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LETTERS TO THE EDITOR

Thermolysis of 1-R_1,R_2-Nitromethyl-3-R-1,2,4-triazoles

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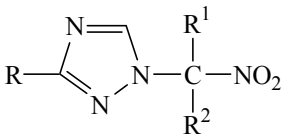
In this work thermolysis kinetics of compounds **I–V** was studied aiming to elucidate influence of additive substituents R_1 and R_2 on the rate and mechanism of decomposition reaction.



R = NO_2, R^1 = R^2 = Br (**I**); R = NO_2, R^1 = Cl, R^2 = Br (**II**); R = NO_2, R^1 = R^2 = Cl (**III**); R = NO_2, R^1 = F, R^2 = Cl (**IV**); R = Cl, R^1 = F, R^2 = H (**V**).

Compounds **I–V** were synthesized and purified by the known methods [1, 2]. The main substance content was no less than 99%. Kinetics were examined by manometric method in accordance with procedure [3].

The thermolysis of compounds **II** and **III** in the melt proceeds till conversion of 40-45% as the first order reaction. The thermolysis of compound **IV** occurs with a small acceleration (the ratio between maximal and initial rate is 2.0). Ratios between substance mass and reaction vessel volume (m/V = 2–24×10^{-4} g cm^{-3}) and between the vessel surface and its volume (S/V = 3.2–4.6 cm^{-1}) do not affect the reaction rate constant suggesting that this reaction is homogeneous. Additives to starting material of gaseous reaction products (P_0 = 106–172 mm Hg), forming during the reaction progress at 8–10% conversion, do not affect the reaction rate constant. This indicates that autocatalysis is absent in the thermolysis of compounds **II–IV** in the melt. The decomposition of compounds **I–IV** in solution and compound **V** in the gas phase to 45–50% conversion is described by equation of the first order reaction. The substance concentration in solution (1–5 wt %) and the dielectric constant of the solvent (6.4–20.6) have no effect on the rate constant. In the gas phase the ratio S/V was no more than 0.55 cm^{-1}.

The kinetic parameters of thermolysis are presented in the table. The solution concentration was 2 wt %. The measurements were performed for solutions in

Kinetic parameters of thermolysis of compounds **I–V**

Comp. no.	Conditions	ΔT, °C	$-\log k_{200°C}$	E_a, kJ mol^{-1}	$\log A$	$-\Sigma E_s$ [a]
I	Solution in DNB	120–150	0.751	147.9	15.58	6.88
	Solution in DBP	120–150	0.865	147.4	15.41	
II	Melt	140–160	1.369	153.5	15.58	6.25
	Solution in DBP	130–160	1.529	153.5	15.42	
III	Melt	145–165	1.932	156.7	15.37	5.62
	Solution in DBP	130–165	2.139	157.3	15.23	
IV	Melt	200–240	4.641	178.7	15.09	1.25
	Solution in DBP	200–240	4.735	180.0	15.14	
V	Gas[b]	250–300	7.545	203.1	14.88	–2.80

[a] ΣE_s is the sum of steric constants of substituents R_1 and R_2 from [4]; [b] S/V = 0.50–0.55 cm^{-1}.

dinitrobenzene (DNB) or dibutylphthalate (DBP), for melts and gas phase.

Analyzing the table data, we state that on passing from compounds **I** to **V** the rate constant decreases by ~7 orders of magnitude. This is mainly connected with the increase in the activation energy by 55.7 kJ mol^{-1}. Thus, mainly the enthalpy component contributes into the reactivity of compounds **I**–**V**. Similar regularities were observed earlier for geminal trinitromethylazoles [5] where the homolytic protocol of decomposing through initial C–NO_2 bond was established. It is presumable that this protocol is realized also at the thermolysis of compounds **I**–**V**. It is possible to consider the order of influence of additive polyfunctional substituents in correlation Eq. (1) and the order of activation energy increase in Eq. (2) as confirmation of this mechanism.

$$\log k_{200^\circ C} = -(0.667\pm0.019)\Sigma E_s - (5.658\pm0.099), \quad r\ 0.998;\ S_y\ 0.323;\ n\ 5, \qquad (1)$$

$$E_a = (5.57\pm0.14)\Sigma E_s + (187.43\pm0.70), \quad r\ 0.999;\ S_y\ 2.301;\ n\ 5. \qquad (2)$$

Negative value of constant δ (–0.667) in Eq. (1) indicates the steric assistance in the thermolysis process.

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