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LETTERS TO THE EDITOR

Thermal Decomposition of 1-R^1-5-R^2-3-Azido-1,2,4-triazoles

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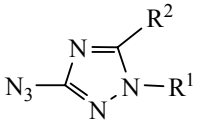
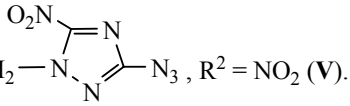
Extending the earlier works [1, 2] on the effect of the nature of the functional substituents on the rate of thermal decomposition of azido-1,2,4-triazoles, a series of 1,5-disubstituted 3-azido-1,2,4-triazoles was studied (Scheme 1).

Compounds **I–V** were synthesized via the known procedures [3]. The kinetics of thermal decomposition was studied by manometric method using glass Bourdon tube pressure gauge [4] in 2% dibutylphthalate solution and (for selected compounds) in melt [2]. The rate constant was not affected by the m/V ratio (m being the specimen mass and V being the volume of the reaction vessel) as well as by the S/V ratio (S being the surface of the reaction vessel), indicating homogeneous mechanism of decomposition. The thermal decomposition in melt and in solution could be described by the first-order reaction rate

Scheme 1.



$R^1 = CH_2CH_2ONO_2$, $R^2 = NO_2$ (**I**); $R^1 = CH_2CH_2N_3$, $R^2 = NO_2$ (**II**); $R^1 = CH_2N(NO_2)CH_3$, $R^2 = NH_2$ (**III**);



$R^1 = CH_3$, $R^3 = N_3$ (**IV**); $R^1 = CH_2N(NO_2)CH_2$, N_3, $R^2 = NO_2$ (**V**).

Activation parameters of thermal decomposition of compounds **I–V** in melt and in dibutylphthalate solution

Comp. no.	ΔT, °C	$k_{160°C} \times 10^4$, s^{-1}	E_a, kJ/mol	log A	$\Delta S^{\neq}_{160°C}$, J mol^{-1} K^{-1}
			Melt		
I	120–160	3.68	145.2	14.08	13.1
II	120–160	5.15	149.8	14.78	26.5
III	140–175	2.59	145.8	14.00	11.6
			2 wt % Solution		
I	130–170	2.53	147.3	14.17	14.9
II	120–160	2.85	144.8	13.92	10.1
III	140–175	2.28	147.1	14.10	13.6
IV	120–170	3.59	147.7	14.37	18.7
V	130–170	2.69	140.2	14.34	18.1

equation up to 45–50% conversion. Concentration of the compound in the solution (1–5 wt %) did not affect the rate constant.

The major gaseous product of thermal decomposition of compounds **I–V** was molecular nitrogen (98–99.6%, GC analysis), suggesting that homolytic reaction of the N^1–N^2 bond rupture in the azido group was the rate-limiting step of thermal decomposition.

Activation parameters of thermal decomposition are represented in the table. From the data it followed that variation of the activation energy of the decomposition in melt (4.7 kJ/mol in the series of compounds **I–III**) and that of the decomposition in the dibutylphthalate solution (7.5 kJ/mol in the series of compounds **I–V**) was somewhat higher than the experimental error (4.1–4.2 kJ/mol).

To conclude, the electron-withdrawing functional substituents in the triazole ring had a slight effect on its reactivity in the reaction of thermal decomposition. The triazole ring itself did not lead to the change of the reaction center in the studied temperature range (for example, in the case of compounds **I–III** that could enter the alternative decomposition reactions).

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