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SHORT COMMUNICATIONS

Effect of the Structure of 2,2,2-Trinitroethyl-*N*-nitroamines on the Rate of Their Thermal Decomposition

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Despite obvious advances, the theory of the reactivity of high-energy compounds, which could allow prediction of their thermal stability, is far from completion [1]. Specifically, this concerns polyfunctional nitro compounds having several reaction centers, for their mutual influence hinders determination of the mechanism of thermal decomposition [2, 3].

The present communication reports on the results of studying thermal decomposition of 2,2,2-trinitroethyl-*N*-nitroamines $RN(NO_2)CH_2C(NO_2)_3$, where R = Me (**I**), Et (**II**), Pr (**III**), CH_2CH_2OH (**IV**), $CH_2CH_2ONO_2$ (**V**), CH_2CH_2CN (**VI**), CH_2COOMe (**VII**), $CH_2C(NO_2)_2CH_3$ (**VIII**), and $CH_2C(NO_2)_3$ (**IX**). Compounds **IX** were synthesized and purified by known methods [4]. The kinetics of their thermal decomposition were studied by the manometric method [1] in *m*-dinitrobenzene ($\varepsilon = 20.6$), 1,3,5-trinitrobenzene ($\varepsilon = 7.21$), and dibutyl phthalate ($\varepsilon = 6.44$). The thermal decomposition of compounds **I**–**IX** followed the first-order kinetics up to a conversion of 40–45%. The kinetic and thermodynamic parameters of the process are given in table. The solvent polarity and substrate concentration (in the range from 2 to 10 wt %) did not affect the rate constant of decomposition, indicating that the process follows a radical mechanism. Theoretically, two radical pathways are possible for decomposition of *N*-nitroamines **I**–**IX**, with initial dissociation of the $C-NO_2$ or $N-NO_2$ bond [1]. According to the data of [2, 3], the decomposition pathway involving cleavage of the $C-NO_2$ is preferable for compounds containing both secondary nitroamino and trintromethyl groups. As might be expected, taking into account the same spatial environment of the trinitromethyl group, the rate of thermal decomposition is described by the Taft equation:

$$\log k_{150°C} = -(4.25 \pm 0.02) + (0.54 \pm 0.02)\sigma^*;$$

$$r = 0.996, \quad s = 0.034, \quad n = 9.$$

The relatively small value of a slope of the above dependence may be due to the radical nature of the process and remoteness of substituents from the reaction center.

Kinetic and thermodynamic parameters of thermal decomposition of 2,2,2-trinitroethyl-*N*-nitroamines **I**–**IX** in *m*-dinitrobenzene ($c = 5\%$)

Comp. no.	Temperature, °C	$k \times 10^5$, s^{-1}	E_a, kJ/mol	$\log A$	$\Delta S^{\neq}$, J × mol^{-1} K^{-1}
I	130–165	5.1	169	16.5	60
II	140–165	5.2	167	16.2	56
III	145–165	5.2	164	16.0	50
IV	135–165	7.3	161	15.8	45
V	145–165	8.7	166	16.4	58
VI	140–160	10.0	164	16.2	54
VII	145–165	14.1	160	15.9	48
VIII	140–160	23.4	156	15.6	43
IX	130–150	52.3	154	15.7	45

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