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# The thermoanalytical study of some aminoderivatives of 1,3,5-trinitrobenzene

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## Abstract

A thermoanalytical study of the aminoderivatives 1-amino-2,4,6-trinitrobenzene (PAM), 1,3-diamino-2,4,6-trinitrobenzene (DATB), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 2,2′,4,4′,6,6′-hexanitrodiphenylamine (DPA), 2,2′,4,4′,6,6′-hexanitrooxanilide (HNO) and 2,4,6-tris(2,4,6-trinitrophenylamino)-1,3,5-triazine (TPM) has been carried out. In the case of TATB, an endothermic change was found in the temperature region 321–326°C by means of DSC. By comparing the melting points of 1,3,5-trinitrobenzene, PAM and DATB, and of the endothermic change of TATB, with the melting points of the derivatives 1,3,5-triazine derivatives, which are structural analogues, it can be deduced that this temperature region corresponds to the melting point range of TATB.

The stability of all the compounds being studied was specified by means non-isothermal thermogravimetry (TGA). Linear dependences were found between the positions of the DTG peaks, or of the TGA onsets, and the weights of the samples. Analysis of the dependences gave results which were correlated with the rate constants of the isothermal thermolysis of the compounds and with their temperatures of explosion. From this analysis the Arrhenius parameters $E = 153.3\ \mathrm{kJ\ mol^{-1}}$ and $\log A = 11$ were determined for the DPA thermolysis in the temperature region 200–300°C.

## INTRODUCTION

Polyaminopolynitroarenes have long been important in technological applications. This group is a good source of potential explosives that possess an optimum combination of explosive and thermostable features [1–7]. This important starting point for the selection and exploitation of these nitroarenes is the study of both their physical and chemical thermostabilities.

With respect to the physical thermostability of polyaminopolynitroarenes, the melting point of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is not still clearly defined. Therefore, this problem has been addressed in the present study.

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TABLE 1

The nitrocompounds studied, their rate constants from isothermal thermolysis (by SMM) and the temperatures of their explosive points

| Substance | | | Rate constants $k_1$ ($s^{-1}$) from SMM application | | | | Temperature of explosive points $T_{expo}$ (°C) for an induction period of 5 s | |
|---|---|---|---|---|---|---|---|---|
| No. | Chemical name | Abbreviation | 250°C | | 300°C | | | |
| | | | $k_{250} \times 10^6$ | Ref. | $k_{300} \times 10^5$ | Ref. | $T_{expo}$ | Ref. |
| 1 | 1-Amino-2,4,6-trinitrobenzene | PAM | 0.35 [a] | 11 | 1.10<br>1.00 | 9, 10<br>9 | 346 | 19 |
| 2 | 1,3-Diamino-2,4,6-trinitrobenzene | DATB | 0.30 [b] | 8 | 0.50<br>1.60 | 9, 10<br>9 | 335 | 20 |
| 3 | 1,3,5-Triamino-2,4,6-trinitrobenzene | TATB | 1.3 [b] | 8 | 13.00 [a]<br>4.50 [b] | 9, 10<br>9 | 320 | 21 |
| 4 | 2,2′,4,4′,6,6′-Hexanitrooxanilide | HNO | 3.20 | 8 | 22.0 | [c] | 384 | 18 |
| 5 | 2,2′,4,4′,6,6′-Hexanitrodiphenylamine | DPA | 28.0 [b,d] | 8 | | | 325 | 22 |
| 6 | 2,4,6-Tris(2,4,6-trinitrophenylamino)-1,3,5-triazine | TPM | 0.25 [b] | 8 | 3.7 [b] | [c] | | |

[a] Thermolysis in the liquid state. [b] Thermolysis in the solid state. [c] Calculated by means of the Arrhenius parameters, given in ref. 8. [d] Value for thermolysis at 200°C.

In order to specify the chemical thermostability of the polyaminopolynitroarenes, the Soviet manometric method (SMM) [8–11], differential scanning calorimetry (DSC) [5, 12–15], differential thermal analysis (DTA) [3, 16, 17] and the American vacuum test [18] have already been applied. The existing literature, however, lacks a more extensive description of the thermogravimetric analysis (TGA) of this problem. Therefore, the present paper considers the thermal reactivity of some polyaminopolynitroarenes by means of TGA.

## EXPERIMENTAL

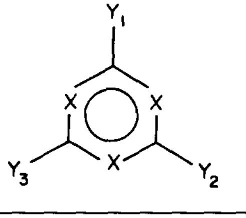
### Materials and data

A list of the studied aminoderivatives of 1,3,5-trinitrobenzene (s-TNB), with their numerical code and abbreviations, is given in Table 1, which also includes the values of the rate constants of the thermolysis of some of the derivatives studied, derived from the SMM technique at 250°C ($k_{250}$) and at 300°C ($k_{300}$). Table 1 also contains published values for the temperature of the explosive points $T_{expo}$ for an induction period of 5 s. The origin and purity of the s-TNB aminoderivatives studied have been previously described in refs. 3, 16 and 17.

Table 2 contains published values of the melting points of s-TNB and its polyaminoderivatives, together with values of the melting points of the

TABLE 2

Survey of the melting points values of 1,3,5-trinitrobenzene (s-TNB), 1,3,5-triazine (s-triazine) and of their aminoderivatives



| Substituents $Y_i$ | | | Melting points (°C) of derivatives | |
|---|---|---|---|---|
| $Y_1$ | $Y_2$ | $Y_3$ | s-TNB ($X = C–NO_2$) | s-Triazine ($X = N$) |
| H | H | H | 122 | 85 |
| $NH_2$ | H | H | 188 | 226 |
| $NH_2$ | $NH_2$ | H | 286 | 323 |
| $NH_2$ | $NH_2$ | $NH_2$ | 321[a]<br>330[b] | 354 |

[a] Initiation of endothermic change (this work) (see Fig. 1). [b] Value from ref. 5.

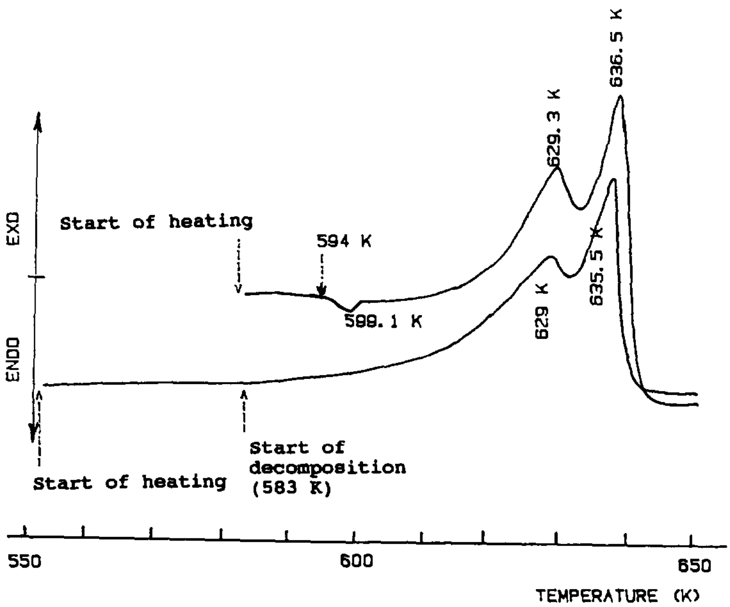


Fig. 1. DSC record of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) (taken from ref. 3).

structurally analogous 1,3,5-triazine derivatives. Some conclusions below concerning the physical thermostability of TATB are based on these values.

## Methods

The methods employed have been described in ref. 3 in the case of the TATB thermolysis using a Perkin-Elmer DSC-1B; this apparatus was calibrated for indium. During measurement, nitrogen was introduced into the furnace, the heating rate was 8 K $\mathrm{min}^{-1}$, the sensitivity was 8 $\mu$cal $\mathrm{s}^{-1}$, and the paper speed in the recorder was 20 mm $\mathrm{min}^{-1}$. TATB was diluted by a glass powder in the ratio 1:1 by weight. The weights of the resulting mixture were 2.2 and 2.5 mg. The corresponding DSC record is shown in Fig. 1.

Thermogravimetric measurements were carried out in a Perkin-Elmer TGA-7, the weighed amounts of samples being up to 10 mg, thermolysed in a nitrogen atmosphere. A linear temperature increase of 20°C $\mathrm{min}^{-1}$ was used; examples of the corresponding TGA curves are shown in Figs. 2–7.

## RESULTS AND DISCUSSION

The DSC curve in Fig. 1 shows that when the heating is started at 307°C (580 K), the endothermic change of TATB begins at 321°C (594 K), peaking at 326°C (599 K). However, if the heating program is started at 277°C (550 K), the beginning of the exothermic decomposition of TATB

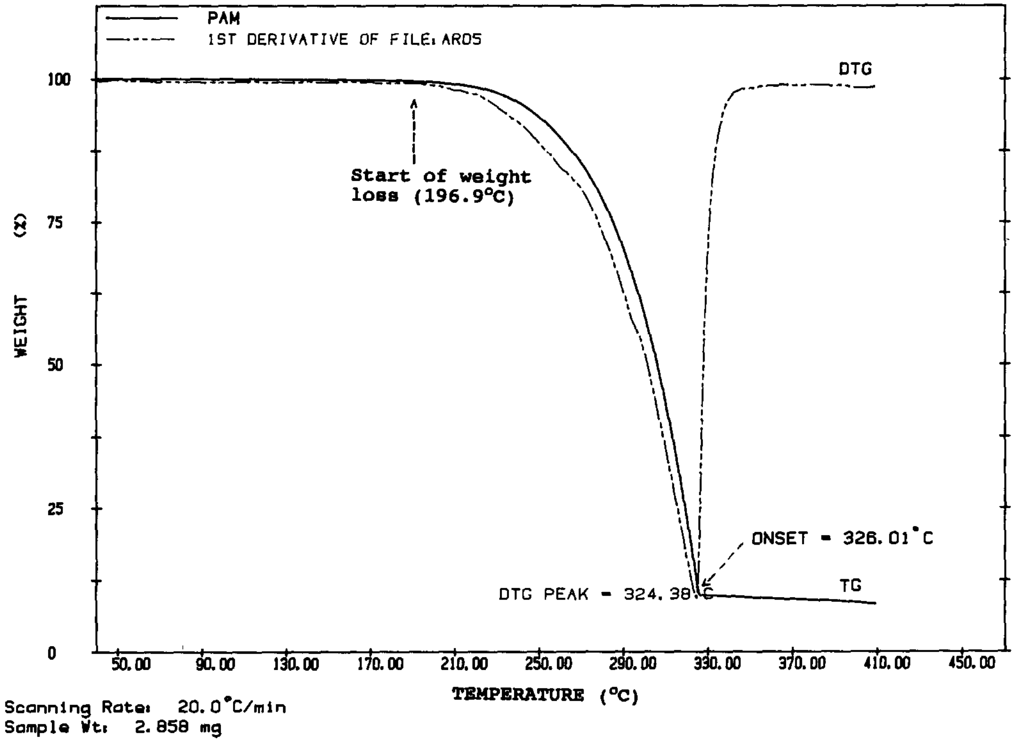


Fig. 2. TGA record of 1-amino-2,4,6-trinitrobenzene (PAM).

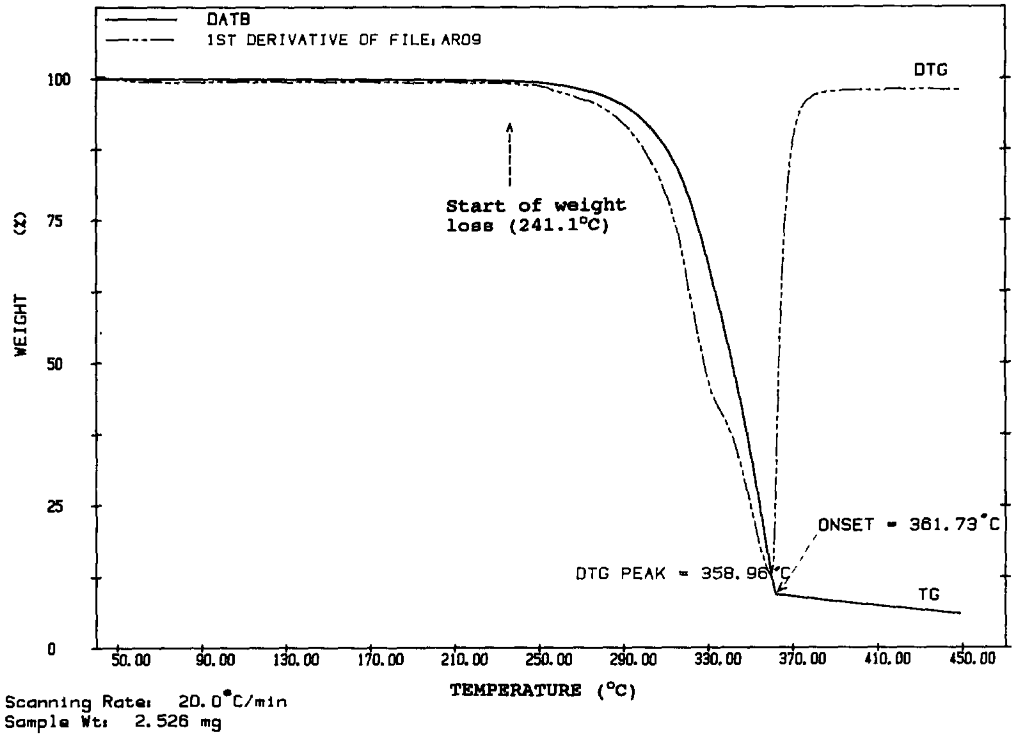
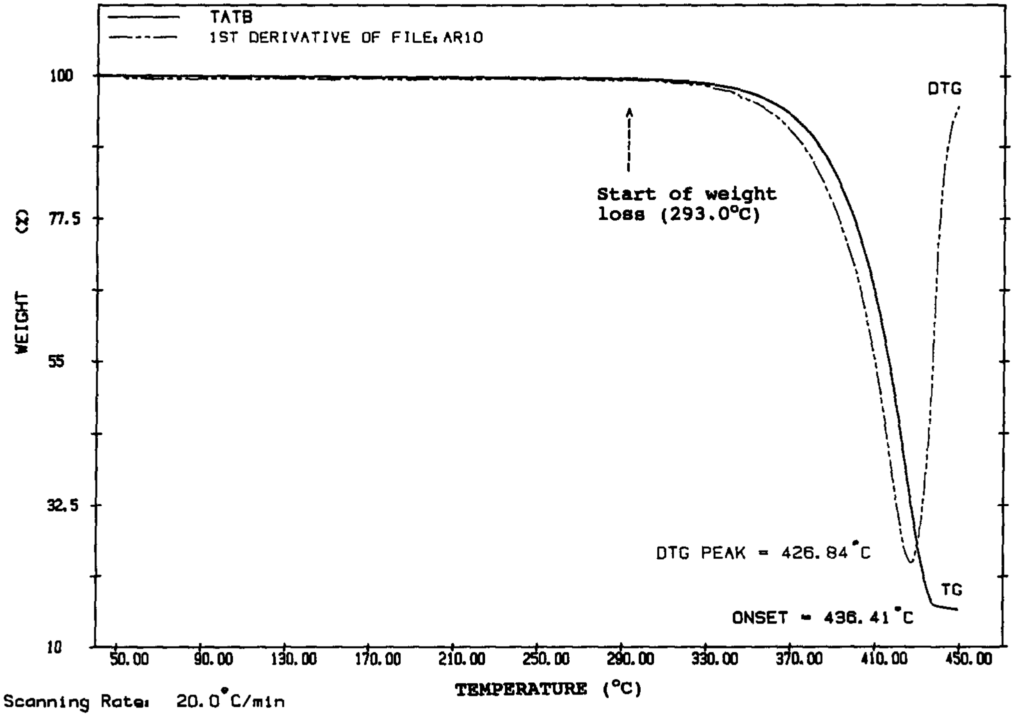
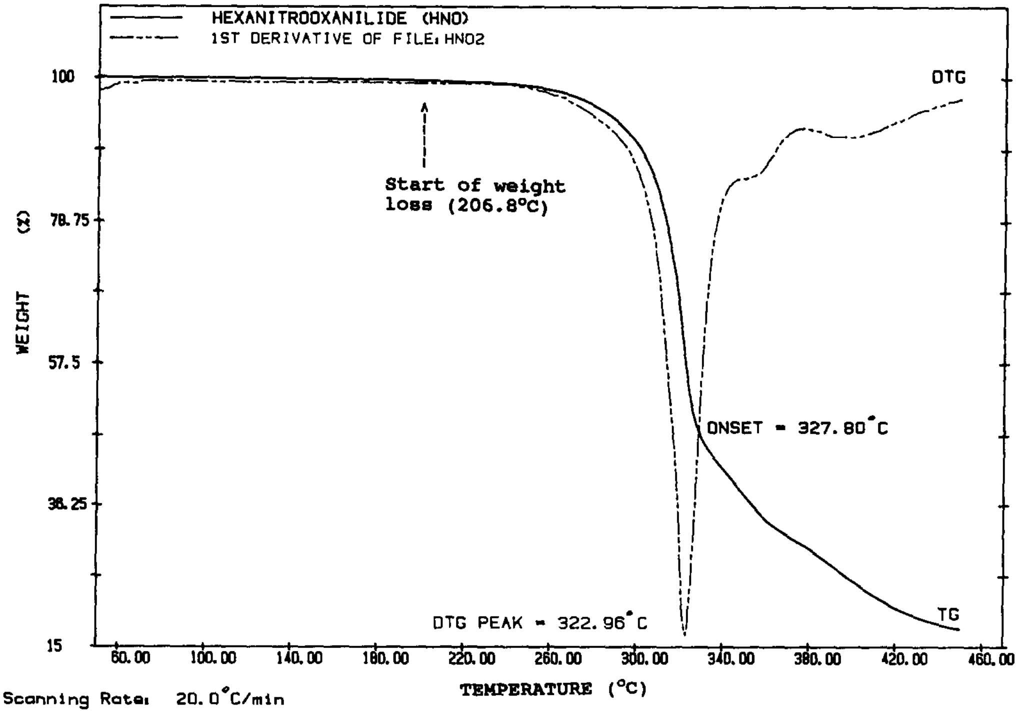


Fig. 3. TGA record of 1,3-diamino-2,4,6-trinitrobenzene (DATB).



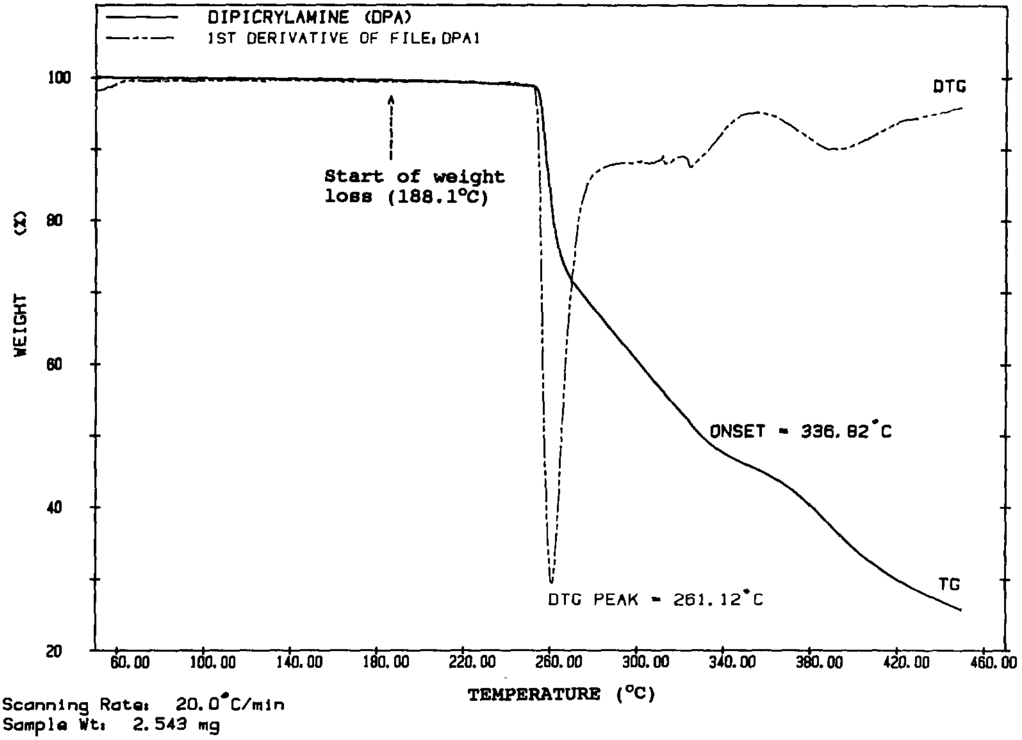
Scanning Rate: 20.0°C/min
Sample Wt: 2.791 mg

Fig. 4. TGA record of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB).



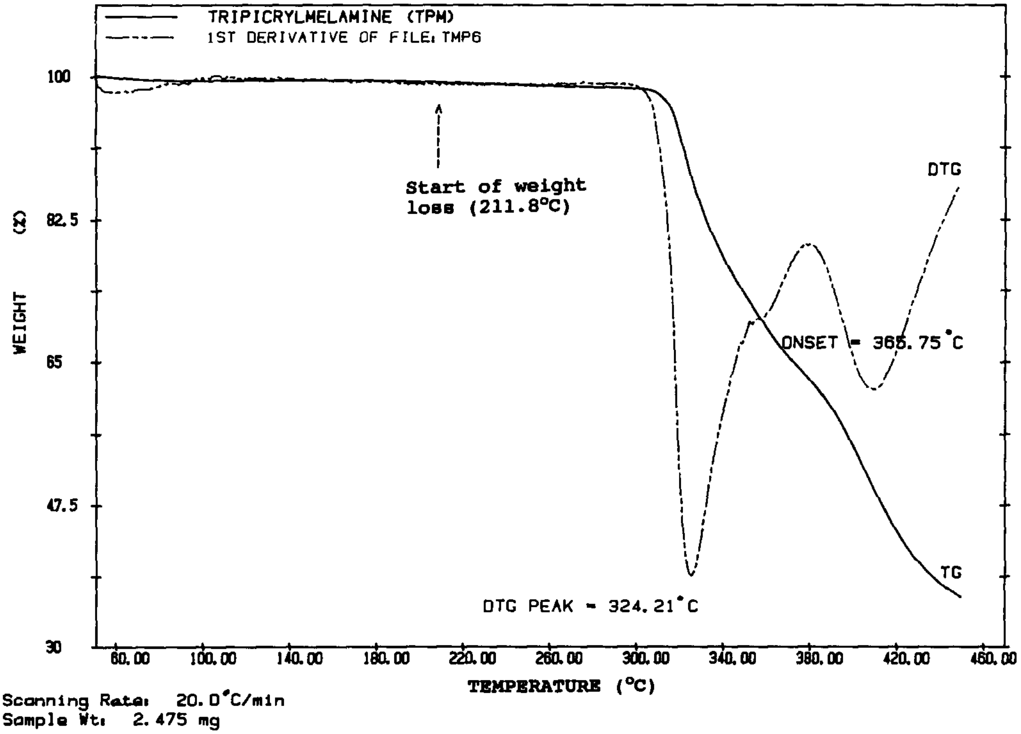
Scanning Rate: 20.0°C/min
Sample Wt: 2.307 mg

Fig. 5. TGA record of 2,2′,4,4′,6,6′-hexanitrooxanilide (HNO).



Scanning Rate: 20.0°C/min
Sample Wt: 2.543 mg

Fig. 6. TGA record of 2,2′4,4′6,6′-hexanitrodiphenylamine (DPA).



Scanning Rate: 20.0°C/min
Sample Wt: 2.475 mg

Fig. 7. TGA record of 2,4,6-tris(2,4,6-trinitrophenylamino)-1,3,5-triazine (TPM).

appears at about 310°C (583 K). The exothermic heat of this decomposition probably exceeds the endothermic effect observed in the former case.

It should be pointed out that Bell et al. [5] state that the melting point of TATB is at 330°C and that Vávra [23], using DTA, determined the endothermic peak of TATB to be at 327°C.

Comparing values of the melting points $Mp_{(ANB)}$ of s-TNB and its polyaminoderivatives with values of the melting points $Mp_{(AT)}$ of the structurally analogous 1,3,5-triazines (see also Table 2), a relationship of the form

$$Mp_{(ANB)} = \exp(4.4550 + 0.0037 Mp_{(AT)}) \qquad (1)$$

resulted, with a correlation coefficient $r = 0.9960$. Equation (1) demonstrates a good correlation of the TATB endothermic change with the trend in melting point values which corresponds to the introduction of aminogroups into the s-TNB molecule. This trend reflects the number and arrangement of the hydrogen bonds in the corresponding aminoderivatives [24–26]. The TATB molecules are bonded by strong hydrogen bonds into continuous gauzes [26].

The instability of the liquid phase at atmospheric pressure is a characteristic peculiarity of many rigid gauzes of TATB type. According to Ubbelohde [27], the proximity of the values for the heat of vaporization and for the formation of crystal lattice defects contribute to this phenomenon. Therefore, there is a high vapor pressure at around their melting points, even over the crystals.

The heat of vaporization of TATB may be characterized by its heat of sublimation [28] $\Delta H_s = 168.2$ kJ mol$^{-1}$ (for the temperature region 129.9–177.3°C). This is close to the activation energy value $E = 174.9$ kJ mol$^{-1}$ [9] (with $\log A = 11.6$) for TATB thermolysis in the temperature region 260–320°C, which was obtained by the SMM, i.e. by isothermal measurement under vacuum. However, a value of $E = 250.6$ kJ mol$^{-1}$ (with $\log A = 19.5$) was obtained from Rogers' isothermal DSC method [12], with the TATB thermolysis being measured under atmospheric pressure. These methods (SMM and DSC), although significantly different, give approximately the same results [29–31] (for DATB, see, for example, refs. 29 and 30).

Thus, it follows that differences in the values of the Arrhenius parameters for TATB thermolysis are connected with the above-mentioned endothermic change of this substance. The influence of this change could be increased by carrying out the TATB thermolysis under SMM conditions. It is essential to add here that the value $E = 174.9$ kJ mol$^{-1}$ correlates in the sense of the modified Evans–Polanyi–Semenov equation [29], with the $E$ values for thermolysis of the s-TNB derivatives in a liquid state, which have a hydrogen atom in the $\gamma$-position towards the nitro group, i.e. possessing the so-called trinitrotoluene mechanism of thermolysis. Rogers' value

$E = 250.6$ kJ/mol, however, correlates well in the same sense [29] with $E$ values for the thermolysis of symmetrically trisubstituted derivatives of s-TNB and also with the $E$ values of PAM and DATB thermolysis [29].

Figures 2–7 illustrate characteristic changes in the TGA records of the nitrocompounds being studied. These changes are largely in the positions of the peaks of the DTG curves (the DTG peaks) and in the positions of the onsets of the TG curves (TGA onsets). The initiation of the weight losses in Figs. 2–7 is designated as losses in the region of 0.48–0.54 wt.%. They correspond with the values for the initiation of thermolysis obtained by DTA applied to the thermostability study of the examined nitrocompounds (see, for example, refs. 3, 16, 17 and 32).

As was found in TGA studies of urea–formaldehyde polycondensates [33] and of commercial explosives [34], the positions of the characteristic changes in the TGA records of the individual nitrocompounds are influenced by the weight of the sample; this relationship is given by the general equation

$$P_i = A_i n + B_i \qquad (2)$$

where $P_i$ is a position of DTG peak ($P_{\text{peak}}$) or of TGA onset ($P_{\text{onset}}$) in °C and $n$ is the weight in mg. The coefficients of eqn. (2) for the individual substances being studied are given in Table 3.

In the TGA study of urea–formaldehyde polycondensates [33] and also in the present case, it is demonstrated that the $A_i$ coefficients of eqn. (2) are linked to the reactivity of the nitrocompounds. In this case the corresponding relationship is given by the general equation

$$A_i = a_i \ln k_t + b_i \qquad (3)$$

where $k_t$ is a rate constant of the thermolysis under SMM conditions at

TABLE 3

Coefficients of eqn. (3)

| Substance | | DTG peaks | | | TGA onsets | | |
|---|---|---|---|---|---|---|---|
| No. | Abbreviation | $A_p$ (°C mg$^{-1}$) | $B_p$ (°C) | Coefficient of correlation | $A_o$ (°C mg$^{-1}$) | $B_o$ (°C) | Coefficient of correlation |
| 1 | PAM | 34.10 | 226.76 | 0.9999 | 33.42 | 230.17 | 0.9998 |
| 2 | DATB | 35.76 | 268.73 | 0.9985 | 35.10 | 273.06 | 0.9999 |
| 3 | TATB | 21.51 | 361.37 | 0.9717 | 22.02 | 366.65 | 0.9744 |
| 4 | HNO | 7.84 | 306.10 | 0.9868 | 8.61 | 309.05 | 0.9906 |
| 5 | DPA | 3.78 | 250.85 | 0.8618 | 3.88 | 254.82 | 0.9990 |
| 6 | TPM | 1.68 | 319.59 | 0.9924 | 1.76 | 323.58 | 0.7838 |

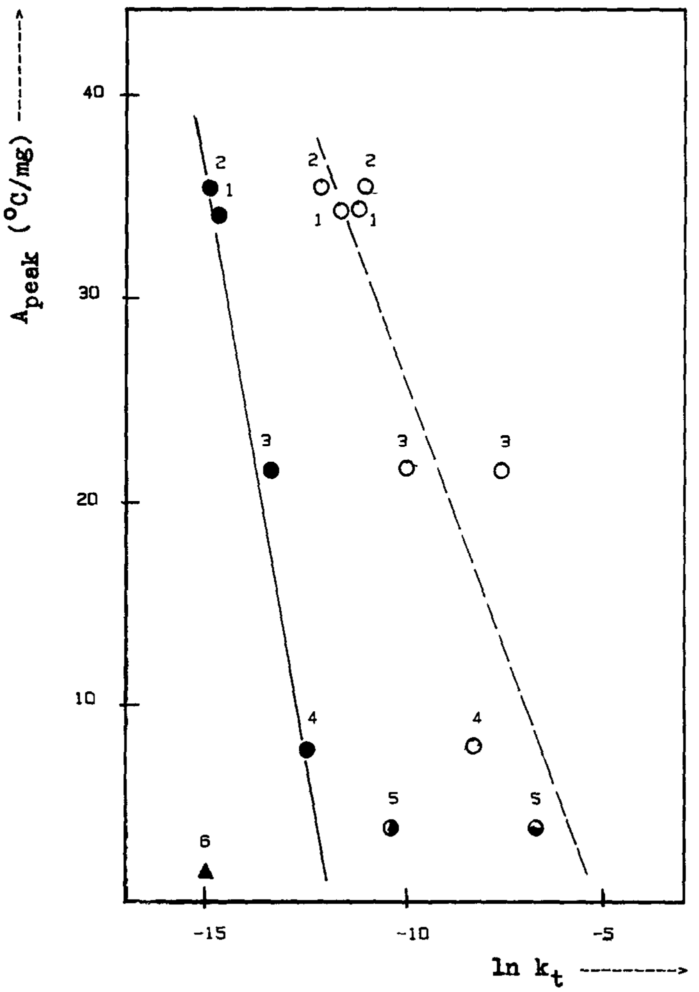


Fig. 8. Graphic representation of eqn. (3) for $A_{peak}$ values: —●—, thermolysis rate constants for 250°C ($k_{250}$); - - ○ - -, thermolysis rate constants for 300°C ($k_{300}$); ▲, value does not correlate; ◑, value does not correlate because it corresponds to the thermolysis at 200°C ($k_{200}$); ⊖, value calculated for 300°C by means of Arrhenius parameters of the DPA thermolysis derived in this paper.

250°C ($k_{250}$) or at 300°C ($k_{300}$). Figure 8 is a graphic representation of eqn. (3) for the data of the DTG peaks, i.e. for $A_{peak}$; a graphic representation of this equation for $A_{onset}$ is very similar. The data for TPM do not correlate in the sense of eqn. (3): its intermolecular interaction factors must be different from those of the other compounds being studied. The published value of $k_{200}$ for DPA thermolysis, the rate constant at 200°C [8] (see Table 1 and also Fig. 8), indicates that the corresponding values of $k_{250}$ and $k_{300}$ could be well correlated in the sense of eqn. (3). If these $k_{250}$ and $k_{300}$ values are computed by the above equation and also using the published $k_{200}$ value, the corresponding Arrhenius parameters $E = 153.3$ kJ mol$^{-1}$ and $\log A = 11$ can be obtained for DPA thermolysis in the temperature region 200–300°C; these parameters were not obtained experimentally.

Comparing all the $B_i$ values, i.e. $B_{peak}$ and $B_{onset}$, of eqn. (2) and the reciprocal values of the temperatures of the explosive points $T_{expo}$ (in °C), the relationship

$$\frac{10^3}{T_{expo}} = 0.0013B_i + 2.6416 \tag{4}$$

resulted, with a correlation coefficient $r = -0.8372$. A similar relationship has already been found for commercial explosives [34], although in this case it was only valid for $B_{onset}$ values. Equation (4) is not valid for the HNO data.

## CONCLUSION

Under certain experimental conditions, the DSC curve of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) can exhibit an endothermic change in the temperature region of 321–326°C. This is in agreement with the observations of other authors [5, 23]. This temperature region is believed to be the TATB melting point range. The endothermic change can cause a discrepancy in the kinetic parameters of the TATB thermolysis measured under vacuum [32] and under atmospheric pressure [12].

Similarly, as in the case of the TGA analysis of urea–formaldehyde polycondensates [33] and of commercial explosives [34], there is a linear dependence between the positions of the characteristic DTG peaks, or the positions of the TGA onsets, and the weight of the sample; this is also observed in non-isothermal thermogravimetric measurements of the aminoderivatives of 1,3,5-trinitrobenzene. There is a general relationship between the section values of the above-mentioned dependence and the temperatures of the explosive points of explosives. The slope of the dependence is closely related to the thermal reactivity [33, 34], with respect to the rate constants of the thermolysis of the studied nitrocompounds using the Soviet manometric method. By means of the latter relationship, the Arrhenius parameters $E = 153.3$ kJ mol$^{-1}$ and $\log A = 11$ can be determined for the non-autocatalyzed thermolysis of 2,2′,4,4′,6,6′-hexanitrodiphenylamine in the temperature region of 200–300°C.

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