*Journal of Thermal Analysis, Vol. 19 (1980) 99–105*

# POSSIBILITIES OF APPLYING THE PILOYAN METHOD OF DETERMINATION OF DECOMPOSITION ACTIVATION ENERGIES

## PART II. POLYAMINO AND POLYHYDROXY DERIVATIVES OF 1,3,5-TRINITROBENZENE

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(Received April 20, 1978; in revised form November 30, 1979)

Activation energies ($E$) of the thermal decomposition and the initial values $T_{\mathrm{D}}$ of the exotherms are determined for trinitroaniline, trinitro-*m*-phenylenediamine, trinitrotriaminobenzene, trinitrophenol, trinitroresorcinol, trinitro-*m*-cresol and hexanitrooxanilide. Linear relationships are derived between the terms $E. T_{\mathrm{D}}^{1-}$ and published kinetics 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 positive influence on their thermal stability has been confirmed, arising from the contact of the measured compounds with the glass surface.

The kinetics of polyamino and polyhydroxy derivatives of TNB have been studied by means of isothermal manometry [1–5]. In this way corresponding data were obtained on the thermal decompositions of liquid 2,46-trinitroaniline (PAM) [1, 5], 1,3-diamino-2,4,6-trinitrobenzene (DATB) [2–5], in the liquid and solid states or in solution [5], 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [1, 3–5] in the solid state or in solution [5], 2,4,6-trinitrophenol (PA) [1], and 1,3-dihydroxy-2,4,6-trinitrobenzene (TNR) [1], in the liquid state.

As in the case of polymethyl and polychloro derivatives of TNB [6], the activation energies of the thermal decompositions of the above substances were determined by the Piloyan method [7], and are reported too in papers [8, 9]. Application of DTA to the study of the thermal stability of PAM is dealt with in paper [10]. Application of the Kissinger method of determination of activation energies in the DTA of PA is the subject of paper [11]. From among other thermoanalytical procedures, DSC has been applied to determine kinetic data on DATB and TATB [12], and both DTA and TG have been employed to study the influence of metals on the thermal reactivity of TATB [13].

## Experimental

### *Materials*

2,4,6-Trinitroaniline (PAM) was obtained by ammonolysis of picryl chloride in methyl alcohol. It was crystallized from an acetone – methyl alcohol mixture, from 65 per cent nitric acid, and finally from acetone; m.p.: 461.1 – 461.6 K.

1,3-Diamino-2,4,6-trinitrobenzene (DATB) was obtained by ammonolysis of 1,3-dichloro-2,4,6-trinitrobenzene in methyl alcohol. DATB was purified by crystallization from a dimethylformamide – ethyl alcohol mixture, with subsequent recrystallization from cyclohexanone; m.p.: 560.1 – 563.1 K with decomposition.

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) was prepared by ammonolysis of 1,3,5-trichloro-2,4,6-trinitrobenzene in methyl alcohol. Its purification consisted in washing with hot distilled water, with subsequent boiling in a large volume of acetone; m.p.: decomposes above 573 K.

2,4,6-Trinitrophenol (PA) was prepared from the technical product by repeated crystallization from distilled water, followed by twofold crystallization from methyl alcohol; m.p.: 394.1 – 394.6 K.

1,3-Dihydroxy-2,4,6-trinitrobenzene (TNR) was prepared from technical styphnic acid, using an analogous purification process as for PA; m.p.: 450.1 – 451.1 K.

3-Methyl-2,4,6-trinitrophenol (TNCr) was obtained by nitration of *m*-cresol with a $H_2SO_4$-$HNO_3$ mixture, followed by threefold crystallization of the product from acetone; m. p. 382. 1 – 382.6 K.

2,2',4,4',6,6'-Hexanitrooxanilide (HNO) was obtained by two-step nitration of oxanilide with a $H_2SO_4$-$HNO_3$ mixture. It was purified by crystallization from nitrobenzene, with subsequent dissolution in 98 per cent $HNO_3$, and precipitation from the resulting solution of 65 per cent nitric acid; m.p.: 584.1 K during decomposition.

The purities of substances were checked by means of thin-layer chromatography [6].

### *Method*

The DTA apparatus, as well as the methods and conditions of measurements are described in the first part [6] of the present paper. Simax or Rasotherm glass was used for production of test-tubes and capillaries to place the samples and thermocouples in the equipment.

## Results and discussion

The obtained Piloyan activation energies $E$ and the initial temperatures of exothermic decomposition $T_D$ are listed in Table 1, together with the Arrhenius parameters $E_M$ and log $A$ which were derived by Andreev [1] and Maksimov and coworkers [2 – 5] from kinetic measurements using manometry.

The results obtained from DTA measurements on PA and HNO and measurements by method A on PAM reveal that a reduction in the weight of sample leads to a moderate shift of the initial exotherm towards lower values. For TNCr, DATB and TATB the trend is in the reverse direction.

The most pronounced change of $E$ values due to the changed sample weight was exhibited by TATB, the changes being small for TNCr and DATB. With the given number of measurements for the individual compounds do not display a systematic dependence the $E$ values upon the sample weight for PA and HNO.

In the case of TNR, activation energies could not be determined by means of the Piloyan method because of the steepness of the initial part of the exotherm.

Table 1

Survey of results

| Substance | Differential thermal analysis data | | | | | | | | Manometric method data | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Method A[8., 9.] | | | | Method B[9.] | | | | | | |
| | Sample weight, mg | Initial decomposition, K | Temperature region, K | $E_M$ 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 |
| PA | 100.4 | 498.9 | 503–523 | 216.83 | 115.6 | 505.8 | 506–517 | 217.51 | 161.18 | 11.7 | 1. |
| | 99.7 | 496.4 | 497–513 | 215.53 | 94.6 | 505.1 | 506–517 | 250.21 | | | |
| | | | | | 80.6 | 503.6 | 505–517 | 183.63 | | | |
| TNR | 96.7 | 447.2 | — | — | — | — | — | — | 144.68 | 11.2 | 1. |
| TNCr | — | — | — | — | 102.7 | 474.0 | 477–484 | 218.85 | — | — | — |
| | | | | | 94.1 | 474.5 | 475–486 | 215.01 | | | |
| | | | | | 82.2 | 476.5 | 477–487 | 213.55 | | | |
| PAM | 106.9 | 513.6 | 516–524 | 290.13 | 102.6 | 521.9 | 523–535 | 220.24 | 129.79 | 7.1 | 1. |
| | 104.0 | 514.5 | 516–524 | 297.09 | 102.3 | 519.9 | 521–535 | 187.55 | | | |
| | 101.2 | 515.1 | 516–524 | 287.67 | 83.0 | 520.8 | 522–531 | 269.95 | | | |
| DATB | 116.3 | 526.4 | 531–541 | 122.29 | 110.3 | 524.1 | 525–535 | 215.90 | 196.77 | 13.2 | 2., 3., 4., 5. |
| | 106.0 | 527.2 | 531–541 | 142.55 | 101.0 | 527.1 | 529–540 | 249.98 | | | |
| | | | | | 92.6 | 527.3 | 529–543 | 243.43 | | | |
| | | | | | 92.5 | 526.5 | 528–538 | 203.89 | | | |
| TATB | 102.0 | 560.6 | 563–581 | 210.21 | 115.5 | 570.5 | 571–587 | 194.84 | 175.00 | 11.6 | 1., 3.–5. |
| | 101.0 | 561.8 | 569–587 | 209.33 | 94.6 | 574.7 | 576–593 | 246.84 | | | |
| | | | | | 80.5 | 571.1 | 573–585 | 273.57 | | | |
| HNO | 107.8 | 550.7 | 553–561 | 146.36 | 111.9 | 546.1 | 547–555 | 274.26 | 215.62 | 16.0 | 1., 3. |
| | 89.0 | 548.8 | 553–561 | 154.99 | 99.9 | 543.1 | 545–553 | 235.38 | | | |
| | | | | | 84.7 | 544.7 | 545–553 | 329.09 | | | |
| | | | | | 76.3 | 540.7 | 543–551 | 285.64 | | | |

All these compounds are characterized by the presence of intramolecular hydrogen-bonds; PAM, DATB and TATB even contain intermolecular hydrogen-bonds [14 – 16]. There is consequently a realistic presupposition of the identity or analogy of the primary step of thermal decomposition of these compounds. i.e. the formation of the aci tautomer is the most probable explanation (see also [6]). There is obviously same similarity with TNB derivatives containing an alkyl substituent or a substituted alkyl substituent [6].

The course of thermal analysis via the aci tautomer can be illustrated by means of one of the most probable mechanism of the initial thermal decomposition of the "isolated" DATB molecule [8].

In the formulation of this mechanism in paper [8], the motivating factors were:

- a general knowledge of the thermal reactivities of polynitroaromatic derivatives containing alkyl, amino or hydroxy groups in the ortho position to the nitro group (see, for example [17, 18];
- knowledge derived from the dehydration of DATB in the form of its 0.99 per cent solution in tetradecane at 253°: this reaction leads exclusively to 4-amino-5,7-dinitrobenzofuran, and not at all to the 5-amino-4,6-dinitro analogue [19];
- the MO diagram of the ground-state of the DATB molecule [20], according to which there is a higher positive charge on the nitrogen atom in the nitro group in position 2 than on the nitrogen atoms of the remaining nitro groups: thereby the higher thermal reactivity of the 2-nitro group in DATB is accounted for.

An analogous mechanism was proposed by Loughran and coworkers [13] for the primary step of the thermal decomposition of TATB. Maksimov and coworkers [5], on the other hand, are of opinion that the elimination of the nitro group may be a primary (monomolecular) fission process in TATB thermal decomposition in both the solid state and solution.

A monomolecular reaction of the given or analogous type (Fig. 1) is a possible primary step in the thermal analysis of the compounds examined within the present paper. The influence of the condensed phase is expected to make itself felt in this reaction through the changed character of bond hybridization of the molecule, due to intermolecular interactions. In the solid-phase decomposition, moreover, the negative influence of the closely arranged molecules within the crystal upon the formation of the activated complex should also be considered. The products, or fragments of the primary monomolecular decomposition, can attack the neighbouring unchanged molecules, or can enter into various reactions with each other. This idea is supported by the dependence of the values of the thermal decomposition kinetic data for organic polynitro compounds upon the technique and physical conditions of thermal measurements.

Intermolecular redox processes, as illustrated for example by the results obtained in the study of the ESR spectra of pyrolysis of some polynitroaromatic compounds [21], can not be taken into account until a more advanced stage of thermal analysis of these compounds is reached.

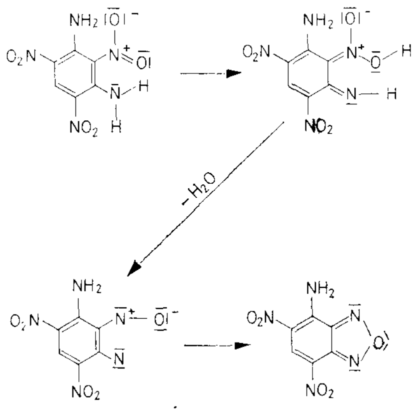

Fig. 1. The probable mechanism of the initial thermal decomposition of the DATB molecule — reproduced from (8.)

From the results of DTA measurements according to method B (thermocouples placed in a glass capillary [6]) it is evident that for HNO there is a slight decrease but for PA, PAM and TATB an increase in the value of the initial temperature of the exotherm $T_D$, as compared with measurements carried out by means of thermocouples placed in a stainless injection needle (method A [6, 8]). No change in $T_D$ was recorded for DATB. Similarly, excluding PAM, the remaining compounds exhibit higher activation energies of decomposition in method B. The increased stability indicated by measurements according to method B may be accounted for as being due to the weakening of the intra- and intermolecular hydrogen-bonds of molecules in the sphere of contact with the surface of the glass, because of the non-bonding interaction of the corresponding hydrogen atoms with protophilic centers on the glass surface of the capillary.

Similarly as for polymethyl and polychloro derivatives of TNB [6, 9], for poly-amino and polyhydroxy derivatives of TNB, relationships were found between the values of the $E \cdot T_D^{-1}$ term and the corresponding kinetic data obtained from the thermal analysis by means of manometry [1 – 5]. For the DTA measurements method A, the following relationship were found on the basis of linear regression analysis [9]:

$$\frac{E}{T_D} = -0.0038 \cdot E_M + 1.0592 \tag{1}$$

$$\frac{E}{T_D} = -0.0374 \cdot \log A + 0.8300 \tag{2}$$

with the correlation coefficient for Eq. (1) $r = 0.9670$, and for Eq. (2) $r = 0.9110$.

From the DTA measurements by method B, separate dependences resulted for decomposition in the liquid and the solid states. On the basis of linear regression analysis, using average values of the $E \cdot T_D^{-1}$ term, the following relationship were found to be most appropriate for decomposition in the solid phase, i.e. for thermal analysis of DATB, TATB and HNO [9]:

$$\log \frac{E}{T_D} = 0.0022 \cdot E_M - 0.7764$$

with the correlation coefficient $r = 0.9839$, and

$$\log \frac{E}{T_D} = 0.0203 \cdot \log A - 0.6183$$

with the correlation coefficient $r = 0.9994$.

For decomposition in the liquid phase, analogous dependences were estimated with the $b$ coefficient values $-0.0003$ and $-0.0020$, respectively, and with the $a$ coefficient values $-0.3165$ and $-0.3536$, respectively. For thermal decomposition of liquid TNCr, as a rough estimate, the result were $E_M = 87.2$ kJ $\cdot$ mol$^{-1}$ and $\log A = 5.5$. The two values are lower than expected, but this can be accounted for by considering the lower number of calibrated points.

The different dependences derived from the DTA measurements by method B provide evidence in favour of the idea of interaction of the hydrogen of inter- and intramolecular hydrogen-bonds of the measured substances with the glass surface. The extent of these interactions will depend upon the state of the pyrolyzed compound, thereby causing ambiguity in the derived relationship.

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The author is obliged to Mrs. Klara Kováčová, M.S. for her most generous help in processing the results of measurements on the Wang 2200 computer.

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