DOI: 10.17516/1998-2836-0157

УДК 547.792:541.127

Kinetics and Mechanism of Thermal Decomposition of 1-R-Substituted bis(1,1-Dinitromethyl-3-Nitro-1,2,4-Triazole-5-yl)

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Received 15.05.2019, received in revised form 01.07.2019, accepted 10.10.2019

Abstract. Thermal decomposition kinetics of 1-substituted bis(1,1-dinitromethyl-3-Nitro-1,2,4-triazole-5-yl) in solution of 1,3-dinitrobenzene is studied with manometric method under isothermal conditions. The limiting stage of thermal decomposition is homolytic break of C-NO_2 bond in gem-dinitromethyl group; activation parameters of this stage are calculated. The reactivity of investigated compounds is analyzed. Correlation dependences between logarithm of rate constant, activation energy and steric constant of substituent R are obtained.

Keywords: kinetics, thermal decomposition, bis(1-R-1,1-dinitromethyl-3-nitro-1,2,4-triazole-5-yl), activation parameters, steric constants, correlation.

Citation: Kruglyakova L.A., Stepanov R.S., Pekhotin K.V., Golubtsova O.A. Kinetics and mechanism of thermal decomposition of 1-R-substituted bis(1,1-dinitromethyl-3-Nitro-1,2,4-triazole-5-yl), J. Sib. Fed. Univ. Chem., 2020, 13(1), 25-30. DOI: 10.17516/1998-2836-0157

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Кинетика и механизм термического разложения 1-R-замещенного бис(1,1-динитрометил-3-нитро-1,2,4-триазол-5-ила)

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Аннотация. Манометрическим методом в изотермических условиях изучена кинетика термического разложения 1-R-замещенных бис(1,1-динитрометил-3-нитро-1,2,4-триазол-5-ила) в растворе 1,3-динитробензола. Определена лимитирующая стадия распада – гомолитический разрыв связи C-NO_2 в гем-динитрометильной группе, для которой найдены активационные параметры. Проведен анализ реакционной способности изученных соединений и получены корреляционные зависимости между логарифмом константы скорости, энергией активации и стерической константой заместителя R.

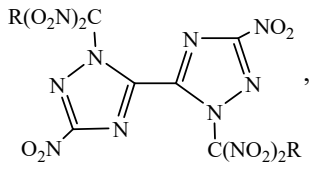
Ключевые слова: кинетика, термическое разложение, бис(1-R-1,1-динитрометил-3-нитро-1,2,4-триазол-5-ил), активационные параметры, стерические константы, корреляция.

Цитирование: Круглякова, Л.А. Кинетика и механизм термического разложения 1-R-замещенного бис(1,1-динитрометил-3-нитро-1,2,4-триазол-5-ила) / Л.А. Круглякова, Р.С. Степанов, К.В. Пехотин, О.А. Голубцова // Журн. Сиб. федер. ун-та. Химия, 2020. 13(1). С. 25-30. DOI: 10.17516/1998-2836-0157

Introduction

In recent years polynitrocompounds on the basis of 1,2,3- and 1,2,4-triazoles, 1,2,3,4-tetrazoles are the subject of numerous studies [1-5] because they are of interest as explosives and components of gunpowders and rocket fuel [3-5]. The practical use of these substances requires knowledge of a complex of properties including thermal stability. Thermal decomposition of nitro derivatives of azoles described in works [6-8], in which the mechanism of decomposition and the dependence between structure and reactivity are established. At the same time, information about the thermal stability of compounds with two triazole cycles in the literature are very limited.

In continuation of the works [6-8] on the influence of substituent nature on the azole′s decomposition rate we for the first time investigated derivatives of bis(1-R-1,1-dinitromethyl-3-nitro-1,2,4-triazole-5-yl)



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where R = CH_3 (I), $CH_2N(NO_2)CH_3$ (II), CH_2CN (III), NO_2 (IV), Cl (V), Br (VI), I (VII).

Experimental Part

Compounds (I-VII) were synthesized and purified by known methods [5, 9], were chromatographically pure and contained not less than 99.5% basic substance.

Thermal decomposition kinetics was studied by manometric method in vacuum using a glass manometer of Bourdon type [6] as well as by photoelectrocolorimetric method on accumulation of nitrogen dioxide [10] during decomposition.

Thermal decomposition rate constants were calculated by the Guggenheim method [11]. The rate constants definition error did not exceed 7%. An r.m.s. deviation for calculation of activation energy was 4,3 kJ·mol^{-1}, and for logarithm of pre-exponential factor 0.11 unit of logarithm.

Experimental Results and Discussion

The study showed that the thermal decomposition of compounds (I-VII) in a solution of 1,3-dinitrobenzene (DNB) described by the equation of first order reaction up to the transformation degree 45-50%. Decomposition rate constants are not affected by the concentration of a substance in a solution within 1-5% (mass). With this in mind, the effect of temperature on the rate constant was studied in 2-2,5% solutions.

Kinetic and thermodynamic parameters of thermal decomposition are shown in Table. Here also substituent′s steric constants E_s are presented, taken from the work of [12].

Analysis of the data in the table shows that with increasing of absolute value of steric constants E_s of substituents R in *gem*-dinitromethyl group the decomposition rate constants reduced for three orders of magnitude. At the same time decrease in value of activation energy from 160,5 to 135,3 kJ·mol^{-1} take place, at practically constant logarithm of pre-exponential factor, equal, on average, 15,66 unit of logarithm. The entropies of activation for investigated compounds (I-VII) are positive.

Similar regularities were observed earlier in thermal decomposition of 1-substituted 3-nitro-1,1-dinitromethyl-1,2,4-triazole, 1,1-dinitromethyl-2-methyl-1,2,3-triazole derivatives, and

Table. Thermal decomposition activation parameters, steric constants of substituents and activation entropies of compounds (I-VII) in 2-2,5% solutions of dinitrobenzene

№	Substituent R	Δ*T*, °C	E_a, kJ·mol^{-1}	lg *A*	$k_{160°C}$, s^{-1}	$\Delta S^{\neq}_{160°C}$, kJ·mol^{-1}·K^{-1}	E_s
I	CH_3	140-180	160,5	15,94	$3{,}81\cdot10^{-4}$	48,7	0
II	$CH_2N(NO_2)CH_3$	140-180	157,3	15,89	$8{,}26\cdot10^{-4}$	47,8	-0,58
III	CH_2CN	140-180	154,2	15,55	$8{,}93\cdot10^{-4}$	41,3	-0,76
IV	NO_2 NO_2*	120-160 120-140	146,5 148,3	15,72 15,88	$1{,}12\cdot10^{-2}$ $9{,}83\cdot10^{-3}$	44,5 47,6	-2,14
V	Cl	110-150	141,0	15,55	$3{,}49\cdot10^{-2}$	41,3	-2,81
VI	Br	110–140	136,1	15,49	$1{,}18\cdot10^{-1}$	40,1	-3,44
VII	I	100–140	135,3	15,48	$1{,}45\cdot10^{-1}$	39,9	-3,62

Note: * – on accumulation of NO_2.

5-dinitromethyl-2-methyl-1,2,3,4-tetrazole [6-8], which limiting thermal decomposition stage includes a homolytic reaction breaking of C-NO_2 bond in geminal dinitromethyl fragment. Obviously, the same mechanism is implemented in thermal decomposition of studied compounds (I-VII). Proof of this are the data obtained during the study of the thermal decomposition kinetics of compound (IV) using photoelectrocolorimetric method for accumulation of nitrogen dioxide. Nitrogen dioxide is a primary product formed during the decomposition. As can be seen from the table, the activation parameters for the compound (IV) found on the accumulation of nitrogen dioxide, are close to that of manometric measurements (the difference does not exceed definition error).

In addition, quantitative description of the reactivity of the studied compounds depending on the nature of substituent also accords well with this mechanism. So, it follows from Fig. 1-2, that thermal decomposition rate constants of substituted bis(1-R-1,1-dinitromethyl-3-nitro-1,2,4-triazole-5-yl), as well as activation energies correlate well with steric constants of substituents.

Found dependencies can be described by regression equations:

$$\lg k_{160^\circ C} = -(0{,}737\pm0{,}017)E_s - (3{,}509\pm0{,}039), \quad (1)$$

$$r = 0{,}998;\ S_y = 0{,}145;\ n = 7,$$

$$E_a = (6{,}99\pm0{,}19)E_s + (160{,}60\pm0{,}44), \quad (2)$$

$$r = 0{,}997;\ S_y = 1{,}65;\ n = 7.$$

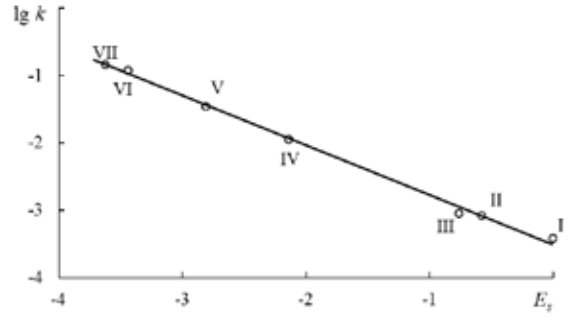

Fig. 1. Dependence lg $k_{160\,^\circ C}$ = f (E_s)

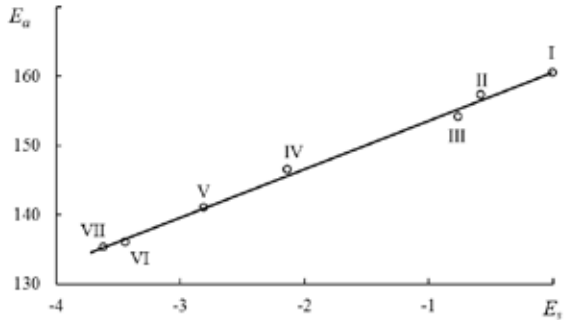

Fig. 2. Dependence E_a = f (E_s)

Equations (1) and (2) can be used for purposeful synthesis of bicyclic derivatives of 1,1-dinitromethyl-1,2,4-triazole with preset parameters on chemical stability.

Conclusion

Thermal decomposition of 1-substituted bis(1,1-dinitromethyl-3-nitro-1,2,4-triazole-5-yl) in a solution of 1,3-dinitrobenzene flows through first-order reactions with primary break of C-NO_2 bond in geminal dinitromethyl fragment. The activation parameters are found for limiting stage. The correlation dependences between the logarithm of the rate constants, activation energies and substituent′s steric constants are obtained, allowing for a preliminary assessment of the thermal stability of the unexplored compounds of this row.

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