

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

PART VI. RELATIONSHIPS FOUND BETWEEN CHROMATOGRAPHIC
AND THERMAL ANALYSIS DATA FOR *N*-SUBSTITUTED
2,6-DINITROANILINES

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The Piloyan activation energies E and initial exotherm temperatures T_D of five *N*-monoalkyl — and four *N,N*-dialkyl-2,6-dinitroanilines were determined. By comparison with R_f factors, or values of R_M functions of paper chromatography, the molecular-structural dependences of the values of E and T_D for the measured compounds were studied. The relationship between the $E \cdot T_D^{-1}$ term and the R_M functions is discussed from the viewpoint of the published data on the conformations of *N*-substituted polynitroanilines.

Study of the relationship found between the Piloyan activation energies E , the initial exotherm temperatures T_D and the molecular structures in the thermal decomposition of *N*-substituted polynitroanilines forms part of earlier papers [1, 2]. Paper chromatography (PC) data [3] provided information on the molecular structures of these compounds. The results obtained in this way for *N*-substituted 2,4-dinitroanilines are discussed in paper [4] and are extended to *N*-substituted 2,6-dinitroanilines in the present paper.

Experimental

Materials

The origin, methods of purification and melting point determination of the *N*-substituted 2,6-dinitroanilines, their R_f factors and R_M functions of their PC, are described in paper [3]. These compounds have also been examined by DTA measurements [5].

Methods

The methods of DTA measurement were detailed in the first part of the present paper [6]. In this paper the DTA measurements were made only by method *A* (i.e. using thermocouples placed in a stainless injection needle). Averaged E and T_D values are given for weighed samples within the range 80–130 mg.

Results and discussion

Table 1 gives average values of the Piloyan activation energies E , as well as the initial exotherm temperatures T_D .

Similarly as in paper [4], a relationship the type shown in Fig. 1 was found between the T_D values and the R_f factors of N -substituted 2,6-dinitroanilines. In Fig. 1 the datum for compound 2 is not correlated with the dependence for N -monosubstituted derivatives.

By means of the dependence illustrated in Fig. 1, the initial temperature of the exotherm was determined by extrapolation for compound 1 ($T_D = 491.6$ K) and

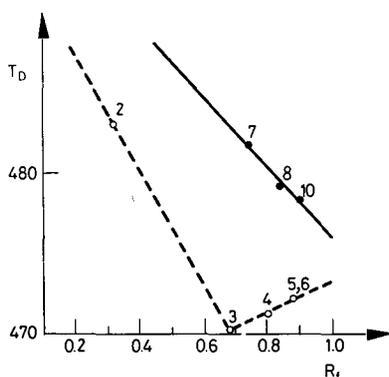


Fig. 1. Relationship between the initial exotherm temperatures T_D and the R_f factors

Table 1
Survey of results

Substance no.	Substance	Initial temperature of exotherm, T_D , K	Temperature range, K	E , $\text{kJ} \cdot \text{mol}^{-1}$
1	2,6-Dinitroaniline	distilled	without decomposition	
2	N-Methyl-2,6-dinitroaniline	483.2	487–496	319.02 ± 37.60
3	N-Ethyl-2,6-dinitroaniline	470.2	473–497	298.63 ± 12.98
4	N-Propyl-2,6-dinitroaniline	471.1	474–491	303.91 ± 11.22
5	N- <i>n</i> -Butyl-2,6-dinitroaniline	472.1	473–485	284.32 ± 23.02
6	N-Cyclohexyl-2,6-dinitroaniline	472.1	475–485	289.76 ± 19.21
7	N,N-Dimethyl-2,6-dinitroaniline	481.7	483–491	303.49 ± 42.96
8	N,N-Diethyl-2,6-dinitroaniline	479.2	453–461	216.58 ± 24.83
9	N,N-Dipropyl-2,6-dinitroaniline	distilled	without decomposition	
10	N-(2,6-Dinitrophenyl)-piperidine	478.2	483–501	195.01 ± 5.48

for compound 9 ($T_D = 493.2$ K). The two compounds distilled without decomposition under the conditions of the experiment (see Table 1).

It follows from Fig. 1 that, starting with compound 3, an increase in the thermal stability due to the increasing volume of the alkyl substituent is characteristic for *N*-monosubstituted 2,6-dinitroanilines.

For *N,N*-disubstitution, however, the relationship between the volume of the alkyl substituent and the thermal stability in the sense of Fig. 1 is not so unambiguous; the relatively high thermal stability of compound 9 is surprising, too.

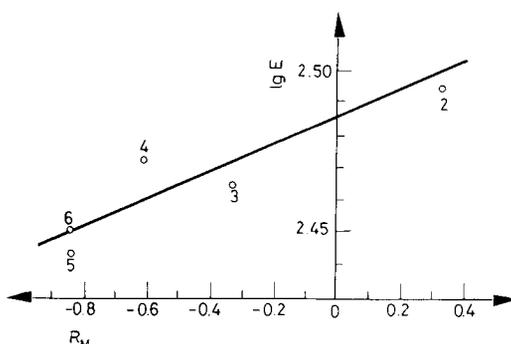


Fig. 2. Relationship between the E values and R_M functions for *N*-monoalkyl-2,6-dinitroanilines

Analogous as for 2,4-dinitroanilines [4], the measured compounds display a certain relationship between the E values and the R_M function values. For *N*-monosubstituted derivatives this relationship is shown in Fig. 2. Unlike the 2,4-dinitro analogues [4], no change in shape of Fig. 2 type was exhibited by the measured *N*-monosubstituted 2,6-dinitroanilines due to the increasing volume of the alkyl substituent.

In *N,N*-dialkyl-2,6-dinitroanilines, the E values are linked with the R_M functions by the relationship of Fig. 3 type. From this relationship the Piloyan activation energy was calculated for compound 9 ($E = 187.10$ kJ · mol⁻¹).

Similarly as for *N*-substituted 2,4-dinitroanilines [4], a graphical representation of the probable relationship between the activation entropies of thermal decomposition of the measured compounds and their molecular structures is illustrated in Fig. 4; on the basis of paper [7], the activation entropy is represented here, to a first rough approximation by the term $E \cdot T_D^{-1}$. The change in entropy due to the increasing volume on *N*-monosubstitution is not so pronounced for the 2,4-dinitro analogues [4]. At the same time, for both *N*-mono- and *N,N*-disubstituted 2,6-dinitroanilines it is expressed by the shape of the dependence of Fig. 4 type.

The differences found between the *N*-mono substituted 2,6-dinitroanilines and the 2,4-dinitro analogues [4] can be interpreted in the knowledge of the molecular structures of polynitroanilines [8–11]: according to Kamlet [8], introduction

of an alkyl group onto the amine nitrogen of 2-monoalkyl- or 2,6-dinitroaniline brings about a deviation of the 2- (or 6-) nitro group from nucleus coplanarity, and can lead to deformation of the amine nitrogen–nucleus carbon bonding angle. Deviation of the amine nitrogen from the benzene nucleus planarity can occur at the same time [8]. Electron spectra show [11] that an increase in the bulk

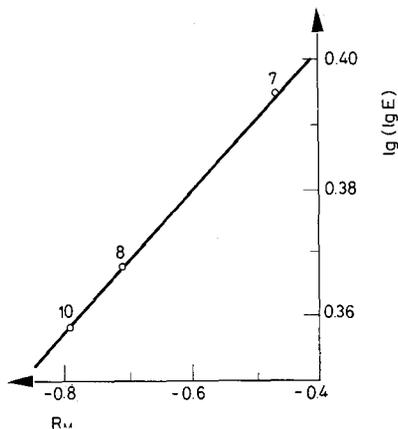


Fig. 3. Relationship between the E values and R_M functions for N,N -dialkyl-2,6-dinitroaniline

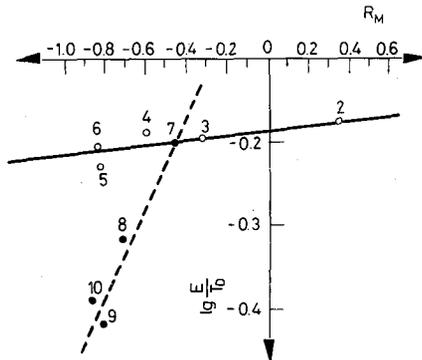


Fig. 4. Relationship between the $E \cdot T_D^{-1}$ terms and the R_M functions: \circ N -monoalkyl- and \bullet N,N -dialkyl-2,6-dinitroanilines

of the N -alkyl group in N -monoalkyl-2,6-dinitroanilines causes no further changes in the molecular geometry [11]. This means that the spatial arrangement of the activated complex in the thermal decomposition of these compounds is negligibly influenced by the size of the alkyl group. This also accounts for the dependences of the types in Figs 2 and 4 for all the measured N -monosubstituted 2,6-dinitroanilines.

Introduction of the nitro group into position 4 in *N*-alkyl-2-nitro- or *N*-alkyl-2,6-dinitroanilines can cause the amino nitrogen to return into coplanarity with the benzene nucleus [8, 9], with a simultaneous deviation of the 2- (or 6-) nitro group from nucleus coplanarity [8, 9].

Due to the conjugation effect, the 4-nitro group, reduces the electron density [11] on both the amine nitrogen and the ortho-nitro oxygen atoms. The donor property of the proton of the amine function is therefore increased more than the acceptor property of the ortho-nitro group is decreased, resulting in a stronger hydrogen-bond [11]. It follows from the results of paper [4] that this leads to the formation of more rigid activated complexes in the thermal decomposition of *N*-alkyl-2,4-dinitroanilines than those exhibited by the 2,6-dinitro analogues. Considering the spatial arrangement in the neighbourhood of the amine nitrogen in the *N*-mono-substituted 2,4-dinitroanilines [8, 9], the influence of the size of the *N*-alkyl substituent or, more particularly, its α -carbon atom branching upon the conformation of the activated complex is naturally more pronounced.

It follows from Fig. 4 that, along with the increasing steric effect exercised by the steric effect of the substituent in the *N,N*-dialkyl-2,6-dinitroanilines, there should be a decrease in the activation entropy. This condition does not contradict the mechanism of thermal decomposition of ortho-nitroaromatic compounds with *N*-heteroparaffinic substituents [12].

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RÉSUMÉ — On a déterminé les énergies d'activation E d'après Piloyan et les valeurs initiales T_D de cinq *N*-monoalkyl- et quatre *N,N*-dialkyl-2,6-dinitroanilines. En se référant aux facteurs R_F ou aux valeurs des fonctions R_M de la chromatographie sur papier, on a étudié la dépen-

dance entre les valeurs de E et de T_D et les caractéristiques moléculaires-structurales. On discute la corrélation entre le terme $E \cdot T_D^{-1}$, d'une part, et les fonctions R_M , d'autre part, du point de vue des données publiées sur la structure des polynitroanilines N -substituées.

ZUSAMMENFASSUNG — Die Aktivierungsenergien E nach Piloyan und die Anfangswerte der Exothermen T_D von fünf N -monoalkyl- und vier N,N -dialkyl-2,6-dinitroanilinen wurden bestimmt. Unter Berücksichtigung des Vergleichs mit den R_F -Faktoren oder Werten von R_M -Funktionen der Papierchromatographie wurden die molekular-strukturellen Abhängigkeiten der Werte E und T_D für die gemessenen Verbindungen untersucht. Die Zusammenhänge zwischen dem Ausdruck $E \cdot T_D^{-1}$ einerseits und den R_M -Funktionen andererseits werden unter Berücksichtigung der über N -substituierten Polynitroanilin-Konformationen veröffentlichten Angaben diskutiert.

Резюме — Определены энергии активации E по Пилояну и начальные экзотермы T_D для пяти N -моноалкил- и четырех N, N -диалкил-2,6-динитроанилинов. Учитывая сравнение с R_F -факторами или значениями R_M -функций бумажной хроматографии, для данных соединений изучены молекулярно-структурные зависимости значений E и T_D . Исходя из опубликованных данных о конформации N -замещенных полинитроанилинов, обсуждены зависимости между выражением $E \cdot T_D^{-1}$ и R_M -функциями.