Journal of Thermal Analysis, Vol. 19 (1980) 417—424

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

PART, V. THE RELATIONSHIP FOUND BETWEEN CHROMATOGRAPHIC AND THERMAL ANALYSIS DATA OF N-SUBSTITUED 2,4-DINITROANILINES

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(Received June 1, 1978; in revised form January 5, 1980)

Piloyan activation energies E as well as initals of exotherm T_D of seven *N*-monoalkyl and five *N,N*-dialkyl-2,4-dinitroanilines were determined. Relationships were found between the T_D values and R_f factors as well as E values and those R_M functions and also the ET_D^{-1} term and R_M functions.

In the previous parts of the paper [1—4] attention was paid to kinetic data of thermal decomposition of compounds contining trinitrophenyl groups in the molecule. Conditions of the DTA measurements were specified [1] for determination of the Piloyan activation energies E [1—4] as well as the initial exotherm temperatures T_D of the measured compounds [1—4]. Relationships of the type [1—5]

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

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

were found to exist between $E \cdot T_D^{-1}$ and published Arrhenius parameters E_M and $\log A$ obtained from the study of polynitroaromatic compounds by isothermal manometry.

The relationship of the Piloyan activation energies E and the values of the initial exotherm temperatures T_D towards the molecular structures was studied in papers [5, 6]. In an attempt to account for this problem, comparison was made with the results obtained from another physical-based procedure for actual analysis, paper chromatography (PC) [6, 7] in this case. *N*-mono- and *N,N*-disubstituted polynitroanilines were selected to serve as model compounds [6, 7].

Experimental

Methods

DTA measurement methods are specified in detail in the first part of the present paper [1]. Measurements using thermocouples placed in a stainless injection

Table 1

Survey of results

Substance No.	Substance	Method A			Method B		
		Initial of exotherm T_D, K	Temperature range, K	E, kJ. mole^{-1}	Initial of exotherm T_D, K	Temperature range, K	E, kJ. mole^{-1}
1	2,4-Dinitroaniline	528.6	533 – 549	196.86±13.56	531.2	533 – 545	233.16±10.00
2	N-Methyl-2,4-dinitroaniline	499,7	503 – 510	277.62±16.58	487.5	492 – 509	204.73±13.15
3	N-Ethyl-2,4-dinitroaniline	491.2	499 – 509	188.28±15.03	481.1	483 – 508	160.73±5.19
4	N-Propyl-2,4-dinitroaniline	483.0	486 – 498	156.14±12.41	480.9	482 – 509	184.80±2.68
5	N-n-Butyl-2,4-dinitroaniline	468.9	470 – 487	132.47±10.00	476.5	478 – 498	203.30±8.12
6	N-Isopropyl-2,4-dinitroaniline	531.2	533 – 541	314.29±9.42	532.9	534 – 544	514.92±5.86
7	N-Isobutyl-2,4-dinitroaniline	482.1	487 – 503	236.97±15.49	478.1	480 – 506	194.30±23.44
8	N-Cyclohexyl-2,4-dinitroaniline	538.1	539 – 548	376.80±13.86	505.5	509 – 528	399.27±31.64
9	N,N-Dimethyl-2,4-dinitroaniline	—	—	—	466.3	468 – 486	266.57±0.70
10	N,N-Diethyl-2,4-dinitroaniline	438.7	440 – 451	315.21±24.07	439.9	442 – 452	286.45±7.53
11	N,N-Dipropyl-2,4-dinitroaniline	—	—	—	436.8	438 – 452	299.91±5.15
12	N,N-Diisopropyl-2,4-dinitroaniline	462.2	467 – 473	145.32±18.75	528.1	530 – 563	269.37±16.41
13	N-(2,4-dinitrophenyl)-piperidine	448.7	—	—	446.0	448 – 468	282.51±4.56
14	N-Phenyl-2,4-dinitroaniline	523.1	524—534	187.69±5.77	—	—	—

needle [1 – 6] are designated in this paper as method A; method B involves measurements using thermocouples placed in a glass capillary [1].

In contrast to previously [1 – 4], in the present paper averaged E and T_D values are given to denote the weighed samples within the range 80 – 130 mg.

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

Sial glass was used to make test tubes to take samples, and capillaries to hold thermocouples.

The PC method is described in paper [7].

Materials

The origin, methods of purification and melting points of the 2,4-dinitroaniline derivatives, and their R_f factors and R_M functions in PC, are described in the paper [7]. These data are also presented in paper [8].

Results and discussion

A survey of average values of the Piloyan activation energies E and average values of the initial exotherm temperatures T_D are given in Table 1.

In the case of N-mono- and N,N-disubstituted polynitroanilines, mutual relationships existing between their T_D values and their R_f factor values in PC have been reported [5, 6]. These relationships are described, in a general form, by the equation [5, 6]:

$$T_D = b_2 \cdot R_f + a_2 \tag{3}$$

A graphical presentation of Eq. 3 for the 2,4-dinitroaniline derivatives in question is given in Fig. 1. Setting out from these dependences, as well as from a knowledge of the conformations of N-mono- and N,N-disubstituted 2,4-dinitroanilines [9, 10], it is possible to arrive at partial conclusions about the relationship existing between the N-substitution and the thermal reactivity of the corresponding derivative.

In the case of N-mono-n-alkyl derivatives of 2,4-dinitroaniline, which exhibit a positively-induced effect of the substituent, the thermal reactivity was found to increase. At the same time the rate of increase upon the DTA method used for measurement (either method A or method B is meant); in other words, it depends upon the material with which the compound being measured is in contact during thermal analysis.

It is in the thermal stability of N-mono-alkyl-2,4-dinitroanilines that the steric effect makes itself felt in the most pronounced way. Branching of the paraffinic substituent on the α-carbon most probably leads to a strong deviation of the amine nitrogen and of the ortho-nitro group from coplanarity with the benzene ring [9] so as to give unfavourable steric and electronic conditions for transition state (see

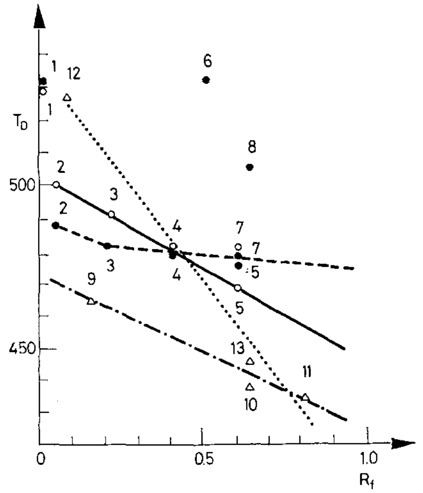

Fig. 1. Graphical representation of Eq. 3: points ○ corresponds to DTA measurements based on method *A*; points ● and △ correspond to DTA measurements based on method *B*

for example [11] or acitautomer [2]) formation. This makes itself felt in the decrease of the thermal reactivity and the increase of the activation entropy (see Figs 4 and 5). Branching on the β-carbon gives rise to a similar, though less pronounced effect. Interaction with the surface of the glass capillary (DTA measurements by method *B*) reduced the mutual difference in the individual thermal reactivities of compounds 5 and 7.

A more considerable steric compression, along with a more pronounced positively-induced action of the alkylamino substituents in *N,N*-dialkyl-2,4-dinitroanilines, brings about the decrease of the thermal stability as compared to the *N*-monoalkyl analogues. The mechanism of their thermal decomposition can be interpreted according to Suschitzki and Sutton [12]: in the thermal decomposition of ortho-nitroaromatic compounds containing N-heteroparaffinic substituents, the acitautomer originates from interaction of the ortho-nitro group with the α-methylene hydrogen [12]. If there is branching in the α-carbons, however, the thermal reactivity will decrease because of the steric conditions.

This decrease of the thermal reactivity, along with the increase of the steric compression, can be illustrated, in the given sense, by means of the series of compounds 13, 11 and 12 (see Fig. 1).

Stabilization on the introduction of isopropyl on the amine nitrogen is so pronounced that, on the basis of the T_D values, the thermal stabilities of compounds 6 and 12 approach the stability of non-substituted 2,4-dinitroaniline (see the results of DTA measurements by method *B*); the stability of compound 6 is higher than those of *N*-aryl derivatives of 2,4-dinitroaniline [6].

In structural analysis, the chromatographic R_M functions are made use of [13].

For N-monosubstituted 2,4-dinitroaniline derivatives, a relationship of general formula [5, 6]

$$\log E = b_3 \cdot R_M + a_3 \tag{4}$$

was found between the R_M functions and the E values.

Graphical representation of Eq. 4 is presented in Fig. 2. For DTA measurement based on method A, relationship 4 splits into three parts. The part including compounds 2, 3, 4 and 5 corresponds to the influence of n-alkyl substituents; the part for compounds 3, 6 and 8 corresponds to branching on the α-carbon in the alkyl substituent; and the part for compounds 5, 7 and 8 is in accordance with the influence exercized by the increased volume of the substituent in the more general sense of the word.

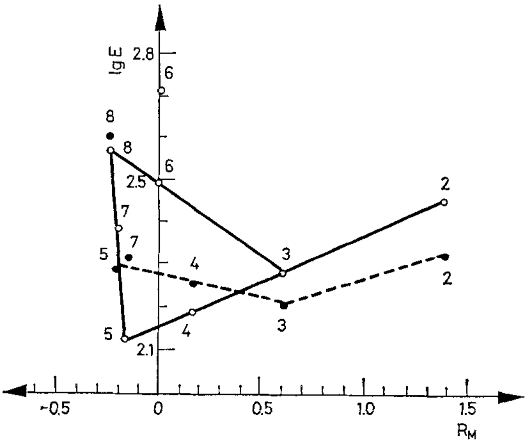

Fig. 2. Graphical representation of Eq. 4: points ○ correspond to DTA measurements according to method A; points ● correspond to DTA measurements according to method B

The course of dependence 4 for DTA measurements by method B is influenced by the interaction of the hydrogen atoms of the amino group with the glass surface (see [2]).

At the same time, however, the shape of dependence 4 for derivatives containing voluminous substituents (i.e. compounds 5, 7 and 8) is practically identical for method A and method B.

For N,N-di-n-alkyl-2,4-dinitroanilines, a relationship

$$\log(\log E) = b_4 \cdot R_M + a_4 \tag{5}$$

was found [5, 6] between E and values of the R_M function. A graphical representation Eq. 5 for DTA measurements by method B is given in Fig. 3.

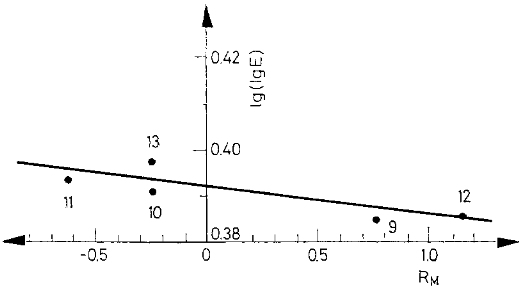

Fig. 3. Graphical representation of Eq. 5; DTA measurements according to method *B*

If the results contained in paper [7] are taken into account, Eqs 4 and 5 can be rewritten as follows:

$$\log E = b_5 \cdot \log N_c + a_5 \tag{6}$$

$$\log (\log E) = b_6 \cdot \log (\log 2 \cdot N_c) + a_6 \tag{7}$$

where N_c is the number of carbon atoms in the *n*-alkyl group of the *N*-substituted polynitroanilines. Relationships 6 and 7 illustrate well the dependence of the Piloyan activation energies E upon the structure of the *N*-*n*-alkyl substituent.

It was found [4, 5] that the term $E \cdot T_D^{-1}$ bears a definite relationship to the activation entropy of thermal analysis, though in itself it cannot be considered to be entropy [4, 5]. In terms of the logarithm of $E \cdot T_D^{-1}$, a probable relationship between the activation entropy of thermal decomposition of the substances under examination and their R_M functions is illustrated graphically in Figs 4 and 5. The relationship has the general form [5]

$$\log \frac{E}{T_D} = b_7 \cdot R_M + a_7 . \tag{8}$$

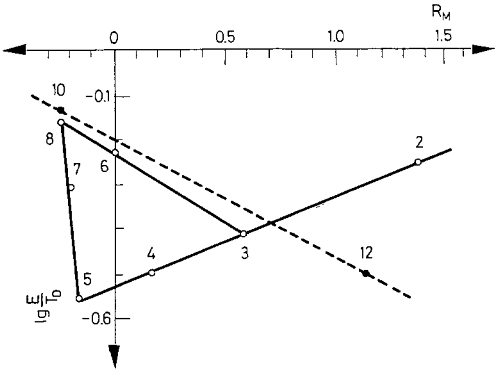

Fig. 4. Relationship (Eq. 8) between $E \cdot T_D^{-1}$ and the R_M function; DTA measurements according to method *A*

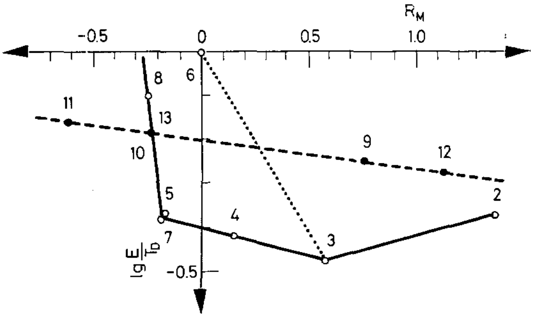

Fig. 5. Relationship (Eq. 8) between $E \cdot T_D^{-1}$ and the R_M function; DTA measurements according to method *B*

It follows from Figs 4 and 5 that, due to branching of the paraffinic substituent on the α-carbon, as well as to the increase of its volume over a given limit for *N*-monoalkyl-2,4-dinitroanilines there should also be an activation entropy increase. This is evidence of the greater number of ways in which the corresponding *N*-alkylamino groups are realized in space than in the case in the molecules of compounds 2, 3, 4 and 5.

Comparison of the dependence illustrated in Fig. 4 with those given in Fig. 5 reveals unambiguously the influence of activation entropy by contact of the compounds with the glass surface of the capillary (method *B*). Analogously to dependence 4 (Fig. 2), Eq. 8 has the same shape for DTA measurements by either method *A* or *B* in the case of compounds 5, 7 and 8.

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The authors would like to thank Mrs. Anna Čollàkovà for careful DTA measurements, and Dr. Ladislav Smolka for help in treatment of the measured results with the Wang 600 computer.

References

1. S. ZEMAN, J. Thermal Anal., 17 (1979) 19.
2. S. ZEMAN, J. Thermal Anal., 19 (1980) 99.
3. S. ZEMAN, J. Thermal Anal., 19 (1980) 107.
4. S. ZEMAN, J. Thermal Anal., 19 (1980) 207.
5. S. ZEMAN, Thermostable Polynitroaromatic Compounds, Part II. Res. Rep., PO 2 – 79, Úrad pro vynálezy a objevy, Prague, Jan. 1979.
6. S. ZEMAN, Thermostable Polynitroaromatic Compounds, Part I. Ph. D. Thesis, Univ. Chem. Technol., Pardubice, June 1973.
7. E. ZEMANOVÁ and S. ZEMAN, J. Chromatogr., 154 (1978) 33.
8. V. KADEŘÁBEK, M. ADÁMEK and J. DENKSTEIN, Chemicky průmysl (Chem. Industry), 28 (1978) 325.
9. M. J. KAMLET, H. G. ADOLPH and J. C. HOFFSOMMER, J. Am. Chem. Soc., 86 (1964) 4018.
10. M. J. KAMLET, J. C. HOFFSOMMER, R. R. MINESINGER and H. G. ADOLPH, J. Org. Chem., 33 (1968) 3070.

11. V. G. Matveev, V. V. Dubikhin and G. M. Nazin, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 474.
12. H. Suschitzki and M. E. Sutton, Tetrahedron Letters, (1967) 3933.
13. L. S. Bark, Progr. Thin-Layer Chromatog. Relat. Methods, 1 (1972) 1.

Résumé — On a déterminé les températures initiales T_D de l'effet exothermique ainsi que les énergies d'activation E d'après la méthode de Piloyan, de sept *N*-mono alcoyl et cinq *N*,*N*-dialcoyl-2,4-dinitroanilines. Une corrélation entre les valeurs T_D et les facteurs R_f de la chromatographie sur papier des dinitroanilines étudiées a été trouvée et discutée, ainsi qu'entre les valeurs E et les fonctions R_M de la chromatographie sur papier. Une relation entre le terme $E \cdot T_D^{-1}$ et les fonctions R_M a également été trouvée.

Zusammenfassung — Die Aktivierungsenergien E nach Piloyan sowie die Anfangswerte der Exothermen T_D wurden für sieben *N*-Monoalkyl- und fünf *N*,*N*-Dialkyl-2,4-dinitroaniline bestimmt. Die Zusammenhänge zwischen den T_D-Werten und den papierchromatographischen R_f-Faktoren der gemessenen Dinitroaniline wurden abgeleitet und erörtert. Desgleichen wurden auch die Zusammenhänge zwischen den E-Werten und den R_M-Funktionen der Papierchromatographie abgeleitet und erörtert. Auch zwischen dem Ausdruck $E \cdot T_D^{-1}$ und den R_M-Funktionen wurde ein Zusammenhang gefunden.

Резюме — Определены энергии активации E по Пилояну и начальные экзотермы T_D семи *N*-моноалкил и пяти *N*,*N*-диалкил-2,4-динитроанилинов. Выведены и обсуждены соотношения между значениями T_D и коэффициентами R_f бумажной хроматографии, а также между E и функциями R_M. Установлены соотношения между выражениями $E \,.\, T_D^{-1}$ и функцией R_M.