SHORT COMMUNICATIONS

Thermal Decomposition of 1-Dinitromethyl-3-nitro-1,2,4-triazole Derivatives in Solution

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In continuation of our previous studies [1, 2] on the relations between the structure and the rate of thermal decomposition of polynitro compounds, we examined a series of 1-dinitromethyl-3-nitro-1H-1,2,4-triazole derivatives **I**–**V**.

I–V
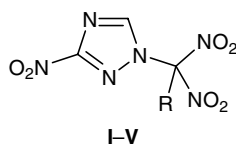
I, R = Me; **II**, R = NO$_2$; **III**, R = Cl; **IV**, R = Br; **V**, R = I.

Compounds **I**–**V** were synthesized and purified by known methods [3]; they contained no less than 99% of the main substance (according to chromatographic data). The kinetics of their thermal decomposition were studied by the manometric technique [2] in dibutyl phthalate. The rate constants of their thermal decomposition do not depend on the concentration in solution in the range 1–5 wt %. The reactions follow the first-order kinetics up to a conversion of 40–50%. The activation parameters of the thermal decomposition of compounds **I**–**V** in dibutyl phthalate (2 wt %) are given below.

Comp. no.	**I**	**II**	**III**	**IV**	**V**
ΔT, °C	140–180	100–140	110–150	110–150	100–140
$k_{100°C} \times 10^5$, s^{-1}	0.02	1.1	3.9	9.4	18.0
E_a, kJ/mol	156	143	133	133	131
$\log A$	15.1	15.1	14.2	14.7	14.6
E_s,[a] kJ/mol	0	–2.14	–2.81	–3.44	–3.62

[a] E_s is the substituent steric constant [4].

It follows from these data that the rate constant of thermal decomposition increases by three order of magnitude in going from compound **I** to **V** and that the energy of activation decreases by more than 20 kJ/mol. An analogous pattern was observed in the decomposition of 5-dinitromethyl-2-methyltetrazole [2], for which homolytic mechanism with initial cleavage of the C–NO$_2$ bond was proved. Presumably, the thermal decomposition of compounds **I**–**V** follows a similar mechanism. This assumption is confirmed by the existence of correlations (1) and (2).

$$\log k_{100°C} = -(6.69 \pm 0.05) - (0.80 \pm 0.02)E_s; \quad (1)$$
$$r = 0.999,\ s_y = 0.051,\ n = 5.$$

$$E_a = (156.05 \pm 2.18) + (6.98 \pm 0.80)E_s; \quad (2)$$
$$r = 0.975,\ s_y = 1.05,\ n = 5.$$

The negative value of δ (–0.80) in equation (1) indicates that steric effect of substituents favors the process. Low values of the energy of activation suggest intermediacy of a semirigid activated complex [5].

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