Russian Journal of General Chemistry, Vol. 72, No. 8, 2002, pp. 1256–1258. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 8, 2002, pp. 1338–1340.
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Kinetics and Mechanism of Liquid-Phase Thermal Decomposition of β-Cyanoethyl-*N*-nitramines

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Received November 8, 2000

Abstract—Termal decomposition of β-cyanoethyl-*N*-nitramine in melt is preceded by protonation of the amino nitrogen atom and is accompanied by evolution of nitrogen(I) oxide with formation of acrylonitrile. Thermal decomposition of bis(β-cyanoethyl)-*N*-nitramine under similar conditions follows a radical mechanism with initial dissociation of the N–N bond. The same mechanism is operative in thermal decomposition of both *N*-nitramines in a dilute dibutyl phthalate solution.

Gas-phase thermal decomposition of primary and secondary *N*-nitramines follows a common radical mechanism involving initial homolytic dissociation of the N–N bond [1, 2]. It is not quite clear whether the same mechanism is general for decomposition of primary and secondary *N*-nitramines in condensed phase. This may be due to various factors which determine the reactivity of *N*-nitramines on heating in condensed phase.

Using β-cyanoethyl-*N*-nitramine (**I**) and bis-(β-cyanoethyl)-*N*-nitramine (**II**) as examples, in the present work we studied the kinetic relations and product structure in the thermal decomposition of primary and secondary *N*-nitramines in melt and in solution in a weakly polar (ε = 6.46) inert aprotic solvent, dibutyl phthalate, with the goal of elucidating the reaction mechanism. Depending on the nitramine structure, their decomposition in melt followed different patterns. The decomposition of nitramine **I** occurred to a conversion of 30–40% and was of the first order. The transformation of compound **II** was characterized by acceleration, and the kinetic curves were S-shaped. We examined the effects of degree of filling of the reaction vessel (*m*/*V*) and of the ratio of the surface of the vessel to its volume (*S*/*V*) on the rate of decomposition. Variation of the *m*/*V* ratio from 1.1×10^{-4} to 1.2×10^{-3} g/cm^3 almost did not affect the rate of decomposition of compound **I**, while the initial rate of gas evolution in the decomposition of compound **II** slightly decreased as the *m*/*V* ratio rose (Fig. 1). Change of the *S*/*V* ratio by a factor of 2–3 had almost no effect on the rate of decomposition of compounds **I** and **II**. These findings indicate that decomposition of *N*-nitramines is not accompanied by heterogeneous processes on the walls of the vessel and is homogeneous.

The decomposition products of compound **I** were nitrogen(I) oxide, molecular nitrogen, traces of carbon dioxide, water, acrylonitrile, and acrylic acid. *N*-Nitramine **II** gave rise mainly to nitrogen(IV) oxide, nitrogen(II) oxide, nitrogen(I) oxide, molecular nitrogen, water, acrylic acid, and acrylonitrile. Some products were not identified. The major gaseous product formed from compound **I** was nitrogen(I) oxide, while decomposition of **II** gives mainly nitrogen(IV) oxide. Study of the kinetics of thermal decomposition of nitramine **I** following the accumulation of nitrogen(I) oxide and of nitramine **II** following the accumulation of nitrogen(IV) oxide showed that the reaction mechanism does not change relative to manometric measurements. The kinetic parameters are summarized in Table 1.

Presumably, the observed acceleration of decomposition of *N*-nitramine **II** is the result of reaction of decomposition products with the substrate. In order to verify this assumption we studied the effect of gaseous and condensed decomposition products on the kinetics of the process (Fig. 2). The results showed

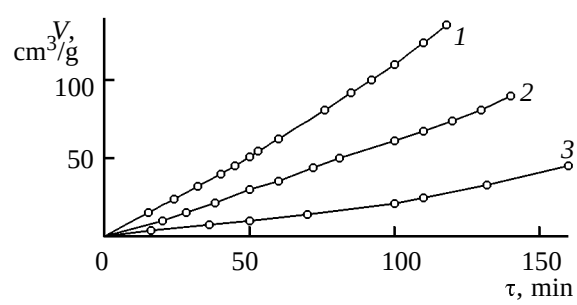

Fig. 1. Effect of the *m*/*V* ratio on the thermal decomposition of bis(β-cyanoethyl)-*N*-nitramine (**II**) at 215°C: (*1*) 1.9×10^{-4}, (*2*) 1.0×10^{-3}, (*3*) 1.2×10^{-2} g/cm^3.

Table 1. Kinetic parameters of thermal decomposition of nitramines **I** and **II** (k and $\Delta S^{\neq}$ at 200°C)

Comp. no.	Conditions	Temperature, °C	$k \times 10^5$, s^{-1}	E_a, kJ/mol	$\log A$	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
I	Melt	140–180	781.3[a]	119.9	11.13	–44.0
	Melt (by N_2O)	140–180	802.6[a]	120.7	11.23	–42.1
	0.3% Solution	200–240	0.65	171.5	13.75	6.2
II	Melt	200–250	1.10	169.6	13.75	6.2
	Melt (by NO_2)	200–230	1.24	170.8	13.95	10.0
	5% Solution	210–250	0.68	172.9	13.92	9.4

[a] Calculated from the activation parameters.

that gaseous products formed at various degrees of conversion either do not affect the kinetic parameters at all or slightly (by a factor of 1.15–1.20) reduce the rate of decomposition. Addition of nitrogen(IV) oxide insignificantly (by a factor of 1.2–1.3) decreases the rate of decomposition of nitramine **II**. Addition of the condensed residue (20–25 wt %) obtained by complete decomposition of **II** to a new portion of the substrate changed of the reaction kinetics, and the initial decomposition rate increased by a factor of ~20. Addition of 5–7 wt % of acrylic acid also sharply accelerated decomposition of **II** (Fig. 2). These data indicate that the decomposition of nitramine **II** is catalyzed by acid condensed products formed during the reaction.

As in melt, thermal decompositions of nitramines **I** and **II** in dibutyl phthalate solution followed different kinetic patterns. Compound **I** decomposed with acceleration, whereas the decomposition of **II** followed first-order kinetics. The specific rate of decomposition of **I** depended on its concentration in solution (Table 2). The concentration of **II** did not affect the rate constant of its decomposition. The activation parameters of thermal decomposition for both nitramines are collected in Table 1. Primarily, we should emphasize the lower activation parameters and greater specific rate of decomposition of compound **I** in melt, as compared to **II**; on the other hand, the Arrhenius parameters for 0.3% solutions of nitramine **I** in dibutyl phthalate almost coincide with those found for nitramine **II**.

The mechanism of thermal decomposition of primary nitramines in condensed state includes their initial ionization [3–7]. By analogy, we can write Eqs. (1)–(4) for nitramine **I**:

$$2NCCH_2CH_2NHNO_2 \rightleftarrows NCCH_2CH_2\overset{+}{N}H_2NO_2 + NCCH_2CH_2\overset{-}{N}NO_2, \quad (1)$$

$$NCCH_2CH_2\overset{+}{N}H_2NO_2 \rightleftarrows NCCH_2CH_2^{+} + NH_2NO_2, \quad (2)$$

Table 2. Effect of the concentration of β-cyanoethyl-*N*-nitramine (**I**) on the rate constant of its thermal decomposition in dibutyl phthalate

Temperature, °C	c, wt %	$k \times 10^5$, s^{-1}	Temperature, °C	c, wt %	$k \times 10^5$, s^{-1}
150	25.2	4.17	200	2.1	7.31
	17.0	2.28		1.2	2.04
	11.2	0.85		0.5	0.70
	5.0	0.15		0.3	0.65

$$NH_2NO_2 \longrightarrow N_2O + H_2O, \quad (3)$$

$$NCCH_2CH_2^{+} \rightleftarrows NCCH{=}CH_2 + H^{+}. \quad (4)$$

Probably, acrylic acid is formed as a result of secondary hydrolysis of acrylonitrile. The formation of nitrogen(I) oxide as the major product (0.98–0.99 mol per mole of the substrate) and acrylonitrile in the decomposition of **I**, as well as the good agreement between the activation parameters determined

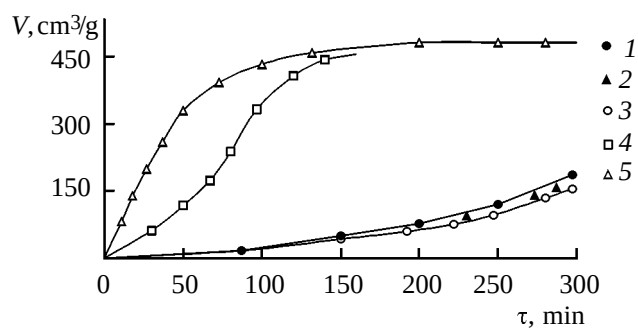

Fig. 2. Effect of gaseous and condensed decomposition products on the thermal decomposition of bis(β-cyanoethyl)-*N*-nitramine (**II**) at 210°C: (*1*) without addition; (*2*) gaseous products, p_0 150–230 mm, conversion 0.9; (*3*) nitrogen(IV)oxide, p_0 125 mm; (*4*) acrylic acid, 10–12 wt % of the initial substrate amount; (*5*) condensed residue obtained by complete decomposition of **II**.

from the accumulation of nitrogen(I) oxide and from gage measurements (Table 1), are important arguents in favor of the mechanism given by Eqs. (1)–(4). Proton transfer from the donor molecule of primary nitramine to a weak acceptor, which may be another nitramine molecule, involves intermediate formation of a molecular H complex [8]. As shown in [7], this stage can be rate-determining in the thermal decomposition of primary nitramines in melt. Nevertheless, the activation parameters found cannot be assigned with certainty to a particular elementary stage, for they characterize the decomposition process (1)–(4) as a whole.

The parameters of the Arrhenius equation for the decomposition of nitramines **I** and **II** in solution are very similar, and they coincide with those found for decomposition of primary nitramines in the gas phase [2] and of secondary nitramines in solution [1], for which a radical mechanism with initial homolytic dissociation of the N–N bond was established. The same mechanism operates for nitramine **II** in melt, as follows, e.g., from the kinetic parameters for accumulation of nitrogen(IV) oxide (Table 1) as the primary product.

To conclude, it should be noted that primary aliphatic nitramines in dilute solutions in weakly polar solvents (where ionization is suppressed almost completely) are capable of decomposing by a radical mechanism via homolytic dissociation of the N–N bond.

EXPERIMENTAL

N-Nitramines **I** and **II** contained no less than 99.9 and 99.7% of the main substance, respectively (GLC). Dibutyl phthalate was treated with an aqueous solution of sodium hydrogen carbonate, washed with distilled water, dried, and distilled twice under reduced pressure. The kinetic measurements were performed by the gage technique [9]; the kinetics of accumulation of nitrogen(I) oxide in the decomposition of **I** were also studied by chromatography using an LKhM-80 instrument equipped with a Polisorb-1 column (18–20°C); the accumulation of nitrogen(IV) oxide in the decomposition of nitramine **II** was monitored by photocolorimetry [10]. Gaseous products (which did not form a condensed phase at room temperature) were quantitated by gas chromatography (see above). Qualitative analysis of the decomposition products was performed by mass spectrometry on an MI-12-01T instrument. The rate constants were calculated by a first-order equation; when the kinetic curves were S-shaped, the rate constants were calculated from the initial rates which were determined by differentiation of the kinetic curves. The error in determination of the rate constants did not exceed 7%, and the energies of activation and preexponential factors were determined with an accuracy of 0.3–0.5 kJ/mol and 0.02 log unit, respectively.

ACKNOWLEDGMENTS

This study was financially supported by the Krasnoyarsk Regional Science Foundation.

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