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

PART IV. 1,3,5-TRINITROBENZENE, 2,2',4,4',6,6'-HEXANITROBIPHENYL,
2,2',2'',4,4'',6,6'',6''-NONANITRO-m-TERPHENYL,
1,4,5,8-TETRANITRONAPHTHALENE AND 2,4,6-TRIPICRYL-1,3,5-TRIAZINE

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The Piloyan activation energies $E$ of decomposition and the initial temperatures $T_e$ of the exotherms of hexanitrobiphenyl (HNB), nonanitro-m-terphenyl (NONA), tripicryl-s-triazine (TPT) and 1,4,5,8-tetranitronaphthalene (TENN) have been determined by means of non-isothermal DTA. Due to its volatility in the zone of the beginning of thermal decomposition only $T_e$ values are specified for s-trinitrobenzene (TNB). From the values of $E \cdot T_e^{-1}$ for HNB and from the derived values of $E \cdot T_e^{-1}$ for TNB on the one hand, and from the published values of the Arrhenius parameters obtained by means of the manometric method on the other, relationships have been derived. The relationship between $E \cdot T_e^{-1}$ and the standard activation entrophy is considered relevant.

This section of the paper deals with 1,3,5-trinitrobenzene (TNB), 2,2',4,4',6,6'-hexanitrobiphenyl (HNB), 2,2',2'',4,4'',6,6'',6''-nonanitro-m-terphenyl (NONA) and 1,4,5,8-tetranitronaphthalene (TENN) as "unsubstituted" polynitroaromatic compounds. 2,4,6-Trimipicryl-1,3,5-triazine (TPT) has also been included in this category, its supporting skeleton being of a heteroaromatic character.

With the use of the isothermal manometric method, kinetic data have been determined for the thermal decompositions of liquid TNB [1-4] and liquid HNB [1,3]. Analogous data on NONA, TENN and TPT have not been found in the literature so far. Determination of the Piloyan activation energies of HNB, NONA and TENN forms a part of papers [5, 6] and determination of these energies of TNB and TPT is presented in paper [6]. Application of the Piloyan method in the thermolysis of HNB and other substance with two picryl groups in the molecule forms a part of paper [7] too.

Experimental

Materials

TNB was obtained from the technical product by means of multiple crystallization from acetone and, in the last stage, from an acetone - methanol mixture. Its m.p. was 395.1 - 396.1 K.

The HNB used was of the same quality as in paper [7].

NONA was synthesized by the earlier described method [8]; it was purified by multiple crystallization from a large volume of a methyl ethyl ketone - ethanol mixture. No traces of melting were found up to 643.1 K.
TENN was prepared by nitrating 1,4,5-trinitronaphthalene using a H$_2$SO$_4$–HNO$_3$ mixture. The product, which was crystallized several times from nitrobenzene and finally from a dimethylsulfoxide – acetone mixture, exhibited a polymorphic transition at 542.9 (initial [9])–549.7 K peak of polymorphic transition; the beginning of sublimation with decomposition was recorded at 581.1 K (by means of DSC) [5].

TPT was prepared by the previously described method [10]. It was purified by double crystallization from an acetone – ethanol mixture. From the TPT adduct with acetone (about 8 per cent acetone) obtained in this way, acetone was removed by vacuum drying at 70 to 80°C. The initial temperature of fusion (by means of DTA) was 621.5 K [6, 9], with decomposition.

The purities of the compounds were checked by thin-layer chromatography against Silufol UV 254, with acetone – cyclohexane in varying ratios as the mobile phase.

Methods

The DTA apparatus and conditions of measurements were described in the first part [11] of this paper. Measurements using thermocouples in a stainless injection needle [5, 6, 9, 11] are denoted as Method A, and measurements by means of thermocouples in a glass capillary [6, 9, 11] as Method B. Simax or Rasotherm glass was employed to make test tubes for samples and capillaries for thermocouples.

Results and discussion

A survey of the obtained Piloyan activation energies $E$ and initial temperatures $T_D$ of exothermic decomposition is given in Table 1, together with the Arrhenius parameters $E_M$ and log $A$, which were derived for TNB and HNB by Andreev [1] and Maksimov and co-workers [2–4].

The influence of the weight of the sample upon the $E$ and $T_D$ values is ambiguous in this category of compounds. In the application of DTA measurements by method A there is a slight decrease of the $T_D$ and $E$ values for HNB with decreasing weight; measurements by method B, however, exhibit an opposite trend of the values for HNB.

With the decrease in the weighed amounts of NONA and of TENN there is a slight increase in the $T_D$ values, regardless of the type of measurement method employed; moreover, for TENN there is a marked increase of the $E$ values. A decrease of the $T_D$ values and an increase of the $E$ values with decreasing sample weight can be observed for TPT.

When DTA method B is applied TNB and HNB exhibit higher thermal stabilities than those found by method A. In these two compounds there is thermal decomposition in the liquid state during measurement. For NONA and TENN, whose thermal decompositions occur in the solid state, the opposite is the case;