [6] of T_D = 520,8 K and E_A = 225.82 kJ · mol^{-1} were found, but for the same compounds with Sial glass the values given in Table 1 resulted.

Comparison of the values for the 2,4-dinitroaniline derivatives [1] with those for the 2,4,6-trinitro analogues leads to the conclusion that introduction of the nitro group into position 6 in 2,4-dinitroanilines unambiguously reduces the thermal stability of the resulting N-monosubstituted 2,4,6-trinitroanilines, and unambiguously increases the thermal stability of the *N,N*-disubstituted 2,4,6-trinitroanilines, as compared with the 2,4-dinitro analogues.

Analogous, introduction of the 4-nitro group into *N*-monosubstituted 2,6-dinitroanilines leads in the case of the *N*-monomethyl derivative to an increase, and in the remaining cases to a decrease of the thermal stability of the resulting 2,4,6-trinitro analogues, as compared with the starting compounds. Substitution in the same sense in *N,N*-disubstituted 2,6-dinitroanilines leads to 2,4,6-trinitro analogues possessing a reduced thermal stability as compared with the starting compounds.

A reduction in thermal stability in the transition from *N*-monosubstituted 2,4-dinitroanilines to the 2,4,6-trinitro analogues can be brought about by steric effects, but above all by the negatively induced effect of the 6-nitro group, which reduces the electron density on the amine nitrogen; the donor property of the proton of the amine function is increased. The increased thermal stability of *N,N*-disubstituted 2,4,6-trinitroanilines as compared with the 2,4-dinitro analogues [1] can be brought about either by a reduction in the resonance interaction $^{+}R_2 = = C_1 \rightarrow C_4 = NO_2^-$ due to deformations caused by introduction of the 6-nitro group [10, 11], or by the influence of the development of steric conditions unfavourable for acitautomer [6] or cyclic activated complex formation by the interaction of the α-methylene hydrogen with the oxygen of the ortho-nitro group [12].

The reduction in thermal stability accompanying the transition from *N*-substituted 2,6-dinitroanilines to the 2,4,6-trinitro analogues is brought about the reduced electron density in the amine nitrogen due to the conjugation effect of the introduced 4-nitro group (see also [2, 13]). In ortho-nitroaromatic compounds having an *N*-heteroparaffinic substituent, the positive influence of the 4-nitro group upon the increase in thermal reactivity has been confirmed [12]. In *N*-monosubstituted derivatives, along with the conjugation effect of the 4-nitro group, the influence of the conformation of the molecule (i.e. "steric enhancement effect" [10]) connected with the introduction of this nitro group into the 2,6-dinitroaniline molecule is also manifested.

It follows from the results of this and previous work [1,2,5–8] that application of the Piloyan method of determination of decomposition activation energy [14] to the differential thermal analysis of polynitroaromates can, under favourable experimental conditions [5] in combination with a suitable method of studying the thermolysis reaction kinetics [5–8] or in combination with a suitable method of structural analysis [1, 2, 15], lead to a satisfactory interpretation of DTA measurements from the points of view of both the reaction kinetics and the molecular structure.

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RÉSUMÉ — On a déterminé les énergies d'activation par la méthode de Piloyan ainsi que les températures initiales T_D de l'effet exothermique de six N-monoalcoyl- et cinq N,N-dialcoyl-2,4,6-trinitroanilines. En se référant aux facteurs R_F ou aux valeurs des fonctions R_M en chromatographie sur papier, on a étudié la dépendance entre les valeurs de E et de T_D sur les caractéristiques moléculaires-structurales de ces composés.

On a également trouvé des rapports entre le terme $E \cdot T_D^{-1}$ et les fonctions R_M. On discute l'influence de l'introduction du groupe 6-nitro dans les 2,4-dinitroanilines N-substituées ainsi que l'influence de l'introduction du groupe 4-nitro dans les 2,6-dinitro analogues sur la stabilité thermique des 2,4,6-trinitroanilines qui en résultent.

ZUSAMMENFASSUNG — Die Aktivierungsenergien E nach Piloyan und die Anfangswerte der Exothermen T_D der sechs N-monoalkyl- und fünf N,N-Dialkyl-2,4,6-trinitroaniline wurden bestimmt. Unter Berücksichtigung des Vergleichs mit R_f-Faktoren oder R_M-Funktionen der Papierchromatographie wurden die molekularstrukturellen Abhängigkeiten der Werte E und T_D dieser Verbindungen untersucht. Zusammenhänge wurden auch zwischen dem Ausdruck $E \cdot Tw_D^{-1}$ und den R_M-Funktionen gefunden. Der Einfluss der Einführung der 6-Nitrogruppe in die N-substituierten 2,4-Dinitroaniline, sowie der Einfluss der Einführung der 4-Nitrogruppe in 2,6-Nitroanaloge auf die Thermostabilität der resultierenden 2,4,6-Trinitroaniline werden erörtert.

Резюме — Для шести N-моноалкил- и пяти N,N-диалкил-2,4,6-тринитроанилинов определены энергии активации E Пилояна, а также начальные экзотермы T_D. Учитывая сравнение с R_f-факторами или R_M — функциями бумажной хроматографии, изучены молекулярно-структурные зависимости значений E и T_D. Найдены также взаимосвязи между выражением E . T_D^{-1} и R_M-функциями. Обсуждено влияние введения нитрогруппы в положение 6 N-замещенных 2,4-динитроаналинов и в положение 4 их 2,6-динитроаналогов на термическую стабильность 2,4,6-тринитроанилинов.