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Kinetics and Mechanism of Thermal Decomposition of Some 1-R-3-Azido-1,2,4-triazoles

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Abstract—The mechanism and kinetics of the thermal decomposition of substituted 3-azido-1,2,4-tri-azoles in the melt and in a solution of dibutyl phthalate or 1,3-dinitrobenzene were studied.

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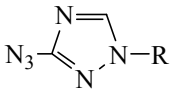
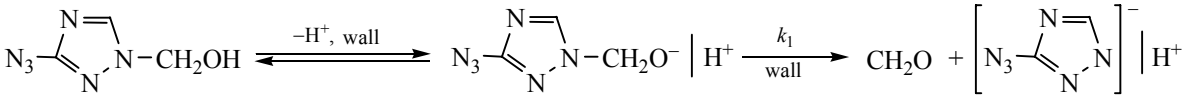
The substituted azidotriazoles are of interest in two aspects. Firstly, they are energy rich components of the solid rocket fuels [1]. Secondly, they can be used as the intermediates in the synthesis of energetic materials.

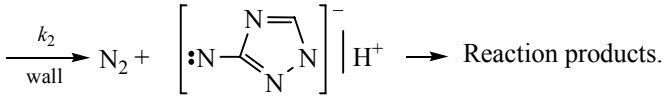
We studied some of the 1-substituted 3-azido-1,2,4-triazoles.



R = H (**I**), CH_2OH (**II**), CH_2CH_2OH (**III**), $CH_2CH_2ONO_2$ (**IV**), $CH_2N(NO_2)CH_3$ (**V**).

Compounds **I**–**V** were obtained and purified by known methods [2]. They were chromatographically pure and contained at least 99.1% of the main substance. The kinetics of the thermal decomposition was studied in the melt and in a 2 wt % dibutyl phthalate or 1,3-dinitrobenzene solution by a static manometric method using a glass Bourdon type pressure gauge [3] as a zero instrument. The concentration of a substance in a solution (1–10 wt %) and the dielectric constant of the solvent had no effect on the rate constant of the thermal decomposition. Up to a conversion of 40–45% the reaction is described by the first order equation. Compounds **I**–**III** at the decomposition in the melt have almost equal activation energy, but the rate constants of the decay of compounds **II** and **III** are twice larger than that of compound **I**. The molecules of **I**–**III** contain labile hydrogen atoms, and their decomposition in the melt is complicated by the ionization on the reaction vessel walls, which can be represented by the following scheme.





A

$k_1/k_2 \sim 2$.

Kinetic parameters of the thermal decomposition of compounds **I–V**

Comp. no.	Reaction conditions	ΔT, °C	$k_{160°C}\times10^5$, s^{-1}	E_a, kJ mol^{-1}	log A	$\Delta S^{\neq}_{160°C}$, J mol^{-1} K^{-1}
II	Melt	130–170	48.8	139.3	13.49	1.8
	Solution in dibutyl phthalate	130–170	21.5	159.4	15.56	41.5
II	Melt	130–150	89.0	140.2	13.86	8.9
III	Melt	130–170	90.1	138.5	13.66	5.1
	Solution in 1,3-dinitrobenzene	130–175	20.8	157.3	15.29	36.3
IV	Melt	130–170	29.5	145.0	13.96	10.8
	Solution in 1,3-dinitrobenzene	130–160	23.0	156.5	14.81	27.1
V	Melt	130–170	24.0	155.2	15.10	32.7
	Solution in dibutyl phthalate	140–170	20.7	154.2	14.92	29.2

The ion pair **A** stabilizes nitrene better than the unionized azole **I** molecule. In a solution of dibutyl phthalate and 1,3-dinitrobenzene, where ionization of compounds **I–III** is absent, the rate of the homolytic thermal decomposition on the N^1–N^2 bond is 2 times lower and does not depend on the nature of the substituent in the position *1* in the triazole ring (see the table).

Finally, we note that for compounds containing the labile hydrogen **I–III** their interaction with the glass wall of the reaction vessel should be taken into account, where the ionization is observed. Therefore, the kinetic parameters E_a and log A in the melt would be lower than in a solution.

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