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NON-ISOTHERMAL DIFFERENTIAL THERMAL ANALYSIS IN THE STUDY OF THE INITIAL STAGE OF THE THERMAL DECOMPOSITION OF POLYNITROAROMATIC COMPOUNDS IN THE CONDENSED STATE *

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ABSTRACT

The activation energies, E, of the decomposition of picramide and its N-methyl-, N-ethyl-, N-n-propyl- and N-n-butyl-derivatives are determined by means of non-isothermal DTA, in its simple form, as well as by the Piloyan method. A relationship is found between the E values of the above-mentioned compounds and the published values of the moments of inertia of the corresponding n-alkyl groups. Taking into account data published previously, which were obtained by application of the Piloyan method in the DTA of polynitroaromates, it is concluded that by suitable selection of DTA measurement conditions, it is possible to record the early part of the exothermal decomposition of the above-mentioned compounds where no autocatalytic influence exists. Attention is also paid to the thermostability of the polynitroaromates due to their contact with the construction materials employed in the course of thermolysis.

INTRODUCTION

Most of the kinetic data concerning the study of the thermal reactivity of organic polynitrocompounds has so far been obtained by means of the isothermal manometric method [1—4]. A similar application of DTA is relatively scarce and, in the past, the Kissinger method was employed [5—9].

Of more recent origin is the application of the Piloyan method in non-isothermal DTA for the determination of the activation energy, E [10] of the decomposition of polynitroaromatic compounds [11—15] and polynitrosoamines [16—18]. As evidenced in work published previously [11—16], the Piloyan method gives good results for measurements under atmospheric pressure providing that:

(a) the temperature difference is measured with such sensitivity and is recorded in such a way as to detect the primary thermolytic processes;

(b) in the region of the primary thermolytic processes there is no melting or dissolution in the decomposition products of those compounds which possess a marked stabilizing effect on the crystal lattice; and

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(c) in the region of the primary thermolytic processes there is no marked phase change "condensed phase—gas" in the compound being measured.

Taking these conditions into account, the E values were obtained which are relevant to both the purity [11,16—18] and molecular structure [11—15, 19] of the compound.

In refs. 12—15, the relationships of the $E\,T_D^{-1}$ term (where T_D is the initial exothermal decomposition temperature) were specified to Arrhenius E_M and $\log A$ parameters, which were obtained by Soviet authors from the study of the initial stage of the thermal decomposition of polynitroaromatic compounds by means of the manometric method. The relationships found are of the general form [12—15]

$$\frac{E}{T_D} = bE_M + a \qquad (1)$$

$$\frac{E}{T_D} = b_1 \log A + a_1 \qquad (2)$$

For N-substituted polynitroanilines, the relationship of the Piloyan energies, E, also with the characteristics of the molecular structure of the stated compounds was also studied [11,12,19]. These characteristics were represented by R_M functions of paper chromatography [20]. For N-mono-n-alkyl-polynitroanilines, it is possible to express the relationships in the form of a general equation [11,12,19]

$$\log E = b_2R_M + a_2 \qquad (3)$$

For N,N-di-n-alkyl-polynitroanilines these relationships have the general form [11,12,19]

$$\log(\log E) = b_3R_M + a_3 \qquad (4)$$

Taking into account the work reported in ref. 20, eqns. (3) and (4) can be re-written

$$\log E = b_4 \log N_c + a_4 \qquad (5)$$

$$\log(\log E) = b_5 \log(\log 2N_c) + a_5 \qquad (6)$$

where N_c is the number of carbon atoms in the n-alkyl group of the corresponding N-substituted polynitroaniline. For the stated compounds a relationship was found between the ET_D^{-1} term and the paper chromatographic R_M functions [12,19]; the said relationship has the general form

$$\log\left(\frac{E}{T_D}\right) = b_6R_M + a_6 \qquad (7)$$

A relationship was also found between the initial exothermal decomposition temperature, T_D, of N-substituted polynitroanilines and their paper chromatographic R_f factors [11,12,19]. Its general expression is

$$T_D = b_7R_f + a_7 \qquad (8)$$

It is necessary, however, to mention the fact that from the molecular structure point of view, the relationships of the type shown in eqn. (8) are more unambiguous than analogous relationships [20] existing between the melting points and the R_f factors of *N*-substituted polynitroanilines. The results of the type shown in eqn. (8) (from ref. 11) also led the authors of ref. 21 to the study of the relationship existing between the R_f factors of the polynitroaniline and polynitrophenol derivatives on the one hand, and peak temperatures of their exothermal decomposition, on the other.

Thermolysis of organic polynitrocompounds in the condensed phase is generally accompanied by autocatalysis. Therefore, attention has been directed in the present work to the determination of the influence of autocatalysis on the region of the start of the exothermic decomposition of the examined compounds. *N*-Mono-*n*-alkyl-picramides were selected as model compounds. Some remarks are also made on the influence of the construction material on the thermal stability of the thermolyzed compounds with which it is in contact.

Data contained in this paper, together with the data from refs. 11—15 and 19, served as one of the starting points in determining the relationship between the data obtained from non-isothermal DTA of polynitroaromatic compounds, on the one hand, and their detonation characteristics on the other [22].

EXPERIMENTAL

Apparatus

All measurements were carried out on a DTA apparatus [23]. The heating rate used was 6°C min^{-1}. Measurements were made in air under atmospheric pressure (in direct contact with the sample and the Al_2O_3 comparison standard).

Some of the measurements were carried out using Fe—Co thermocouples enclosed in Type 19112e No. 36-1 stainless steel injection needles produced by Chirana, Stará Turá, CSSR, and are labelled method A. Method B involved measurements using Fe—Co thermocouples enclosed in capillaries made of Sial glass.

An EZ-11 recorder (Laboratorní přístroje, Prague) was used for recording temperature differences. During the measurements, the recorder worked within a range of 0.5 mV over the whole scale, i.e. 0—355°C, and the paper speed was 20 mm min^{-1}. A more detailed description of the apparatus is contained in ref. 13.

Samples

Origin, method of purification and melting point determinations of the 2,4,6-trinitroaniline (picramide) and its *N*-methyl-, *N*-ethyl-, *N*-*n*-propyl- and *N*-*n*-butyl-derivatives are described in ref. 20.

Procedure

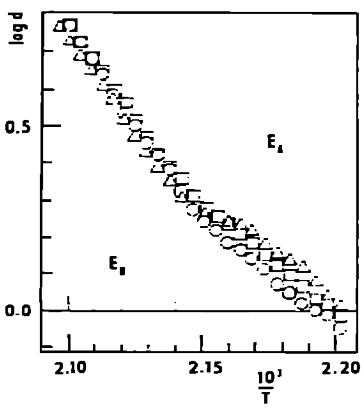
The conclusions reached in the present work were arrived at by considering the DTA measurements of pure picramide derivatives with sample weights of 80—150 mg. A more detailed description of the procedure is contained in ref. 13.

The results of the DTA measurements obtained by method A are average values of two measurements [11,12] and those for method B are average values of three measurements [12].

RESULTS AND DISCUSSION

Semi-logarithmic analysis of the initial part of the exotherm of *N*-ethylpicramide, within the limits of the Piloyan method [13], is represented graphically in Fig. 1. By carrying out this analysis in a broader temperature range, a divided linear dependence results: log $d - 10^3T^{-1}$, where d is the deviation in mm of the exotherm from the baseline. For *N*-monoalkylpicramides, measured by means of the DTA according to method A, three sections were thus specified in ref. 11: the corresponding E values were labelled E_A (i.e. immediately after the initial exothermal decomposition temperature, T_D), E_B and E_C. A survey of E_A and T_D values is given in Table 1. Table 2 contains data from DTA measurements according to method A: they are related to E_B and E_C values.

Zeman [11] used published values of the moments of inertia, I [24] to derive the corresponding molecular structure dependencies for methyl-, ethyl-, *n*-propyl- and *n*-butyl-groups in the corresponding *N*-monoalkylpicramides.



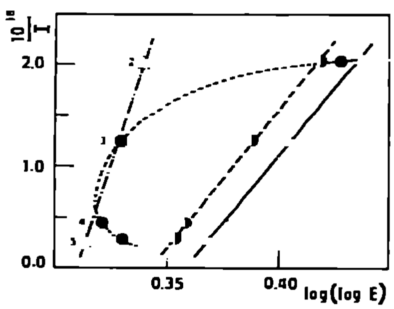


Fig. 1. Piloyan linearization of the initial part of the *N*-ethyl-picramide exotherm. Weight of sample: ○, 84.3 mg; □, 96.3 mg; △, 121.0 mg. (Substraction of temperature difference in length units; d in mm).

Fig. 2. Graphic representation of eqn. (9). DTA measurements according to method A: ○, E_A values; ◗, E_B values; ●, E_C values. DTA measurements according to method B: △, E_A values.

TABLE 1

Survey of T_D and E_A values

Substance no.	Picramide	Method A [11,12]			Method B [12,19],		
		T_D (K)	Temp. range (K)	E_A (kJ mole^{-1})	T_D (K)	Temp. range (K)	E_A (kJ mole^{-1})
1	Unsubstituted	514.6	516—524	291.48 ± 2.43	518.2	522—532	201.04 ± 11.23
2	*N*-Methyl-	499.2	503—511	553.06 ± 28.44	476.1	479—497	153.90 ± 12.06
3	*N*-Ethyl-	469.2	471—478	343.89 ± 14.11	468.1	470—478	136.61 ± 6.61
4	*N*-*n*-Propyl-	467.1	468—475	249.40 ± 25.45	458.8	460—478	120.83 ± 9.96
5	*N*-*n*-Butyl-	467.7	470—491	213.64 ± 5.61	453.4	455—471	114.04 ± 2.72

TABLE 2

Survey of E_B and E_C values (DTA measurements according to method A [11])

Substance no.	Picramide	Temp. range (K)	E_B (kJ mole^{-1})	Temp. range (K)	E_C (kJ mole^{-1})
1	Unsubstituted	525—543	132.55 ± 5.65	543—573	112.91 ± 6.19
2	*N*-Methyl-	513—519	418.42 ± 11.85	521—527	446.93 ± 13.39
3	*N*-Ethyl-	479—495	274.81 ± 3.77	497—507	137.20 ± 4.35
4	*N*-*n*-Propyl-	475—495	192.46 ± 3.81	499—517	125.60 ± 4.18
5	*N*-*n*-Butyl-	493—501	182.29 ± 7.91	503—521	137.66 ± 1.29

Using E_A and E_B values, on the one hand, and moments of inertia values, I, of alkyls on the other, a relationship of a more general shape was specified as being the most suitable [11]

$$I^{-1} = b_S \log(\log E) + a_S \qquad (9)$$

The same relationship also holds best for the E_A values resulting from DTA measurements using method B [12]. Figure 2 is a graphic representation of eqn. (9) which reveals that E_c values do not correlate with this equation.

Taking into consideration the dependencies represented in Figs. 1 and 2, it can be stated that the exotherm sections, to which the E_A or E_B values correspond, are immediately linked with the molecular structure. This means that the influence exercised by autocatalysis, in the same way as the influence exercised by the contact of thermolyzed compounds with the air atmosphere, will not make itself felt here. However, the E_c values do correspond to the fission processes exercising a marked influence of catalysis upon the kinetics of the decomposition.

The relationships represented in Figs. 1 and 2 bear evidence that under the experimental conditions used in the present work, it is possible to record the initial, most probably monomolecular, stage of polynitroaromatic thermolysis. The condensed phase would then occur in this stage through the influence brought about by the changed character of the molecular bonding hybridization due to intermolecular interactions; in disintegration of the solid phase, the negative influence of closely arranged molecules within the crystal will also contribute to the formation of an activated complex.

Due to the absence of autocatalysis in the initial stage of the thermolysis of picramide derivatives (generally, polynitroaromatic compounds), in the sense of the present work, the existence of relationships (1)—(8) can be accounted for. Similarly, as in ref. 4, it is possible to account for the relationship found between T_D values and those of the temperature limit T_{max} of the exploitation of polynitroaromatic compounds as secondary thermostabile explosives [25]. As follows from ref. 25, T_{max} values may be derived from the results of the kinetic measurements on the basis of the manometric method.

As seen from Table 1, the influences exerted by the construction materials with which the examined compounds are in contact during the thermolysis are linked with the kinetics of the fission processes. In the present case, it is the packing material of the thermocouples which may be of some influence. These problems were partially dealt with in refs. 4, 12—15 and 19, and in the present work it is illustrated in Fig. 2. In conclusion, the glass, acting as a destabilizer makes itself felt in those compounds which are liable to chemical interaction with a nucleophile (e.g. polychlorotrinitrobenzenes or nucleophilic attack in the methyl group of polymethyltrinitrobenzenes and others); it also manifests itself in those compounds which possess a most pronounced stabilizing influence on the crystal lattice [4]. In substances exhibiting strong intra- and intermolecular hydrogen bonds within the molecule, such as polyaminotrinitrobenzenes [14], the contact of the compound with the glass increases its stability: the introduction of one substituent into the amine nitrogen in the compounds of the above-mentioned category, however, causes a decrease in the thermal stability in the derivative (as compared with stainless steel).

As far as the type of glass is concerned, no practical differences were observed between separate measurements: capillaries of both Simax and Rasotherm glass were used in each case. Somewhat different values, however, resulted from DTA measurements when Sial glass was employed: for picramide with Rasotherm glass, average values of $T_D = 520.8$ K and $E_A = 225.82$ kJ mole^{-1} resulted [12,14], but for the same compound when Sial glass was employed, the values given in Table 1 were obtained.

CONCLUSIONS

By the application of non-isothermal DTA in its simple form to the study of the thermolysis of polynitroaromatic compounds, registration of that part of the exothermic decomposition can be achieved if suitable conditions are selected, wherein no autocatalysis has yet made itself felt and where no influence of the contact between the compound being measured with the air atmosphere is manifested.

In measurements of this kind, it is possible to make use of the Piloyan method determining activation energies, E, of the decomposition. This method can be applied not only to thermolysis in the solid phase, but also to the decomposition of the liquid phase of the compounds mentioned above.

The resulting E values, as well as those of the initial exothermal decomposition temperature (T_D), are dependent not only upon the molecular structure but also upon the construction material with which the thermolyzed compound is in contact. The dependence of the mentioned values upon construction materials is one of the factors rendering the interpretation of the DTA results difficult from the point of view of reaction kinetics. In combination with a suitable method for the study of reaction kinetics or if combined with a suitable method of structural analysis, it is possible, however, to obtain a satisfactory interpretation of DTA results both from the point of view of reaction kinetics and molecular structure.

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