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Thermal Decomposition of Some Metal Salts of *N*-Nitro-2-cyanoethylamine

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Abstract—Thermal decomposition kinetics of sodium, potassium, rubidium, and copper salts of *N*-nitro-2-cyanoethylamine has been studied in melt by manometric method combined with IR spectroscopy. The rate constant has been practically independent of the metal cation nature. Thermal decomposition mechanism has been suggested, the limiting stage being homolysis of the C–N bond to form cyanoethyl and metal nitramide radicals. Parameters of the Arrhenius equation and activation entropy have been determined for the limiting stage.

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Salts of primary nitramines are important energetic materials; furthermore, they are interesting modifiers of the pre-flame burning processes [1] and components of pyrotechnic compositions for security systems [2].

In this work we studied thermal decomposition kinetics of $NCCH_2CH_2\bar{N}(NO_2)M^+$ with $M^+ = Na^+$ (**I**), K^+ (**II**), Rb^+ (**III**), and Cu^{2+} (**IV**) in melt, in order to elucidate the effect of cation metal nature on the thermal decomposition rate, mechanism, and activation parameters.

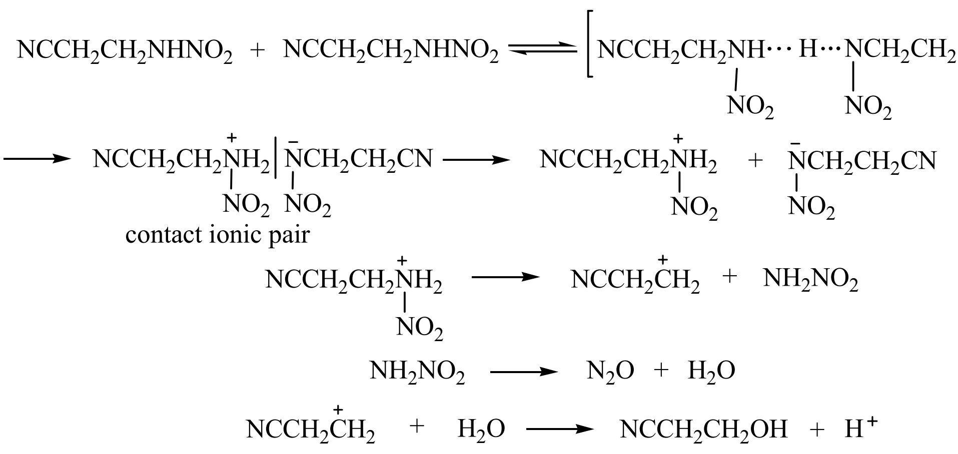
Kinetic experiments showed that thermal decomposition of the salts could be described by the first-order kinetics up to conversion of 40–45% (slightly dependent on the salt nature). The rate constant was independent of the ratio of the substance mass to the reaction vessel volume (m/V) in the range of 10^{-2}–10^{-4} g/cm^3 and on the ratio of the reaction vessel surface to its volume (S/V) in the range of 4.1–6.3 cm^{-1}. This proved the absence of any chain process or heterogeneous processes at the walls and in the volume of reaction vessel and indicates the homogeneity of thermal decomposition. The found activation parameters are given in the table.

Despite slight variation of the activation parameters E_a and log A, the rate constant of thermal decomposition was practically independent of the cation nature ($k_{200°C}$ was of 2.01×10^{-5} s^{-1} on the average). Similar trend was observed previously in the study of thermal decomposition of metal derivatives of cupferonates in melt [4].

That was likely due to the increase in the distance between the ions in the melt as compared to that in the crystal; therefore, their Coulomb interactions became much weaker and consequently reduced their mutual polarization. Hence, the acid's anion was the reactive form of salt.

Kinetic parameters of of thermal decomposition of salts of *N*-nitro-2-cyanoethylamine

Comp. no.	Cation or compound	ΔT, °C	E_a, kJ/mol	log A	$k_{200°C} \times 10^5$, s^{-1}	$\Delta S^{\neq}_{200°C}$, J mol^{-1} K^{-1}
I	Na^+	180–230	169.0	13.91	1.78	9.3
II	K^+	180–230	170.0	14.00	1.69	11.0
III	Rb^+	180–220	166.2	13.66	2.04	4.5
IV	Cu^{2+}	180–220	167.9	13.94	2.52	9.9
V	$NCCH_2CH_2N(NO_2)H$ [3]	140–180	119.9	11.13	778.1	–43.9



$$\mathrm{NCCH_2CH_2NHNO_2 + NCCH_2CH_2NHNO_2 \rightleftharpoons \left[NCCH_2CH_2\underset{NO_2}{N}H\cdots H\cdots\underset{NO_2}{N}CH_2CH_2CN\right]^{\neq}}$$

$$\longrightarrow \underset{\text{contact ionic pair}}{\mathrm{NCCH_2CH_2\underset{NO_2}{\overset{+}{N}}H_2\,|\,\underset{NO_2}{\overset{-}{N}}CH_2CH_2CN}} \longrightarrow \mathrm{NCCH_2CH_2\underset{NO_2}{\overset{+}{N}}H_2 + \underset{NO_2}{\overset{-}{N}}CH_2CH_2CN} \qquad (1)$$

$$\mathrm{NCCH_2CH_2\underset{NO_2}{\overset{+}{N}}H_2 \longrightarrow NCCH_2\overset{+}{C}H_2 + NH_2NO_2} \qquad (2)$$

$$\mathrm{NH_2NO_2 \longrightarrow N_2O + H_2O} \qquad (3)$$

$$\mathrm{NCCH_2\overset{+}{C}H_2 + H_2O \longrightarrow NCCH_2CH_2OH + H^+} \qquad (4)$$

As followed from the activation parameters (typical of ionic reactions), compound **V** in the melt was decomposed following the first-order kinetics via the acid catalysis mechanism [3].

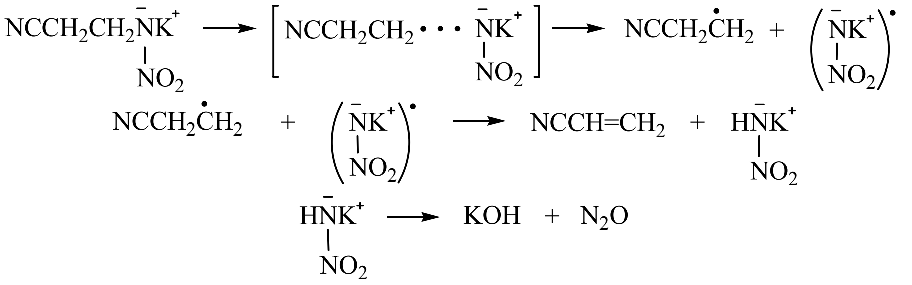
Kinetics of thermal decomposition of compound **V** in the melt was studied following N_2O accumulation at 140–180°C; the activation parameters were found: E_a 120.7 kJ/mol, log A 11.23, $k_{200°C}$ 799.8 × 10^{-5} s^{-1}, practically equal to those determined by manometric method (see table).

As was discussed in [5, 6], upon decomposition of primary nitramines in aqueous solutions of acids, where more higher rate of protons transfer observed, the process was limited by decomposition of protonated form of nitramine [reaction (2)]. However, thermal decomposition of nitramine **V** in the melt and in organic solutions showed lower rate of proton transfer [7] as compared with that in aqueous solution, and the decomposition occurred via the formation of molecular and molecular-ionic complexes of primary nitramines [8, 9]. Taking into account the above-mentioned considerations, the limiting stage of thermal decomposition of compound **V** could be expressed as reaction (1).

In order to elucidate the mechanism of thermal decomposition of salts **I–IV**, IR analysis of the products was performed using compound **II** as representative example (conversion of 8–10% at 180°C). The major products were found to be acrylonitrile (ν = 2220 cm^{-1}), N_2O (ν = 2224, 1280, and 589 cm^{-1}), and potassium hydroxide (ν = 3600 cm^{-1}). Minor amounts of acrylic acid (ν = 1690 cm^{-1}) and acrylamide (ν = 1660 and 3550 cm^{-1}) were detected.

Hence, the analysis of the thermal decomposition products and accounting for the determined activation parameters it was possible to suggest the following homolytic decomposition mechanism of salts **I–IV**.

Reaction (5) was the rate-limiting one.



$$\mathrm{NCCH_2CH_2\underset{NO_2}{\overset{-}{N}}K^+ \longrightarrow \left[NCCH_2CH_2\cdots\underset{NO_2}{\overset{-}{N}}K^+\right] \longrightarrow NCCH_2\dot{C}H_2 + \left(\underset{NO_2}{\overset{-}{N}}K^+\right)^{\bullet}} \qquad (5)$$

$$\mathrm{NCCH_2\dot{C}H_2 + \left(\underset{NO_2}{\overset{-}{N}}K^+\right)^{\bullet} \longrightarrow NCCH{=}CH_2 + H\underset{NO_2}{\overset{-}{N}}K^+} \qquad (6)$$

$$\mathrm{H\underset{NO_2}{\overset{-}{N}}K^+ \longrightarrow KOH + N_2O} \qquad (7)$$

To conclude, the metal cation nature did not influence the rate constant of thermal decomposition of *N*-nitro-2-cyanoethylamine metal salts in melt, whereas the nature of anion was important.

EXPERIMENTAL

Thermal decomposition kinetics of compounds **I–IV** was studied in melt by a manometric method using a glass Bourdon's manometer [10] at residual pressure of air in a reactionary vessel of 10^{-2}–10^{-1} mmHg. Gaseous decomposition products were analyzed by IR spectroscopy (the UR-10 instrument, KBr gas cuvette). The condensed product was purified with dichloroethane–chloroform mixture, dried, and analyzed by IR spectroscopy (Nicolet IMPACT-400, KBr, resolution of 4 cm^{-1}, 32 scans, DTGS detector).

The rate constants were calculated by the Guggenheim method [11]. Error of the rate constant determination was below 7.3%; mean-square errors of activation energy and of pre-exponential factor were 6.3 kJ/mol and 0.54 logarithmic units, respectively.

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