

DOI: 10.17516/1998-2836-0281

УДК 541.127:547.861

Thermal Decomposition Kinetics of 2-R-2,2-dinitroethyl 2,4,6-trinitrobenzoates

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Received 14.11.2021, received in revised form 21.02.2022, accepted 07.04.2022

Abstract. The manometric and photoelectrocolorimetric methods as well as IR spectroscopy and chromatomass spectrometry were used to study the kinetics of thermal decomposition of 2-substituted gem-dinitroethyl 2,4,6-trinitrobenzoates. The mechanism of the limiting stage of the process was established. The activation parameters of the limiting stage are determined; this stage is the break of the C-NO₂ bond in the gem-dinitro group. The correlation between the reactivity (logarithms of rate constants, activation energies) and steric constants of the substituent R in the alcohol component of the ester was established.

Keywords: kinetics, thermal decomposition, gem-dinitroethanol, trinitrobenzoic acid, mechanism, activation parameters, steric constants of substituent, correlation.

Citation: Kruglyakova, L.A., Pekhotin, K.V. and Golubtsova, O.A. Thermal decomposition kinetics of 2-R-2,2-dinitroethyl 2,4,6-trinitrobenzoates. *J. Sib. Fed. Univ. Chem.*, 2022, 15(2), 170–175. DOI: 10.17516/1998-2836-0281

Кинетика термораспада сложных эфиров 2-R-2,2-динитроэтанола и 2,4,6-тринитробензойной кислоты

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Аннотация. Манометрическим и фотоэлектроколориметрическим методами с использованием ИК-спектроскопии и хромато-масс-спектрометрии изучена кинетика и установлен механизм термического разложения 2-замещенных гем-динитроэтиловых эфиров 2,4,6-тринитробензойной кислоты. Определены активационные параметры лимитирующей стадии процесса, которой является разрыв связи C-NO₂ в гем-динитрогруппе. Установлена корреляционная зависимость между реакционной способностью (логарифмами констант скорости, энергиями активации) и стерическими константами заместителя R в спиртовой составляющей сложного эфира.

Ключевые слова: кинетика, термическое разложение, гем-динитроэтанол, тринитробензойная кислота, механизм, активационные параметры, стерические константы заместителя, корреляция.

Цитирование: Круглякова, Л. А. Кинетика термораспада сложных эфиров 2-R-2,2-динитроэтанола и 2,4,6-тринитробензойной кислоты / Л. А. Круглякова, К. В. Пехотин, О. А. Голубцова // Журн. Сиб. федер. ун-та. Химия, 2022, 15(2). С. 170–175. DOI: 10.17516/1998-2836-0281

Introduction

The derivatives of polynitro alcohols (acetals, ethers and esters) are energetic compounds and may be of interest as promising plasticizers of the polymer base of mixed solid rocket fuels, as well as components of explosive compositions for various purposes [1–7]. The negative inductive effect of nitro groups in polynitro alcohols leads to a change in their reactivity compared to unsubstituted alcohols, due to a decrease in the basicity of polynitroalcohols and nucleophilicity on oxygen atom of the hydroxyl group [1, 6]. This complicates the further synthesis of acetals from them, as well as esters of aliphatic and aromatic acids containing volumetric substituents [1]. Information on the kinetics and mechanism of thermal decomposition of polynitroalcohol ethers in the literature is very limited. At the same time, it was previously shown that the thermal decomposition of 2-nitroethanol esters of various aliphatic acids proceeds through a quasi-heterolytic mechanism with the formation of the corresponding acid and nitroethylene [8]. The reaction rate increases with a decrease in pK_a of the acid. However, this increase is not as large as can be expected from the values of pK_a for a known reason – poor conductivity of induction and steric effect by the carboxyl group. The introduction of the second nitro group into the alcohol component changes the reaction mechanism, in which the limiting stage is already homolytic breaking of the C-NO₂ bond. In this regard, it is interesting to identify the relationship of the reactivity of esters in the reaction of thermal decomposition with the nature of the substituent R in the alcohol component. This will make it possible to predict the targeted synthesis of

compounds of this class with the specified parameters for chemical stability and guarantee their safe production, processing and operation.

We studied the thermal decomposition kinetics of the reaction series of the general formula



where R = F (I), CH₃ (II), CH₂N(NO₂) CH₃ (III), NO₂ (IV), Cl (V), CH₂C(NO₂)₂CH₃ (VI), Br (VII).

Experimental Part

Compounds (I)-(VII) were synthesized and purified by means of known methods [1]. For investigation the chromatographically pure compounds were taken, contained the basic substance about 99,4–99,6 %.

Thermal decomposition kinetics was studied by manometric method using a glass manometer of Bourdon type [8] at residual pressure in the reaction volume 10⁻²–10⁻¹ mm of mercury. Photoelectrocolorimetric method was moreover used to determine the rate of accumulation of nitrogen dioxide during the reaction.

Gaseous products of thermal decomposition were analyzed on a mass spectrometer in a special gas cell made of KBr on the IR spectrometer UR-10. Condensed decomposition products identified on the MX-1312 effusion chromatomass spectrometer (squalane capillary column temperature 60–80 °C, effusion chamber temperature 105 °C, detector temperature 100 °C, injector temperature 130–150 °C).

The rate constants of thermal decomposition were calculated by the Guggenheim method. The error in determining of the activation energy did not exceed 3.5 kJ·mol⁻¹, and for the pre-exponential factor – 0.23 log units.

Experimental Results and Discussion

The study of thermal decomposition kinetics of compounds (I)-(VII) was carried out in a solution of 1,3-dinitrobenzene (DNB), and compounds (II) and (V) also in the melt. It was found that in the melt and solution thermal decomposition of the studied compounds was described by the first-order rate equation up to conversion of 45–50 %. The rate constant in the melt is not affected by the ratio of the substance mass to the volume of the reaction vessel ($m/V = 10^{-4}$ – 10^{-2} g·cm⁻³) and the ratio of the reaction vessel surface to its volume ($S/V = 0,8$ – $4,2$ cm⁻¹). Those observations evidenced about homogeneity of the reaction not only in volume, but also on the walls of the reaction vessel. Furthermore, the addition of gaseous products formed during thermal decomposition in the melt at a conversion degree of 15 and 25 % to the initial substance does not affect the thermal decomposition rate of compounds (II) and (V).

Experiments on thermal decomposition in the solution of DNB showed that the substance concentration in the solution in the range of 2–6 wt.% does not affect the decomposition rate constant of compounds (I)–(VII). Therefore, the dependence of the rate constant on temperature we studied in 2–3 % solutions of DNB.

The parameters of the Arrhenius equation are given in the table 1.

Analysis of the table data shows that the nature of the substituent R strongly affects the rate constants and the activation parameters of the thermal decomposition. Thus, during the transition

Table 1. Activation parameters of thermal decomposition of compounds (I–VII)

№	Substituent R	ΔT , °C	Decomposition conditions	$k_{160\text{ }^\circ\text{C}}$, s ⁻¹	E_a , kJ·mol ⁻¹	lg A	$DS_{160\text{ }^\circ\text{C}}^*$, J·mol ⁻¹ ·K ⁻¹	E_s *
I	F	185–223	solution	$6,62 \cdot 10^{-8}$	186,7	15,34	37,3	1,56
II	CH ₃	170–220	solution melt **	$7,02 \cdot 10^{-7}$ $1,44 \cdot 10^{-6}$	180,6 179,5	15,63 15,81	42,8 46,3	0
III	CH ₃ N(NO ₂)CH ₂	170–220	solution	$2,08 \cdot 10^{-6}$	174,2	15,33	37,1	-0,58
IV	NO ₂	160–180	solution	$2,67 \cdot 10^{-5}$	165,1	15,34	37,3	-2,14
V	Cl	150–170	solution melt***	$1,07 \cdot 10^{-4}$ $1,57 \cdot 10^{-4}$	161,0 160,3	15,45 15,53	39,4 40,9	-2,81
VI	CH ₃ C(NO ₂) ₂ CH ₂	150–170	solution	$1,59 \cdot 10^{-4}$	158,9	15,36	37,6	-3,22
VII	Br	140–160	solution	$2,24 \cdot 10^{-4}$	157,6	15,36	37,7	-3,44

Notes: * – the steric constants E_s are taken from the work [9], ** – on accumulation of NO₂ during decomposition.

from compound (I) to compound (VII), the decomposition rate constant in the solution increases by more than three orders of magnitude, and the activation energy decreases by about 30 kJ·mol⁻¹. The reason for this is seen in the increasing in the volume of α -substituent R in the 2,2-dinitroethyl fragment of the ester. A similar picture was observed earlier in the case of thermal decomposition of geminal dinitro alkanes in the gas phase [10] и polyfunctional geminal dinitro compounds in inert solvents [4, 9].

The found regularities of changes in reactivity due to the spatial interaction of the substituent R with the reaction center – carbon atom in the geminal dinitro group in compounds (I)–(VII). They are presented in fig. 1 and 2.

It can be seen from figures 1 and 2 that the points of compounds (I)–(VII) fit well into straight lines, which are described, respectively, by the following regression equations:

$$\lg k_{160\text{ }^\circ\text{C}} = - (0,722 \pm 0,011) E_s - (6,100 \pm 0,026) \quad (1)$$

$$r=0,999; S_y=0,128; n=7$$

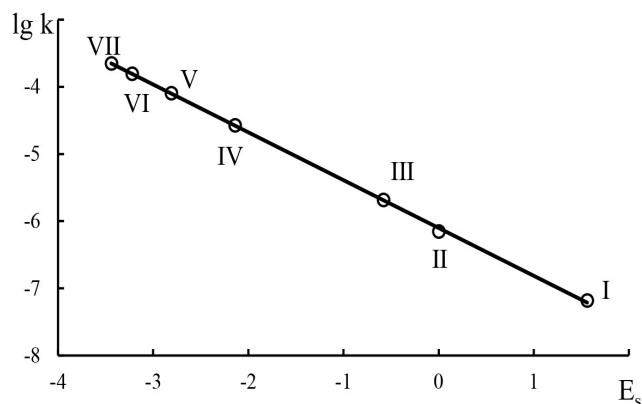


Fig. 1. Dependence $\lg k_{160\text{ }^\circ\text{C}} = f(E_s)$ for compounds (I)–(VII). The point numbers correspond to the compound numbers in the table

$$E_a = (6,04 \pm 0,25) E_s + (178,34 \pm 0,57) \quad (2)$$

$$r=0,995; S_y=2,62; n=7$$

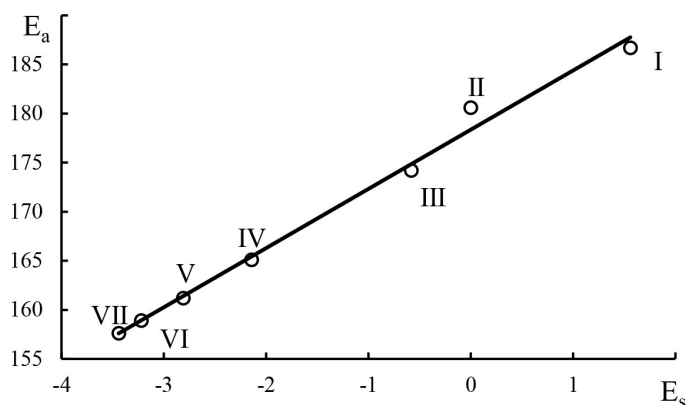
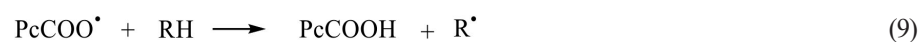
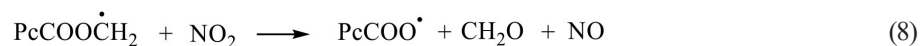
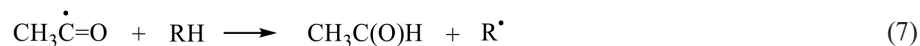
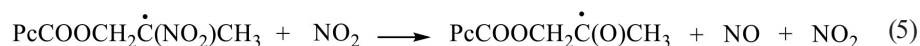
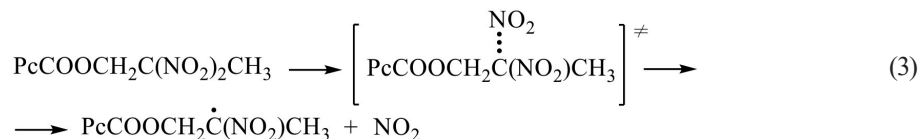
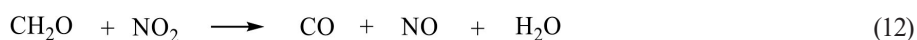


Fig. 2. Dependence $E_a = f(E_s)$ for compounds (I)–(VII).

The qualitative composition of gaseous thermal decomposition products of compounds (II), (V) at a conversion degree of 20–30 % was as follows: NO, CO₂, CO, H₂O, N₂O, N₂, HCN (traces). In the condensed residue at a conversion degree of compounds (II) of 5–7 % at 170 °C, ester of 2,4,6-trinitrobenzoic acid and 2-ketopropanol was identified. In addition, at a conversion degree of 20–25 % of compounds (V) at 170 °C, the formation of 2,4,6-trinitrobenzoic acid, 2,4,6-trinitrobenzene was recorded, as well as some other products that could not be identified.

Photoelectrocolorimetric study of the kinetics of nitrogen dioxide accumulation during thermal decomposition of compounds (II), (V) showed that it coincides with that for manometric measurements for total gas release ~ up to 35–38 % transformation, which in combination with the found condensed and gaseous decomposition products of the compound (II) allows to present a kinetic scheme of the thermal decomposition of the latter:





where Pc – 2,4,6-trinitro-C₆H₂.

The limiting stage of thermal decomposition here is a reaction (3) involving a homolytic break in the C-NO₂ bond in the geminal dinitro group. Within the framework of the mechanism (3)–(12), the found regularities of the influence of the nature of the substituent R in compounds (I)–(VII) on the rate constant, Arrhenius parameters and activation entropy are logically explained. Correlation equations (1)–(2) are of scientific and practical interest for predicting of chemical stability in the synthesis of 1-R-1,1-dinitro ethanol esters of aromatic or heterocyclic acids.

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