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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 VIII. POLYNITRO DERIVATIVES OF TOLUENE AND NAPHTHALENE

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By means of non-isothermal DTA in its simple form the initial exotherm temperatures $T_D$ of 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2,4,6-trinitrotoluene, 1,5-dinitronaphtalene, 1,8-dinitronaphthalene and 1,4,5,8-tetranitronaphthalene have been determined. By application of the Piloyan method to these measurements, the activation energies $E$ arising from the decompositions of these compounds were established. The results are discussed from the point of view of the molecular structures of the polynitro compounds.

As mentioned in the first part of the present series [1], of the polynitrotoluenes, the thermal reactivity of 2,4,6-trinitrotoluene (TNT) has been studied. Considerably less attention has been paid in this respect to dinitrotoluenes: the kinetics of thermal decomposition of 2,4- and 2,6-dinitrotoluene (2,4-DNT and 2,6-DNT) have been studied by means of the manometric method, in both gaseous [2] and liquid [3] phases.

DTA was recently applied to the study of the thermal reactivity of 2,4-DNT [4]. In the past, DTA has been made use of in the case of 2,4-DNT only for the examination of its thermal stability [5, 6]. Results have also been published on the determination of the heats of decomposition of 2,4-DNT and TNT by means of DSC [7]. From among the more recent studies of TNT decomposition, referred to in [1], mention may be made of the determination of the kinetic parameters of the above process from ESR investigations [8].

Of the polynitronaphthalenes, only the thermal decomposition of 1,5-dinitronaphthalene (1,5-DNN) has recently been investigated, in the gaseous phase [2]. Analogously as for 2,4-DNT, with the dinitronaphthalenes DTA was made use of in the past only to establish the thermal stability [6]. More recently, the thermal reactivities of 1,5- and 1,8-DNN, 1,4,5-trinitronaphthalene (TNN) and 1,4,5,8-tetranitronaphthalene (TENN) have been investigated using DTA, by means of the Piloyan method of determination of decomposition activation energies ($E$) [9—11]. This is also true of the thermal reactivites of 2,4- and 2,6-DNT [9] and TNT [1,9,10]. The data obtained in this way on TENN and TNT have already been published [1,11]: within the present paper, data are given on the low nitrated analogues mentioned below.

## Experimental

### *Materials*

2,4-DNT and 2,6-DNT were obtained from technical products by repeated crystallization from ethanol. 2,4-DNT had m.p. 342.6 – 343.5 K, and 2,6-DNT had m.p. 338.4 – 339.1 K. The TNT used was of the same quality as in [1].

1,5-DNN and 1,8-DNN were obtained from the technical mixture of the two isomers by crystallization from cyclohexanone. Residues of the 1,5-isomer were removed from 1,8-DNN by means of reduction with sodium sulphite, with subsequent crystallization from an isopropanol-acetone mixture and, in the last stage, from isopropanol. 15-DNN was crystallized three times from cyclohexanone and finally once from acetone. 1,5-DNN had m.p. 488.7 – 489.6 K, and 1,8-DNN had m.p. 443.5 – 444.6 K.

TNN was prepared by 1,5-DNN nitration [12]. It was purified by crystallization from pyridine, then from acetone, and finally from benzene. TNN had m.p. 421.1 – 421.9 K. The TENN used was of the same quality as in [11].

### *Methods*

Methods of DTA measurement are detailed in [1]. In the present work, the DTA measurements were made only by method *B* (i.e. using thermocouples placed in a glass capillary). Simax or Rasotherm glass was used to produce test-tubes for samples and capillaries for holding the thermocouples.

## Results and discussion

It is evident from the survey in Table 1 that with decreasing sample weight there is a shift of the initial exotherm temperature $T_D$ towards higher values for TNT, 1,5-DNN and TNN. For 1,8-DNN and TENN, decrease of the sample weight leads to decreasing values of $T_D$.

In 1,8-DNN and 2,6-DNT, there is a marked relationship between the $E$ values and the sample weights. Such a relationship is less obvious for TNN and TENN.

According to the $T_D$ and $E$ values, the most stable of the measured polynitrotoluenes is 2,4-DNT, followed by TNT, the most reactive being 2,6-DNT. The stabilizing influence of the nitro group introduced into the 4-position in 2,6-DNT obviously makes itself felt here. This influence can also be observed in the structural analogues of polynitro derivatives of N-methylaniline for example [13 – 15].

During the thermolysis of nitrobenzene derivatives which have a hydrogen atom in the $\gamma$-position to the nitro group, the primary process is the migration of this hydrogen atom towards the oxygen of the nitro group *via* a six-membered cyclic transition state [16 – 18], during thermal decomposition in the condensed state, an acitautomer of ortho-quinoid type might arise (see e.g. [18 – 19]) as the primary intermediate of the reaction.

For hydrogen migration in the above sense, at least approximate planarity of the groups which participate in the reaction is necessary. Introduction of the nitro

Table 1

Survey of results

| Substance | Sample weight, mg | Initial temperature of exotherm, $T_D$, K | Temperature region, K | $E$, kJ · mol$^{-1}$ | Arrhenius parameters from manometric method | | |
|---|---|---|---|---|---|---|---|
| | | | | | $E_M$, kJ · mol$^{-1}$ | log $A$, s$^{-1}$ | Reference |
| 2,4-DNT | 107.1 | 515.6 | 517–529 | 243.62 | 139.56 | 9.0 | [3] |
| | 105.7 | 514.1 | 515–529 | 216.26 | | | |
| | 78.3 | 516.4 | 517–529 | 239.93 | | | |
| 2,6-DNT | 156.1 | 497.7 | 499–508 | 198.08 | 198.87 | 14.3 | [3] |
| | 80.6 | 498.3 | 500–510 | 187.57 | | | |
| | 54.4 | 497.1 | 499–509 | 159.15 | | | |
| TNT | 123.8 | 512.1 | 513–527 | 219.33 | 144.44 | 9.3 | [24] |
| | 113.2 | 512.7 | 513–527 | 196.64 | | | |
| | 96.4 | 512.9 | 513–527 | 220.58 | | | |
| | 67.1 | 513.1 | 515–525 | 212.30 | | | |
| 1,8-DNN | 102.2 | 559.7 | 561–571 | 158.66 | | | |
| | 102.0 | 559.2 | 561–577 | 151.08 | | | |
| | 90.4 | 555.9 | 557–570 | 139.28 | | | |
| 1,5-DNN | 111.9 | 568.4 | 570–581 | 218.40 | – | – | – |
| | 96.6 | 569.2 | 570–585 | 173.77 | | | |
| | 78.4 | 569.7 | 571–585 | 177.96 | | | |
| TNN | 119.6 | 545.4 | 547–561 | 313.07 | – | – | – |
| | 91.9 | 550.4 | 551–563 | 409.27 | | | |
| | 84.7 | 551.3 | 552–565 | 409.99 | | | |
| TENN | 118.5 | 571.1 | 572–585 | 318.08 | 223.05 | 15.0 | calculated according to [11] |
| | 102.7 | 570.9 | 571–595 | 251.85 | | | |
| | 84.7 | 573.1 | 574–585 | 280.01 | | | |
| | 72.2 | 570.2 | 571–579 | 283.01 | | | |

group into the 4-position in 2,6-DNT (or in 2,6-dinitro-*N*-methylaniline [14]) should increase the non-coplanarity of the 2- (or 6-) nitro group and the steric enhancement of resonance [20–22]. At the same time, there is also an electron density decrease on the oxygen atoms of this nitro group (see [14, 23]). These changes in the electron configuration and spatial arrangement of the reaction centre of the molecule can bring about the lower thermal reactivity of TNT as compared with that of 2,6-DNT.

The decrease in thermal stability accompanying the introduction of the nitro group into the 6-position in 2,4-DNT can be attributed both to the influence exercised by the steric compression and to the influence exercised by the electron density decrease on the carbon atom of the methyl group. The former influence is linked with the volume of the nitro group, while the latter is conditioned by the negatively inductive, or negatively conjugated effect.

In [1], a relationship has been derived for polymethyltrinitrobenzenes, between $E \cdot T_{\mathrm{D}}^{-1}$ on the one hand, and the Arrhenius parameters $E_{\mathrm{M}}$ and $\log A$ (obtained by Soviet authors using a manometric method) on the other hand. The values of $E \cdot T_{\mathrm{D}}^{-1}$ for 2,4-DNT satisfactorily fit this relationship: calculation gave $E_{\mathrm{M}} = 137.94$ kJ $\cdot$ mol$^{-1}$ and $\log A = 8.12$ s$^{-1}$, in good agreement with the experimental data (see Table 1). In contrast, there is no correlation of $E \cdot T_{\mathrm{D}}^{-1}$ for 2,6-DNT: calculation gave $E_{\mathrm{M}} = 150.55$ kJ $\cdot$ mol$^{-1}$ and $\log A = 9.31$ s$^{-1}$, which differ considerably from the experimental data (see Table 1). These facts provide evidence of the influence of the 4-nitration of 2,6-DNT and the 6-nitration of 2,4-DNT upon the thermal stability of the resulting TNT.

The trend in the order of thermal stabilities of 1,5-DNN, 1,8-DNN and TNN is quite within the expected limits. The lower stability of 1,8-DNN as compared with that of the 1,5-isomer is brought about particularly by steric factors.

The stabilizing influence of the crystal lattice within this compound [26] is due to the perfect symmetry of the TENN molecule [25], as well as to the perfect fixation of the charges in it: after the above-mentioned influence had been removed by conversion of TENN into a solution of 1,3,5-trinitrobenzene, an initial exotherm temperature $T_{\mathrm{D}} = 517$ K [9, 26] was determined. It is thus evident that in the naphthalene series too the thermal stability of the resulting polynitro derivatives decreases due to nitro group cumulation within the molecule. The influence of the cumulation is enhanced by steric factors: in our case it is caused by the entry of the nitro group into vicinal peri-positions of naphthalene.

The existing literature does not contain any studies of the primary processes of thermal decomposition of polynitronaphthalenes, whereas the problems of the polynitro derivatives of benzene have received sufficient attention. Of course, knowledge obtained from the thermal decomposition of benzene polynitro derivatives cannot be applied simply to the thermal decomposition of polynitronaphthalenes, in view of the special features exhibited by the molecular structure and chemical reactivity of naphthalene. For example, considering the knowledge of the mass-spectral fragmentation of dinitronaphthalenes [27], it can be expected that the primary step of thermal decomposition of 1,8-DNN in both gaseous and condensed phases will be homolysis of the $C-NO_2$ bond; this correspond to our ideas of thermal decomposition, e.g. 1,3-dinitro- and 1,3,5-trinitrobenzene [2, 28]. In the case of 1,5-DNN, however, again considering the conclusions of [27], the primary step of the thermal decomposition should be attack on the carbon or hydrogen in position 8 by a free electron pair of the nitro group oxygen in position 1: depending upon the electron density of the 8⊠ (or 4⊠) position [27], the fission would go via a five or six-membered transition state.

It is therefore probable that activated complexes in the thermal decomposition of 1,8-DNN and TENN will be structurally different from the activated complexes arising from 1,5-DNN and TNN. This presents complications in the calculation of the Arrhenius parameteres $E_{\mathrm{M}}$ and $\log A$ for 1,5- and 1,8-DNN, TNN and TENN; application of the relationship between $E \cdot T_{\mathrm{D}}^{-1}$ on the one hand and $E_{\mathrm{M}}$ or $\log A$ on the other hand, derived in [11] for "sterling" polynitroaromatic compounds, may not be suitable for this purpose. More definite conclusions may be arrived at after the missing data on the study of the thermal reactivity of polynitronaphthalenes in the condensed state by means of the manometric method have been published.

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Résumé — On a déterminé par ATD les températures initiales $T_D$ des phénomènes exothermiques du 2,4-dinitrotoluène, 2,6-dinitrotoluène, 2,4,6-trinitrotoluène, 1,5-dinitronaphtalène, 1,8-dinitronaphtalène, 1,4,5-trinitronaphtalène et 1,4,5,8-tétranitrophtalène. Les énergies d'activation $E$ de la décomposition de ces composés ont été déterminées à l'aide de la méthode de Piloyan. Les résultats obtenus sont discutés sous l'aspect de la structure moléculaire de ces composés.

ZUSAMMENFASSUNG — Durch nicht-isotherme DTA in ihrer einfachen Form wurde der Beginn $T_D$ der Exothermen von 2,4-Dinitrotoluol, 2,6-Dinitrotoluol, 2,4,6-Trinitrotoluol, 1,5-Dinitronaphthalin, 1,8-Dinitronaphthalin, 1,4,5-Trinitronaphthalin und 1,4,5,8-Tetranaphthalin bestimmt. Durch Anwendung der Methode von Piloyan auf diese Messungen wurden die aus der Zersetzung o.a. Verbindungen herrührenden Aktivierungsenergien $E$ spezifiziert. Die erhaltenen Ergebnisse werden unter dem Aspekt der Molekularstruktur der untersuchten Polynitroverbindungen erörtert.

Резюме — Посердством неизотермического ДТА в его простой форме были определены начальные $T_D$ эксотерм 2,4-динитротолуола, 2,6-динитротолуола, 2,4,6-тринитротолуола, 1,5- и 1,8-динитронафталинов, 1,4,5-тринитронафталина и 1,4,5,8-тетранитронафталина. Применяя к этим измерениям метод Пилояна, были установлены энергии активации $E$ реакций разложения этих соединений. Полученные результаты обсуждены с точки зрения молекулярной структуры изученных полинитросоединений