Kinetics of the thermal decomposition of dinitramide
3.* Kinetics of the heat release during the thermal decomposition of dinitramide ammonium salt in the liquid phase

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The kinetic regularities of the heat release during the thermal decomposition of liquid $NH_4N(NO_2)_2$ at 102.4—138.9 °C were studied. Kinetic data for decomposition of different forms of dinitramide and the influence of water on the rate of decomposition of $NH_4N(NO_2)_2$ show that the contributions of the decomposition of $N(NO_2)_2^-$ and $HN(NO_2)_2$ to the initial decomposition rate of the reaction at temperatures about 100 °C are approximately equal. The decomposition has an autocatalytic character. The analysis of the effect of additives of HNO_3 solutions and the dependence of the autocatalytic reaction rate constant on the gas volume in the system shows that the self-acceleration is due to an increase in the acidity of the $NH_4N(NO_2)_2$ melt owing to the accumulation of HNO_3 and the corresponding increase in the contribution of the $HN(NO_2)_2$ decomposition to the overall rate. The self-acceleration ceases due to the accumulation of NO_3^- ions decreasing the equilibrium concentration of $HN(NO_2)_2$ in the melt.

Key words: dinitramide ammonium salt, decomposition, kinetics, mechanism.

The ammonium salt of dinitramide, $NH_4N(NO_2)_2$ (ADNA), is a representative of the class of onium salts formed due to the proton transfer from an acid to a base. We have previously studied such high-energy onium salts as ammonium, hydroxylammonium, and hydrazonium, nitrates and perchlorates and established[2] that their thermolysis results first in the equilibrium proton transfer from the cation to the anion to form the acid and base, which undergo subsequent thermal transformations. In particular, ammonium salts decompose through the thermal reactions of the corresponding acids or their interaction with ammonia and the NH_4^+ ion. This mechanism is determined by the great difference between the rates of thermal decomposition of the anion and the corresponding acid, and even a very low equilibrium concentration of the acid is sufficient for a high decomposition rate.

Dinitramide salts differ substantially from the other ammonium salts, for example, nitrate and perchlorate: they are characterized by a higher rate of decomposition of the $N(NO_2)_2^-$ anion due to the relatively low energy of the $N-NO_2$ bond. On going from the $N(NO_2)_2^-$ anion to the $HN(NO_2)_2$ molecule, the rate of thermal decomposition increases substantially,[3] but this increase is not as high as that observed in the case of HNO_3 or $HClO_4$ on going from the anion to the molecule.

Quantitative data on the rate of thermal decomposition of $NH_4N(NO_2)_2$ have been presented for the first time in the lecture of one of the authors.[4] The main kinetic regularities of the thermal decomposition of ADNA in the liquid-phase have also been studied,[5] and it has been shown that the difference between the rates of decomposition of ammonium and potassium salts is not high. The main kinetic scheme of decomposition[5] including the reactions of both the anions and dinitramide molecules has been presented.

In this work, we studied the kinetic regularities of the heat release during the thermal decomposition of $NH_4N(NO_2)_2$ in the liquid phase. Based on the previously obtained data on the kinetics of decomposition of different forms of dinitramide,[1,3] we determined the contribution of dinitramide molecules $NH_4N(NO_2)_2$ and other compounds formed in equilibrium from dinitramide in the salt melt to the overall rate of decomposition. In addition, we attempted to elucidate the peculiarities of the thermal decomposition of ADNA compared to other ammonium salts.

Experimental

The starting sample of ADNA synthesized by a known procedure[6] was additionally purified by fusing *in vacuo* at 99 °C for 40 min to remove highly volatile admixtures. The kinetics of heat release was studied on a dynamic microcalorimeter[7] in glass ampules (inner volume ~2 cm^3), which were pre-evacuated, sealed, and thermostatted in the calorimeter cell. This procedure makes it possible to study decomposition of solutions at temperatures higher than their boiling points

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* For Part 2, see Ref. 1.

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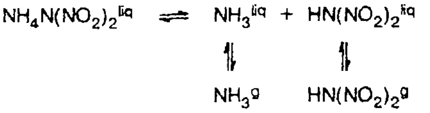
retaining volatile reaction products unchanged. The glass ampule was filled and placed in a metallic ampule of the calorimeter in a darkened room.

The accumulation of HNO_3 in samples during decomposition was determined after exposure of the glass ampule during some time period followed by measuring the pH of an aqueous solution placed in the ampule. The consumption of anions $N_3O_4^-$ was monitored spectrophotometrically by absorption at 285 nm. The content of water in samples during decomposition was determined by the Fischer method. The concentrations of NH_4^+ and NO_3^- ions were determined from conditions of mass equilibrium.

Results and Discussion

ADNA and other onium salts are characterized by the equilibrium dissociation to the initial base and acid followed by the transition of a portion of the dissociation products to the gas phase. The equilibrium vapor pressure over the salt is created by the sum of partial pressures of ammonia and dinitramide.



$$\begin{array}{ccccc} NH_4N(NO_2)_2{}^{liq} & \rightleftharpoons & NH_3{}^{liq} & + & HN(NO_2)_2{}^{liq} \\ & & \updownarrow & & \updownarrow \\ & & NH_3{}^{g} & & HN(NO_2)_2{}^{g} \end{array} \qquad (1)$$

(Indices "liq" and "g" refer to the liquid and gas phases, respectively).

The thermal decomposition in the salt melt can occur, in principle, through both the decomposition of the acid (as for other ammonium salts) and the decomposition of the anion; the ratio of the decomposition rates of different forms of dinitramides has been considered previously.[1,3] Based on these data, we can evaluate the role of undissociated dinitramide molecules in the decomposition of the salt melt.

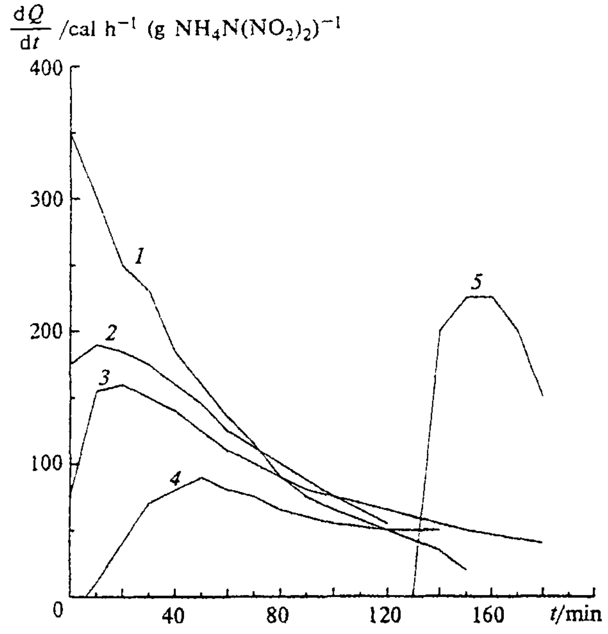


Fig. 1. Time dependence of the rate of heat release during the decomposition of $NH_4N(NO_2)_2$ at different T/°C and V^g/cm^3 mol^{-1}: *1*, T = 50.8 and V^g = 49600; *2*, T = 138.9 and V^g = 26400; *3*, T = 132.6 and V^g = 12500; *4*, T = 121.8 and V^g = 9300; *5*, T = 110.3 and V^g = 4400.

Table 1. Kinetic parameters of the thermal decomposition of dinitramide ammonium salt

T /°C	$V^g \cdot 10^{-3}$ /cm^3 mol^{-1}	$k_1 \cdot 10^5$ s^{-1}	$k_2 \cdot 10^3$
102.4	3.0	0.09	0.18
103.6	2.0	0.11	0.19
106.2	3.7	0.22	0.17
106.2	3.1	0.25	0.19
110.3	3.0	0.31	0.42
114.6	2.5	0.44	0.89
121.8	2.65	0.75	1.25
121.8	5.7	0.62	1.20
121.8	9.2	0.53	0.80
121.8	10.50	0.56	0.50
121.8	30.0	0.50	0.14
121.8	41.0	0.66	0.09
132.6	5.2	4.25	—
132.6	32.0	4.2	—
138.9	88.0	8.9	—

Note. V^g is the free gas volume of the system per mole of the starting salt.

The kinetics of heat release was studied in the 102.4—138.9 °C temperature range. Several curves of the heat release are presented in Fig. 1, and the kinetic data obtained are given in Table 1.

The thermal decomposition of $NH_4N(NO_2)_2$ occurs in two stages. After cessation of the first stage, the reaction is sharply retarded, but the decomposition continues with a low rate at the second stage of the reaction. This rate becomes considerable at high temperatures, and $NH_4N(NO_2)_2$ decomposes completely. To analyze the regularities of a change in the rate of heat release during the decomposition of the salt melt, we calculated the dependences of the specific rate at the first stage of the process $(dQ/dt)/[Q_1(1 - \eta)]$ on the conversion degree $\eta = \int_0^t (dQ/dt)dt/Q_1$, where Q_1 is the thermal effect of the first stage of the reaction (Fig. 2). It can be seen that the reaction is self-accelerated to the conversion degrees $\eta \approx$ 0.25—0.30, and at the very beginning, the rate of the process can be described by the first-order equation of autocatalysis:

$$d\eta/dt = k_1(1 - \eta) + k_2\eta(1 - \eta), \qquad (2)$$

where k_1 is the rate constant of the initial stage, and k_2 is the self-acceleration constant.

The Q_1 value increases with the temperature increase and ranges from 8.6 to 42.0 kcal mol^{-1}. Based on the analysis of the decomposition products and equations of

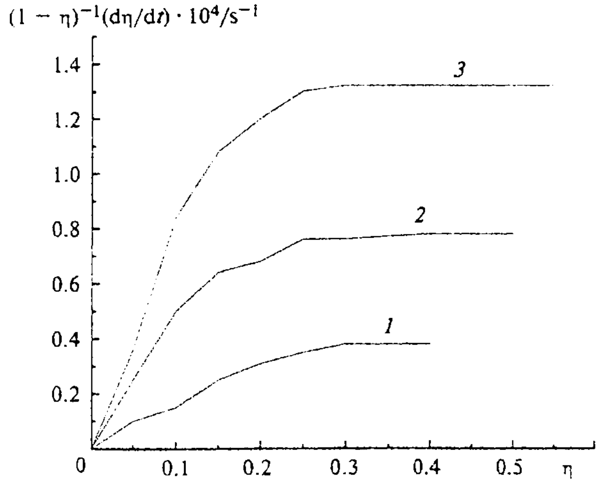


Fig. 2. Dependence of the specific rate on the conversion at the first stage of decomposition of $NH_4N(NO_2)_2$ at different T/°C and V^g/cm^3 mol^{-1}: *1*, $T = 103.0$ and $V^g = 2500$; *2*, $T = 109.4$ and $V^g = 2600$; *3*, $T = 114.6$ and $V^g = 2500$.

mass equilibrium by elements at 106.2 °C, we established that when the conversion of the starting salt is 8.5%, the decomposition proceeds according to the stoichiometric equation

$$NH_4N(NO_2)_2 = 0.81\ NH_4NO_3 + 0.76\ N_2O + 0.376\ H_2O + 0.14\ HNO_3 + 0.35\ N_2. \qquad (3)$$

Taking into account the value of the standard enthalpy of formation of $NH_4N(NO_2)_2$ (−35 kcal mol^{-1}),[8] the heat of this reaction, neglecting the heat of melting of $NH_4N(NO_2)_2$ and heats of dissolvation of $NH_4N(NO_2)_2$ and NH_4NO_3 in the reaction products, is 52.1 kcal mol^{-1}. Therefore, the decomposition of the salt by 16—80% corresponds to the conversion degree $\eta = 1$ depending on the temperature. The value of self-acceleration depends strongly on the free volume of the system referred to one mole of the starting salt (V^g) and decreases as this volume increases.

The V^g value has almost no effect on the rate constant of the initial stage of the reaction k_1, and its temperature dependence is described by the equation $k_1 = 7.7\cdot10^{14}\exp[-34600/(RT)]$ s^{-1} which is sufficiently close to the corresponding dependence obtained previously[4] from the rate of gas evolution and at considerably higher values of V^g ($\geq 2\cdot10^5$ cm^3 mol^{-1}): $k = 10^{14.4}\exp[-35500/(RT)]$ s^{-1}. Taking into account the increase in Q_1 as the temperature increases, we can write the temperature dependence of the initial rate of heat release in the form

$$(dQ/dt)_{t=0} = k_1Q_1 = 7.4\cdot10^{19}\exp[-40700/(RT)]\ \text{cal (g s)}^{-1}.$$

The comparative study of the rates of thermal decomposition of the $NH_4N(NO_2)_2$ and $KN(NO_2)_2$ melts and the change in the rates due to dilution of these melts with water (which is one of the products of decomposition of $NH_4N(NO_2)_2$) shows that the decomposition of the $KN(NO_2)_2$ melts on the addition of water is described by the kinetic equation of the first-order reaction up to $\eta \approx 0.75$. The addition of water in the $NH_4N(NO_2)_2$ melt at 106.2 °C favors a decrease in the degree of self-acceleration of the reaction, and the process occurs without acceleration when the concentration of water is ≥74 mol.%.

The $NH_4N(NO_2)_2$ melt mainly consists of the NH_4^+ and $N(NO_2)_2^-$ ions; in addition, it contains very small amounts of the NH_3 and $HN(NO_2)_2$ molecules formed from the starting salt according to equilibrium (1). The rate of decomposition of the $N(NO_2)_2^-$ ions in an aqueous solution has been previously determined;[3] of course, this rate changes on going to the melt. The rate constant of decomposition of the $N(NO_2)_2^-$ anion depends on the properties of the medium; in an aqueous solution, the solvation of the ion by the H_2O molecules facilitates its thermal decomposition. For example, the rate of decomposition of an aqueous solution of $KN(NO_2)_2$, where the formation of the $HN(NO_2)_2$ molecules due to the hydrolysis of the salt is almost ruled out because of the strong acidic properties of dinitramide, is 15—20-fold higher than the rate of decomposition of this salt in the melt also containing no dinitramide molecules. When a solution of $KN(NO_2)_2$ is diluted with water, the rate of decomposition referred to a mole of the salt increases monotonically. When water is added to the $NH_4N(NO_2)_2$ melt, the rate of thermal decomposition of the salt first decreases and begins to increase only when the water content is >5 mol.%, and its minimum value is twofold lower than the rate of decomposition of the salt in the melt. This difference can be due only to the ionization of the dinitramide molecules, which are present in the melt of the ammonium salt and contribute to the rate of decomposition; their transformation into the anions in the reaction

$$HN(NO_2)_2 + H_2O \rightleftharpoons H_3O^+ + N(NO_2)_2^-$$

decreases the rate of the process.

The decrease in the reaction rate when water is added to the $NH_4N(NO_2)_2$ melt, taking into account an increase in the rate in the same concentration range in a solution of $KN(NO_2)_2$, makes it possible to estimate the contribution of the decomposition of the $HN(NO_2)_2$ molecules to the overall rate of decomposition of the salt melt. At 106 °C it is ~50%, and the contributions of the decompositions of the $HN(NO_2)_2$ molecules and $N(NO_2)_2^-$ anions to the overall process are approximately equal. Using as a rough estimation the ratio of the rate constants of decomposition of the nondissociated dinitramide molecules and dinitramide anions in an aqueous solution extrapolated to 106 °C by the published data,[3] we calculated the equilibrium content of dinitramide in the melt of its ammonium salt: $C_{HN(NO_2)_2} = 8.7\cdot10^{-6}$ mol L^{-1}. The real value can differ several times from that presented above because of the different effects of the H_2O molecules on the rate of decomposition of the dinitramide anions and molecules. Since the nondissociated molecule and the anion decompose with different activation energies (for the anions E_a is 13.5 kcal mol^{-1} higher), and the equilibrium concentration of dinitramide changes as the temperature changes, a change in the contribution of the decomposition of dinitramide to the overall rate of the process can be expected. Presently, we have no data for calculation of the temperature dependence of equilibrium (1) in the liquid phase, but comparison with the other onium salts[2] suggests that the enthalpy of this reaction, which determines the temperature dependence of the dissociation equilibrium, is lower in magnitude (ΔH = 3—8 kcal mol^{-1}) and has an opposite sign compared to the difference between the activation energies of decomposition of the dinitramide molecule and its anion. As a result, the contribution of the decomposition of $HN(NO_2)_2$ to the overall rate of the decomposition of ADNA should decrease slightly as the temperature increases. On going to the solid phase, the situation can change, because the necessity to deform the crystal lattice should result in shifting equilibrium (1) to the left and a decrease in the concentration of dinitramide and, hence, the contribution of its decomposition to the overall process.

The fact that $NH_4N(NO_2)_2$ decomposes in two stages can be explained by the effect of the reaction products on the equilibrium concentration of $HN(NO_2)_2$. Due to the equilibrium processes of the transfer of the proton from the $HN(NO_2)_2$ molecule to the decomposition products (H_2O and the NO_3^- ion), the concentration of $HN(NO_2)_2$ becomes substantially lower than the equilibrium concentration of the acid corresponding to Eq. (1). As a result, the rate of decomposition of $NH_4N(NO_2)_2$ approaches the rate of decomposition of the $N(NO_2)_2^-$ anions surrounded by a solvate shell of the NH_4^+ cations, and this rate, as mentioned above, is approximately half as low as the initial rate of the salt decomposition. Then the reaction occurs with a low and slowly changing rate until all $N(NO_2)_2^-$ anions in the system decompose.

In the experiments when the decomposition of the salt was brought almost to the end, the total heat of decomposition (Q_{tot}) (with the formation of liquid H_2O) was 41—43 kcal mol^{-1}. The difference between Q_{tot} and the heat of the process calculated from Eq. (3) can be evidence for a change in the stoichiometry of the reaction during the decomposition and for an increase in the contribution of a less exothermic reaction when the conversion of decomposition increases. As follows from the analysis of the kinetic curves of accumulation of the products of the $NH_4N(NO_2)_2$ decomposition, nitric acid is formed at all stages of the process. At first, when the accumulation of the acid in the system is insignificant, ammonium ion should be mainly oxidized to N_2O. In this case, the acid and base are consumed in an equimolar ratio:

$$NH_4N(NO_2)_2 \rightleftharpoons NH_3 + HN(NO_2)_2,$$

$$HN(NO_2)_2 \rightarrow H\dot{N}NO_2 + NO_2,$$

$$H\dot{N}NO_2 \rightarrow \dot{O}H + N_2O,$$

$$\dot{O}H + NO_2 \rightarrow HNO_3,$$

$$NH_4^+ + HNO_3 \rightarrow NH_3NO_2^+ + H_2O,$$

$$NH_3NO_2^+ \rightarrow N_2O + H_3O^+,$$

$$H_3O^+ + NH_3 \rightleftharpoons NH_4^+ + H_2O.$$

The following reaction corresponds to the overall equation:

$$NH_4N(NO_2)_2 = 2\ H_2O^{liq} + 2\ N_2O + 62\ \text{kcal mol}^{-1}. \quad (4)$$

The oxidation of the ammonium ion to nitrogen by the products of the decomposition of dinitramide or its ion results in the accumulation of HNO_3, and the consumption of the acid is lower than that of the base:

$$N(NO_2)_2^- \rightarrow \dot{N}NO_2^- + NO_2,$$

$$NH_4^+ + \dot{N}NO_2^- \rightarrow NH_3 + H\dot{N}NO_2,$$

$$H\dot{N}NO_2 + NO_2 \rightarrow HN(O)NO_2 + NO,$$

$$HN(O)NO_2 \rightarrow HNO + NO_2,$$

$$HNO \rightarrow 0.5\ H_2N_2O_2 \rightarrow 0.5\ N_2O + 0.5\ H_2O,$$

$$NO + NO_2 \rightleftharpoons N_2O_3,$$

$$NH_3 + N_2O_3 \rightarrow N_2 + H_2O + HNO_2,$$

$$NH_4^+ + HNO_2 \rightarrow N_2 + 2\ H_2O + H^+,$$

$$N(NO_2)_2^- + H^+ \rightarrow HN(NO_2)_2 \rightarrow HNO_3 + N_2O.$$

The overall reaction

$$NH_4N(NO_2)_2 = N_2 + 0.75\ N_2O + 1.75\ H_2O + \\ + 0.5\ HNO_3 + 73.5\ \text{kcal mol}^{-1} \quad (5)$$

is the second channel of consumption of the NH_4^+ cation.

The stoichiometry of the oxidation *via* this channel is that 0.5 moles of HNO_3 are formed per mole of the decomposed $NH_4N(NO_2)_2$. However, the real contribution of this route to the overall process is low: according to Eq. (3), 0.14 moles of HNO_3 are formed per mole of the decomposed $NH_4N(NO_2)_2$. The decomposition of NH_4NO_3 results in the formation of 0.11 moles of HNO_3.[9] After the maximum reaction rate is achieved, the oxidation of the NH_4^+ ions to N_2O (see Eq. (4)) ceases, and they are mainly retained in the form of NH_4NO_3, consuming only in reaction (5), whose contribution to the overall process is small. The process mainly occurs through the decomposition of $NH_4N(NO_2)_2$ to N_2O and NH_4NO_3 according to the overall equation

$$NH_4N(NO_2)_2 \rightarrow NH_4NO_3 + N_2O + 33 \text{ kcal mol}^{-1} \quad (6)$$

with a small contribution of the oxidation of NH_4^+ to N_2 according to Eq. (5). The contribution of reactions (4) and (5) to the overall process increases as the temperature increases.

The self-acceleration of the process (the k_2 constant in Eq. (2)) depends sufficiently strongly on the free gas volume V^g and decreases with its increasing. At $V^g \approx$ 4000 cm^3 mol^{-1}, the temperature dependence of k_2 has the form

$$k_2 = 5.6 \cdot 10^{12}\exp[-22200/(RT)] \text{ s}^{-1}.$$

The accumulation of HNO_3 in the system is the most probable reason for the self-acceleration of the thermal decomposition at the initial stages of the reaction. The effect of a 26% aqueous solution of HNO_3 (which corresponds to the content of HNO_3 (%) with respect to the sum of HNO_3 and H_2O in the melt at the moment of achievement of the maximum decomposition rate) on the kinetics of thermal decomposition of the $NH_4N(NO_2)_2$ melt was studied (Fig. 3). The acid was introduced in amounts of 3.86 and 1.34 wt.% HNO_3 of the weight of $NH_4N(NO_2)_2$, *i.e.*, 1.97 and 0.68 mol.% HNO_3, respectively, with respect to the number of moles of the salt. When pure $NH_4N(NO_2)_2$ decomposes, 0.5 mol.% HNO_3 is present in the system at the moment of achievement of the maximum rate. The increase in the initial rate is proportional to the molar concentration of the added HNO_3, and its 2.8-fold increase results in a 2.7-fold increase in the rate. The acceleration of the process due to both direct addition of the acid and formation of the acid during the decomposition is proportional, on the average, to the molar concentration of HNO_3 in the system at the given moment.

We studied the effect of the main decomposition product, NH_4NO_3, on the rate of the process. It was established that even in the presence of 4—5 mol.% NH_4NO_3 at 106 and 141 °C, both the initial rate of the process and the degree of self-acceleration decrease by 1.4—1.5 times. When the content of NH_4NO_3 is equal to 20—30 mol.%, almost no self-acceleration is observed, and the initial rate decreases by 30—40%.

A more considerable decrease in self-acceleration of the process is achieved when additives of NH_4F are added to the $NH_4N(NO_2)_2$ melt. The corresponding kinetic curves obtained at 122.6 °C are presented in Fig. 4. It can be seen that the initial reaction rate remains almost unchanged, and no acceleration is observed for a sufficiently long time, but then it becomes quite pronounced, although the former value of the maximum rate is not achieved.

Thus, additives of compounds decreasing the equilibrium concentration of dinitramide (bases or salts of acids that are weaker than $HN(NO_2)_2$) decrease the degree of self-acceleration of the process.

Different routes of increasing the rate of the processes due to the accumulation of HNO_3 in the system are possible. For example, the accumulation of HNO_3 was established[2] to be a reason for self-acceleration of the thermal decomposition of ammonium nitrate, and the HNO_3 molecules participate directly in the oxidation of the NH_4^+ ion at the stage determining the rate of thermal decomposition. This reaction cannot play a substantial role in the decomposition of ADNA, because its rate is 10^7—10^8 times lower than that of decomposition of the dinitramide salts. The reaction of HNO_3 with

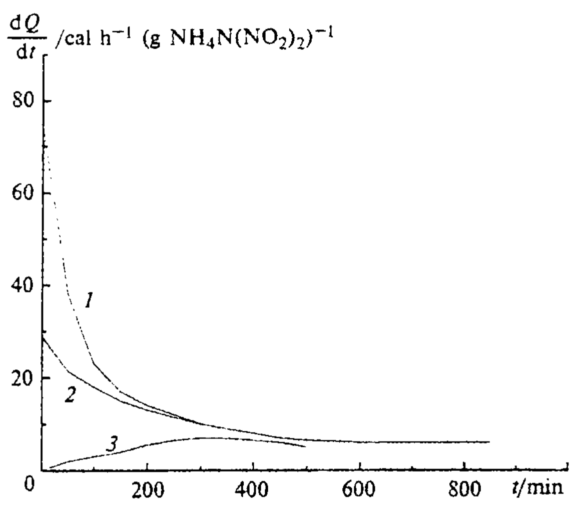


Fig. 3. Time dependence of the rate of heat release during the decomposition of $NH_4N(NO_2)_2$ at 106.2 °C and V^g = 2100 cm^3 mol^{-1} in the presence of additives of 26% HNO_3 (*1*, *2*) and without additives (*3*). Concentration of the additive (wt.%): 3.86 (*1*) and 1.34 (*2*).

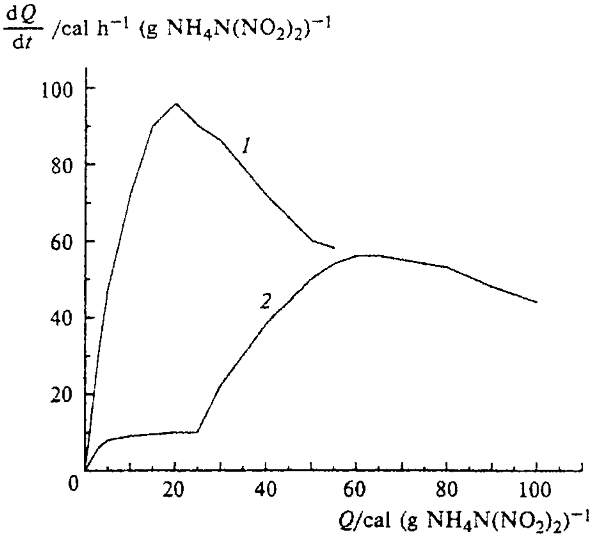


Fig. 4. Dependence of the rate of heat release on the current heat during the decomposition of $NH_4N(NO_2)_2$ at 122.6 °C and V^g/cm^3 mol^{-1} = 6900 (*1*) and 8100 (*2*) (in the presence of 1.49 wt.% NH_4F).

dinitramide in aqueous solutions of nitric acid accompanied by the equilibrium formation of mixed anhydride followed by its thermal decomposition has been described.[1] This reaction leads to a substantial acceleration of the decomposition of dinitramide at 0—20 °C. However, due to the relatively low activation energy of this reaction, its contribution decreases with the temperature increase and at $T > 100$ °C does not play a substantial role in the overall rate of the process, so that the acceleration of the decomposition of ADNA should follow a different mechanism.

Nitric acid reacts with $N(NO_2)_2^-$ anions, somewhat increasing the content of the nondissociated dinitramide molecules in the system due to the reaction

$$HNO_3 + N(NO_2)_2^- \rightleftharpoons NO_3^- + HN(NO_2)_2. \qquad (7)$$

In an aqueous solution, dinitramide is a stronger acid than HNO_3, and their pK_a are equal to −4.85 [3] and −1.6,[10] respectively. In the ionic melt of $NH_4N(NO_2)_2$ with a low dielectric constant, processes of ion association have a substantial effect on the pK_a values of acids.[11] In NO_3^- and $N(NO_2)_2^-$ ions, the charge is delocalized approximately to equivalent extents, and their polarizabilities are close. It can be assumed that the depths of the association processes involving NO_3^- and $N(NO_2)_2^-$ ions are approximately equal, which results in retention of the difference between the pK_a values of HNO_3 and $HN(NO_2)_2$ on going from an aqueous solution to the melt of $NH_4N(NO_2)_2$. When the ratio of decomposition rates of the anions and nondissociated dinitramide molecules is assumed unchanged on going from an aqueous solution to the melt of ADNA, the difference between the pK_a values of $HN(NO_2)_2$ and HNO_3 in the ADNA melt should be about −3.3 (which is quite real) for the description of the experimentally observed increase in the rate of decomposition of ADNA during the process or the addition of HNO_3. Thus, an increase in the content of dinitramide due to equilibrium (7) is the most probable reason for an increase in the rate of decomposition of ADNA as the acidity of the melt increases. This reason is also fundamental for the decomposition of many other ammonium salts. However, in the case of ammonium nitrate or perchlorate, the addition of an excessive base, for example, ammonia, decreases the rate of decomposition, while the rate of decomposition of ADNA, in principle, cannot be less than the rate of decomposition of the anions, which can increase substantially in the presence of ammonia. This increase in the rate of decomposition of the anions is observed, for example, in aqueous solutions.

The decrease in the degree of self-acceleration, when acids weaker than nitric acid are introduced into the salt melt, confirms the effect of the accumulation of HNO_3 on the acceleration of the thermal decomposition of ADNA. This additive can decrease the equilibrium concentration of HNO_3 and, hence, $HN(NO_2)_2$.

The experimentally observed dependence of k_2 on V^g is determined by the transition of some HNO_3 molecules to the gas phase. Using Henry's equation for evaporation of HNO_3:

$$n^{g}_{HNO_3} \cdot RT/V^{g} = K_H(HNO_3) \cdot n^{liq}_{HNO_3},$$

the kinetic equation of decomposition of $HN(NO_2)_2$:

$$d\eta/dt = k \cdot n^{liq}_{HN_3O_4},$$

equilibrium conditions with respect to HNO_3 when it is accumulated during the process:

$$n^{g}_{HNO_3} + n^{liq}_{HNO_3} = \alpha\eta,$$

the expression for the equilibrium constant K_N from Eq. (7), and Eq. (2) for autocatalysis, we obtain

$$\frac{1}{k_2} = \frac{n^{liq}_{NO_3^-}}{kK_N\alpha} + \frac{K_H(HNO_3) \cdot n^{liq}_{NO_3^-}}{RTkK_N\alpha} \cdot V^{g}, \qquad (8)$$

where $n^{g}_{HNO_3}$, $n^{liq}_{HNO_3}$, $n^{liq}_{HN_3O_4}$, and $n^{liq}_{NO_3^-}$ are the numbers of moles of the corresponding components in the gas and liquid phases per mole of the initial mixture; $K_H(HNO_3)$ is Henry's constant for the transition of HNO_3 from the liquid to the gas; k is the rate constant of decomposition of $HN(NO_2)_2$; and $\alpha = 0.14$ is the number of moles of HNO_3 formed during the decomposition of one mole of the salt. It is accepted that $HN(NO_2)_2$ does not go to the gas, and in the melt the total number of moles of the components $\Sigma n \approx n^{liq}_{NH_4N_3O_4} = 1$ (this is acceptable for the initial stages of decomposition). If $n^{liq}_{NO_3^-} \approx$ const, which is observed at the initial stages of decomposition of ADNA when reaction (4) mainly occurs, a linear dependence of $1/k_2$ on V^g should be fulfilled. This dependence obtained

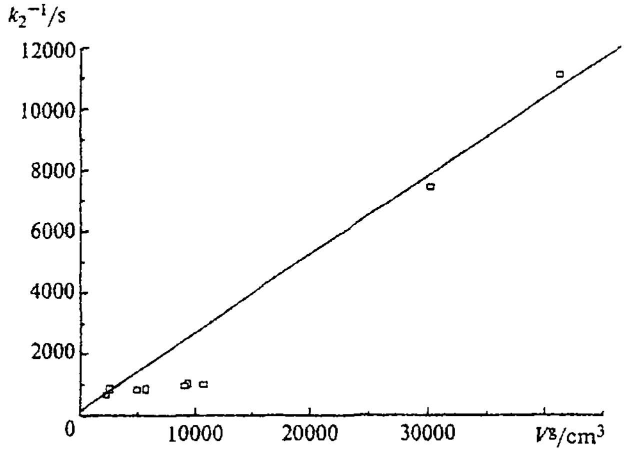


Fig. 5. Dependence of $1/k_2$ on the free gas volume of the system (V^g) during the decomposition of $NH_4N(NO_2)_2$ at 121.8 °C.

from the data in Table 1 is presented in Fig. 5. Thus, fulfillment of Eq. (8) confirms the determining role of evaporation of HNO_3 in the dependence of the self-acceleration on V^g. The equilibrium pressure of the $HN(NO_2)_2$ vapor and the $K_H(HN(NO_2)_2)$ value should be much lower than those for HNO_3 because of the great molecular weights of these molecules and the much higher degrees of their ionization in the melt compared to that of HNO_3; therefore, the k_1 constant is independent of V^g.

When reaction (6) begins to play the main role, the $n^{liq}_{NO_3^-}$ value increases strongly and, hence, the k_2 value decreases, and the self-acceleration of the process ceases. The addition of NH_4NO_3 to the melt has a similar effect, decreasing the k_2 value. Thus, the mechanism suggested for the thermal decomposition describes all kinetic regularities observed and explains the specific features of the decomposition of ADNA compared to other ammonium salts.

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