Kinetics of the thermal decomposition of dinitramide

2.* Kinetics of the reactions of dinitramide with decomposition products and other components of a solution

A. I. Kazakov, Yu. I. Rubtsov, G. B. Manelis, and L. P. Andrienko*

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588

The kinetic regularities of the thermal decomposition of dinitramide in aqueous solutions of HNO_3, in anhydrous acetic acid, and in several other organic solvents were studied. The rate of the decomposition of dinitramide in aqueous HNO_3 is determined by the decomposition of mixed anhydride of dinitramide and nitric acid (N_4O_6) formed in the solution in the reversible reaction. The decomposition of the anhydride is a reason for an increase in the decomposition rates of dinitramide in solutions of HNO_3 as compared to those in solutions in H_2SO_4 and the self-acceleration of the process in concentrated aqueous solutions of dinitramide. The increase in the decomposition rate of nondissociated dinitramide compared to the decomposition rate of the $N(NO_2)_2^-$ anion is explained by a decrease in the order of the $N-NO_2$ bond. The increase in the rate constant of the decomposition of the protonated form of dinitramide compared to the corresponding value for neutral molecules is due to the dehydration mechanism of the reaction.

Key words: dinitramide, thermal decomposition, mechanism, kinetics; mixed anhydride of dinitramide and nitric acid.

In the previous report,[1] we have presented the main kinetic regularities of the thermal decomposition of anions of nondissociated and protonated forms of dinitramide in water and solutions of H_2SO_4. These regularities make it possible to estimate decomposition rates within wide ranges of temperatures and the acidities of solutions. However, these forms of dinitramide can also react with the components of the solution and the products of the thermal decomposition. These reactions affect the rate of the overall process and, in many cases, lead to a substantial increase in the rate during the decomposition.

It is known that the thermal liquid-phase decomposition of the ammonium salt of dinitramide occurs with substantial autoacceleration.[2] An increase in the rate during the decomposition is also observed for the thermolysis of some solutions of dinitramide. In this work, we studied the kinetic regularities of the reactions of dinitramide with the products of its thermal decomposition and the other components of the system. These regularities make it possible to evaluate a change in the rate during the decomposition and when the reaction medium is changed. Based on the available data on the kinetic regularities of the thermal decomposition of dinitramide, we considered possible mechanisms of these reactions and discussed the reasons for the differences between the rates of the thermal decomposition of the anions, nondissociated and protonated dinitramide molecules.

Experimental

Procedures for the preparation of solutions of dinitramide and study of the kinetics of heat release are similar to those described previously.[1]

The effect of nitric acid on the kinetic regularities of the thermal decomposition of dinitramide was studied for solutions of $NH_4N(NO_2)_2$ (0.1—0.3 wt.%) in aqueous HNO_3 (56—90 wt.%) in the temperature range from −9.7 to 99.9 °C according to a procedure similar to that used previously[1] for studying the kinetics of the decomposition of $NH_4N(NO_2)_2$ in solutions of H_2SO_4.

The kinetics of the thermal decomposition of the ammonium salt of dinitramide in anhydrous acetic acid (the content of H_2O was not higher than 0.004 wt.%, as determined from the electroconductivity of the acid) was studied in the 19.3—103.5 °C temperature range. An attempt to study acetic solutions of dinitramide was unsuccessful, because the decomposition occurred very rapidly, almost immediately after mixing, and the kinetics cannot be studied.

The pK_a values of dinitramide in acetic acid were estimated by the measurement of the electroconductivity of the solution of dinitramide with the concentration of $1.1 \cdot 10^{-2}$ mol L^{-1}. To calculate pK_a, the electroconductivity values were extrapolated to the zero time, because the conductivity of the solutions changes in time due to their low stability. We obtained $pK_a = 8.1 \pm 0.5$, while $pK_a = -4.85$ in an aqueous solution of dinitramide.

---

* For Part 1, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 41—47, January, 1998.

Results and Discussion

The dynamics of the accumulation of the main decomposition products and their effect on the rate of the process were studied first of all to analyze the reasons for the autoacceleration of the thermal decomposition of solutions of dinitramide and its ammonium salt. HNO_3 and N_2O are the main products of the decomposition of dinitramide, and a decrease in the content of the $N(NO_2)^-$ anions corresponds to the kinetics of the heat release according to the stoichiometric equation (reaction (1)).

$$HN(NO_2)_2 = HNO_3 + N_2O \qquad (1)$$

According to the kinetics of the heat release, nitric acid is formed upon decomposition of solutions of $NH_4N(NO_2)_2$ during the whole process. The NH_4^+ ions are consumed, and H_2O is accumulated at the initial stage of the process, while NH_4NO_3 is accumulated at the later stages. In an aqueous solution of $HN(NO_2)_2$ with a concentration >1 mol.%, the decomposition occurs with noticeable autoacceleration. The dependence of the specific reaction rate on the conversion (η) is shown in Fig. 1. The autoacceleration is described by the first-order equation of autocatalysis and almost ceases at η = 0.20—0.25. The autoacceleration degree of the decomposition increases as the acid concentration increases at a constant temperature or as the temperature increases at a constant concentration of dinitramide. Similar kinetic dependences are observed for the thermal decomposition of the melt of the ammonium salt of dinitramide (they will be considered in detail in the next publication[3]).

Examination of the effect of HNO_3 on the reaction is first of all required for understanding the kinetic regularities and the mechanism of the thermal decomposition of dinitramide and its salts. The rate of the decomposition of dinitramide in aqueous HNO_3 at low temperatures and the same acidity is several orders of magnitude higher than that in H_2SO_4. When the temperature increases, these differences decrease, and at ~100 °C the rates of the decomposition of dinitramide in H_2SO_4 and HNO_3 almost coincide. The obtained values of the rate of the thermal decomposition are presented in Table 1.

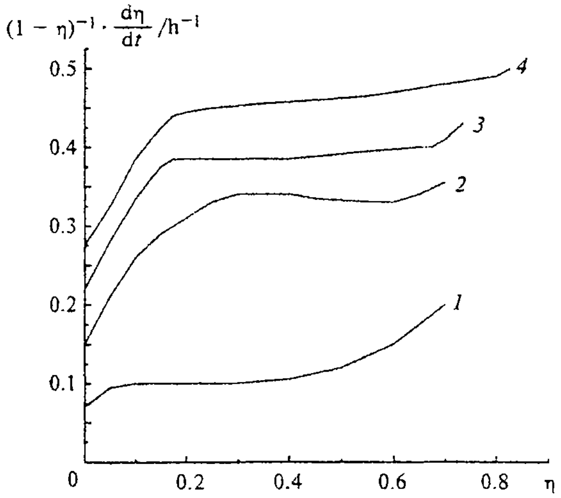


Fig. 1. Dependences of the specific reaction rate on the conversion for the decompsition of aqueous solutions of $HN(NO_2)_2$ at 105.9 °C: $C_{HN(NO_2)_2}$ (mol.%) = 2.26 (*1*), 3.05 (*2*), 3.43 (*3*), 3.79 (*4*).

In the acidity range studied, the rates of the decomposition of dinitramide are proportional to the square of the acidity (h_0), but the reaction has the first order during the process. This character of the dependence cannot be explained by the determining role of direct interaction of the dinitramide molecules and HNO_3, since the concentration of HNO_3 in the acidity range studied increases weakly, and improbably high order (~20) is obtained for the k_{exp}/h_0 dependence on C_{HNO_3} (k_{exp} is the experimental reaction rate constant). The reversible formation of the mixed anhydride of nitric acid and dinitramide (reaction (2)) followed by its thermal decomposition (reaction (3)), which determines the rate of the whole process, seems to be most probable:

$$HN(NO_2)_2 + HNO_3 \overset{K}{\rightleftharpoons} N_4O_6 + H_2O, \qquad (2)$$

$$K = a_{anh} \cdot a_{H_2O}/(a_{HNO_3} \cdot a_{ac}),$$

$$N_4O_6 \xrightarrow{k_{anh}} N_2O_5 + N_2O, \qquad (3)$$

$$N_2O_5 + H_2O \rightleftharpoons 2\ HNO_3,$$

Table 1. Rate constants of the decomposition of dinitramide (0.1—0.3 wt.%) in aqueous solutions of HNO_3

C_{HNO_3} (mol.%)	T /°C	$k \cdot 10^5$ /s^{-1}
11.14	99.9	6.7
13.48	99.9	9.3
14.37	99.9	12.0
18.33	99.9	18.0
19.26	99.9	14.0
21.88	99.9	38.0
21.88	99.9	35.0
24.74	9.9	68.0
26.66	30.3	1.8
27.06	99.9	170.0
27.87	99.9	16.0
29.65	99.9	37.0
41.51	10.6	1.9
41.54	30.3	11.0
43.01	30.3	16.0
43.38	10.6	0.9
45.89	10.6	6.9
46.47	3.8	2.8
46.47	21.7	14.0
46.47	30.3	49.0
49.39	10.6	21.0
50.97	10.6	17.0
51.29	10.6	14.0
51.64	−1.1	5.8
51.64	3.8	12.0
51.64	30.3	80.0
57.82	10.6	57.0
58.4	−9.7	6.5
58.4	−1.1	32.0
58.4	3.8	33.0
58.4	30.3	250.0
60.27	−1.1	16.0
71.86	−1.1	31.0
71.86	−1.1	66.0

where a_{anh} and a_{ac} are the activities of the anhydride N_4O_6 and dinitramide, respectively, and K is the equilibrium constant.

The expression for the rate constant, according to Eq. (3), has the form

$$-(\mathrm{d}C/\mathrm{d}t)_{t=0} = k'_{anh}C_{anh}\gamma_{anh}/\gamma^{\neq}_{anh} =$$
$$= k'_{anh}K(a_{HNO_3}a_{ac}/a_{H_2O})\cdot(1/\gamma^{\neq}_{anh}),$$

where k'_{anh} is the rate constant of the decomposition of the anhydride N_4O_6 in the gas phase; γ_{anh} and $\gamma^{\neq}_{anh}$ are the activity coefficients of the anhydride and the activated complex in the solution, respectively.[4] Taking into account the dependence of a_{ac} on the acidity of the medium and assuming that C_{ac}, $C_{anh} \ll C_0$ (C_0 is the analytical concentration of $NH_4N(NO_2)_2$ in the solution, the latter equation can be transformed to the expression

$$-(\mathrm{d}C/\mathrm{d}t)_{t=0} = k_{exp}C_0 = (k_{anh}K/K_a)a_{HNO_3}h_0C_0/a_{H_2O},$$

where $k_{anh} = k'_{anh}\gamma_{ac}/\gamma^{\neq}_{anh}$ is the rate constant of the decomposition of the anhydride in the solution, γ_{ac} is the activity coefficient of dinitramide, K_a is the constant of the acid dissociation of dinitramide in the reaction

$$HN(NO_2)_2 \rightleftharpoons N(NO_2)^- + H^+,$$

$$K_a = a_{H^+}a_{an}/a_{ac},$$

a_{an} is the activity of the $N(NO_2)^-$ anion.

It can be seen in Fig. 2 that a linear dependence with $\tan\alpha = 1$ is fulfilled between $\log k_{exp}$ and $\log(a_{HNO_3}/a_{H_2O}) - H_0$ (H_0 is the acidity function). The temperature dependence of k_{exp} was calculated from the experimental data:

$$k_{exp} = k_{anh}K/K_a = 10^{2.8}\exp(-7.3\cdot10^3/T)\ (\mathrm{s}^{-1}).$$

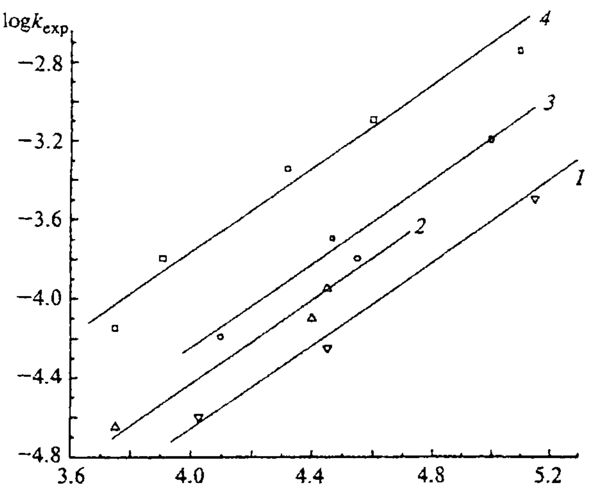


Fig. 2. Dependences of $\log k_{exp}$ on $\log(a_{HNO_3}/a_{H_2O}) - H_0$ for the decomposition of $HN(NO_2)_2$ in aqueous HNO_3 at different temperatures: T/°C = −1.1 (*1*), 3.8 (*2*), 10.6 (*3*), 30.3 (*4*).

Taking into account the temperature dependence of K_a, we have

$$k_{anh}K = 8.7\cdot10^3\exp(-4.7\cdot10^3/T).$$

The first order during the reaction can be explained by the fact that the C_{HNO_3} value remains almost unchanged during the decomposition and even somewhat increases due to reaction (1). The dependences of $\log k_{exp}$ on H_0 for the decomposition of dinitramide in aqueous H_2SO_4 and HNO_3 at −1.1 °C and 99.5 °C are presented in Fig. 3. At −1.1 °C (curve *1*) and $H_0 > 1$, the HNO_3 molecules are almost absent, and the rate is determined by the decomposition of the $N(NO_2)^-$ anions and the same in solutions of H_2SO_4 and HNO_3. At the higher acidity, the mixed anhydride is formed and decomposes in HNO_3 more rapidly, and at $H_0 < 1$ the rate of the decomposition in nitric acid is much higher than that in sulfuric acid.

Since the temperature dependence of k_{exp} for N_4O_6 is weaker than those of the experimental rate constants of the thermal decomposition of $HN(NO_2)_2$ and the $H_2N(NO_2)_2^+$ cations, when the temperature increases, the difference between the decomposition rates in H_2SO_4 and HNO_3 decreases, and at 99.5 °C (see Fig. 3, curve *2*) the reaction with HNO_3 followed by the decomposition of the anhydride determines the rate of the whole process only when $H_0 < -5.5$. At the lower acidity, the rate is determined by the decomposition of the $HN(NO_2)_2$ and $H_2N(NO_2)_2^+$ molecules according to the kinetics studied previously,[1] and the observed rates coincide with the rates of the decomposition of dinitramide and its protonated form in H_2SO_4. Thus, the reaction of dinitramide with HNO_3 enhances very strongly the overall rate of the decomposition at low

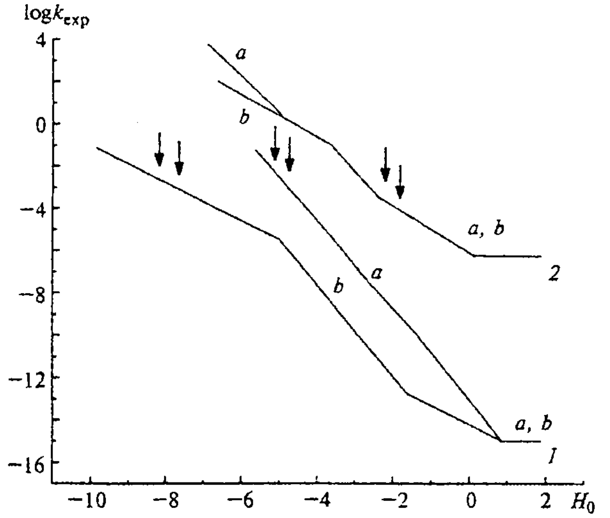


Fig. 3. Dependences of $\log k_{exp}$ on H_0 for the decomposition of $HN(NO_2)_2$ in solutions of HNO_3 (*a*) and H_2SO_4 (*b*): *1*, at −1.1 °C; *2*, at 99.5 °C. The experimental range of H_0 is bounded by arrows.

Table 2. Rate constants of the decomposition of the ammonium salt of dinitramide in AcOH

$C_{NH_4N(NO_2)_2} \cdot 10^3$ /mol L^{-1}	T /°C	$k \cdot 10^5$ /s^{-1}	$C_{NH_4N(NO_2)_2} \cdot 10^3$ /mol L^{-1}	T /°C	$k \cdot 10^5$ /s^{-1}
4.1	19.3	7.2	2.9	40.6	32.0
6.4	19.3	7.5	1.1	52.5	49.0
1.1	19.3	7.0	2.0	52.5	42.0
2.8	29.6	11.0	4.1	52.5	47.0
7.6	29.6	10.0	3.9	52.5	47.0
5.2	29.6	10.0	2.1	52.5	31.0
0.7	40.6	34.0	1.9	87.2	200.0
1.9	40.6	33.0	3.8	87.2	200.0
2.7	40.6	31.0	3.8	103.5	260.0

temperatures and in media with high acidity, but it does not play a substantial role in the decomposition of the ammonium salt of dinitramide at ≥100 °C.

The kinetic law of the first order is fulfilled during the decomposition of $NH_4N(NO_2)_2$ in AcOH with different concentrations of the salt in the original solution. The obtained values of the rate constants are presented in Table 2. The rate of the thermal decomposition of acetic solutions of $NH_4N(NO_2)_2$ is several orders of magnitude higher than that in aqueous solution and depends strongly on the content of water in the solutions: the rate of the decomposition at 87.2 °C decreases by 55 times on going to technical-grade glacial acetic acid (0.4 wt.% H_2O). Specific features of the thermal decomposition of dinitramide in acetic acid are important for the comparison of the homolytic and heterolytic routes of its decomposition. The low dielectric constant of AcOH ($\varepsilon = 6.2$) makes the complete dissociation of dissolved compounds difficult, therefore, all heterolytic decomposition processes should be strongly retarded in acetic acid. At the same time, AcOH, having a low proton affinity, is a differentiating solvent and decreases the strength of all acids dissolved in it. On going from an aqueous solution of dinitramide to a solution in acetic acid, pK_a increases by ~13, and for the other strong acids, this change is also 13±2 units, *i.e.*, the relative strength of acids, in particular, dinitramide and HNO_3, remains unchanged on going from aqueous to acetic solutions.

Extrapolation of the data on the acidity functions of solutions of H_2SO_4 in AcOH [5] to neat AcOH gave the h_0 value equal to ~10. The comparison of this value to the K_a value of dinitramide in acetic acid shows that dinitramide should exist almost completely in a molecular form. The observed rate of the decomposition of $HN(NO_2)_2$ in AcOH is an order of magnitude higher than that in solutions of H_2SO_4 with the same content of $HN(NO_2)_2$. There are no grounds to expect a substantial increase in the rate constant of the decomposition of $HN(NO_2)_2$ (k_{ac}) on going from aqueous to acetic solutions. Thus, the decomposition of the protonated $H_2N(NO_2)_2^+$ molecules, whose decomposition rate is considerably higher, is most probable. This is also supported by a sharp decrease in the decomposition rate when the content of water in acetic acid increases slightly, because this can strongly reduce only the concentration of the protonated form due to a decrease in the acidity of a solution of AcOH.

The initial rate of the decomposition of dinitramide in acetic acid can be written in the form

$$(dC/dt)_{t=0} = k_{exp}C_0 = k_pC_0h_0/K_p,$$

where k_p and K_p are the rate constant of the decomposition of the protonated $H_2N(NO_2)_2^+$ form and the equilibrium constant of its dissociation in a solution of acetic acid, respectively:

$$H_2N(NO_2)_2^+ \rightleftharpoons H^+ + HN(NO_2)_2.$$

Based on the experimental data, we obtained the following temperature dependence of the rate constant of the decomposition of $NH_4N(NO_2)_2$ in AcOH:

$$k_{exp} = 2.5 \cdot 10^2 \exp(-4.4 \cdot 10^3/T)\ (s^{-1}).$$

Assuming that the true rate constant of the monomolecular decomposition of the protonated form in solutions of H_2SO_4 and AcOH are equal, we estimated

$$K_p = 10^{10.6} \exp(-3.5 \cdot 10^3/T).$$

The concentration of the protonated form of dinitramide decreases as the temperature increases, therefore, the temperature dependence of k_{exp} in an acetic solution is weaker than in an aqueous solution.

The kinetics of the heat release in the decomposition of solutions of $NH_4N(NO_2)_2$ in acetonitrile, nitrobenzene, and DMF with a salt concentration of ~1% was studied in special experiments. The kinetic curves of the decomposition of $NH_4N(NO_2)_2$ in DMF obtained at 122.6 °C are presented in Fig. 4. When the salt decomposes in acetonitrile, the initial rate and the total reaction heat increase strongly (as compared to an aqueous solution), which testifies that $NH_4N(NO_2)_2$ directly reacts with the solvent. At the initial stage, the rate of the thermal decomposition of the salt in nitrobenzene is very close to that of the decomposition of the $NH_4N(NO_2)_2$ melt, but further the oxidation of nitrobenzene begins, which involves the decomposition products, and the total heat of the process increases strongly. The rate of the heat release in the thermal decomposition of mixtures of $NH_4N(NO_2)_2$ with DMF changes very slightly during the reaction. The dependence of the initial rate of the decomposition at 122.6 °C on the composition of the solution is shown in Fig. 5, and at this temperature the system is homogeneous in the whole concentration range. The initial rate is described by the equation of the third-order reaction: the second order with respect to the salt and the first order with respect to DMF. When the salt concentration is 5 mol.%, the initial rate of the decomposition of $NH_4N(NO_2)_2$ in DMF is lower than that of the decomposition of its melt

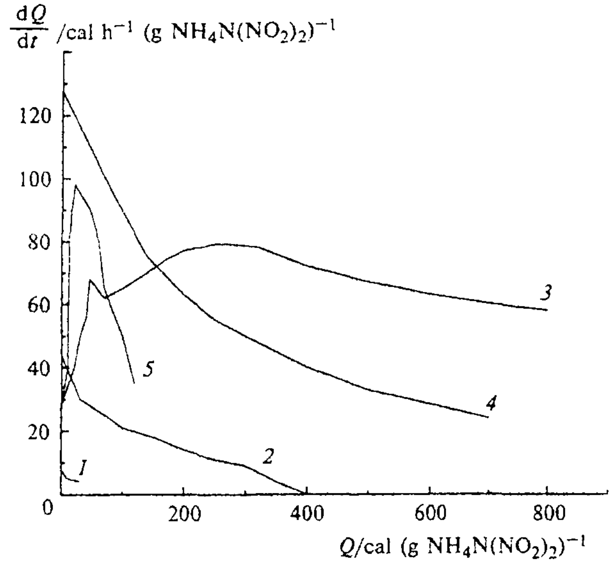


Fig. 4. Dependences of the rate of the heat release on the amount of the heat yielded during the decomposition of $NH_4N(NO_2)_2$: *1*, in DMF (1.28 mol.% of the salt); *2*, in water (1.24 mol.%); *3*, in nitrobenzene (1.09 mol.%); *4*, in acetonitrile (1.28 mol.%); *5*, in the melt.

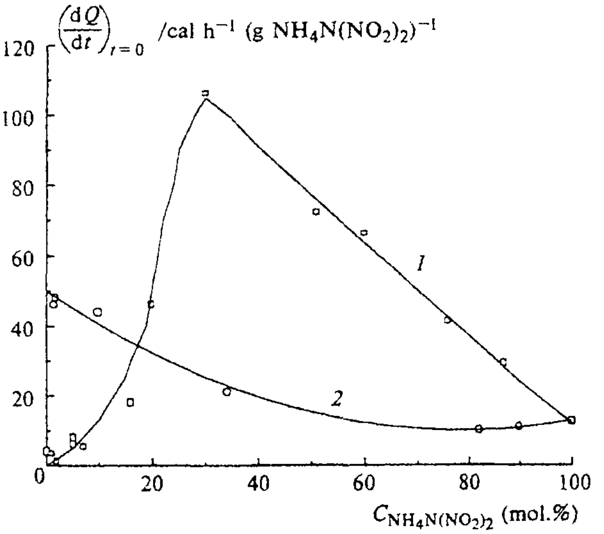


Fig. 5. Dependences of the initial rate of the heat release in the $NH_4N(NO_2)_2$—DMF (*1*) and $NH_4N(NO_2)_2$—H_2O (*2*) systems on the concentration of $NH_4N(NO_2)_2$ in the mixture at 122.6 °C.

and lower than the initial reaction rate in aqueous solutions with the same concentration of the salt. At the same time, in the region of the $NH_4N(NO_2)_2$ concentrations of 25—75 mol.%, the initial rate of the decomposition is substantially greater than that in aqueous solutions.

A sufficiently fast interaction between the salt and solvent is observed in mixtures of $NH_4N(NO_2)_2$ with DMF for the major part of the compositions of the solution. Analysis of the kinetic peculiarities and the mechanism of this process is beyond the scope of this work. The observed rate of heat release is a sum of the rates of this process and inherent thermal decomposition of the dinitramide molecules and its anions. In this case, it is important that in dilute solutions of the salt, where the rate of the reaction between the salt and DMF is low due to the second order of the reaction with respect to $NH_4N(NO_2)_2$, the overall rate of the heat release is 3—4 times lower than the rate of the decomposition of $NH_4N(NO_2)_2$ in the melt and aqueous solution. Therefore, the inherent rate of the decomposition of $NH_4N(NO_2)_2$ in DMF is also substantially lower than those in the melt or an aqueous solution. This decrease can be related, first of all, to a decrease in the concentration of the dinitramide molecules due to their ionization in the solution. DMF is a more basic solvent than water, and the acid dissociates in this medium more deeply than in an aqueous solution. In dilute aqueous solutions, the contribution of the decomposition of the nondissociated dinitramide molecules is low, solutions of dinitramide and its potassium salt decompose at equal rates, but the rate of their thermal decomposition increases due to the solvation of the $N(NO_2)_2^-$ anions by water molecules, and, therefore, dilute aqueous solutions of $HN(NO_2)_2$ and its salts decompose at a higher rate than the $NH_4N(NO_2)_2$ melt. When $NH_4N(NO_2)_2$ is dissolved in DMF, the solvation likely changes slightly the rate of the decomposition of the anions, or at least does not substantially increase it; therefore, we can observe a decrease in the rate of the decomposition of the salt in DMF as compared to that in the melt.

The virtual absence of autoacceleration during the reaction confirms that the dinitramide molecules in DMF are considerably more strongly ionized than in the melt, since the accumulation of the nondissociated $HN(NO_2)_2$ molecules under these conditions should result in a considerable increase in the decomposition rate.

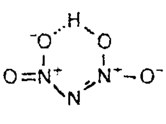
Thus, the kinetic regularities of the decomposition of solutions of $NH_4N(NO_2)_2$ in DMF support the fact that its thermal decomposition occurs through the decomposition of both the anions and nondissociated $HN(NO_2)_2$ molecules.

Analyzing the mechanism of the thermal decomposition of dinitramide, one should take into account that, due to some specific features of the structure, it is similar to nitronic acids, which are well known in the chemistry of nitro compounds. These acids are characterized by the tautomeric transformation of the nitro form into the acido form. For dinitramide, this tautomeric equilibrium has the form

$$O_2N{-}NH{-}NO_2 \rightleftharpoons [O_2N{-}N{-}NO_2]^- + H^+ \rightleftharpoons$$
$$\rightleftharpoons O_2N{-}N{=}NOOH.$$

In media with a high dielectric constant, for example, in aqueous and acidic solutions, processes of ionization and proton exchange occur with high rates, therefore, the tautomeric equilibrium is rapidly established.

Based on the IR spectra of dinitramide, the authors of Ref. 6 suggested a somewhat different structure of the acido form (**A**). Analyzing probable mechanisms of the decomposition, one should take into account the possibility that the reaction occurs through both the acido and nitro forms, and the decomposition of one of them should be accompanied by a decrease in the content of both forms of dinitramide due to the fast establishment of the tautomeric equilibrium.



A

The activation energy of the decomposition of the $N(NO_2)_2^-$ anion in the solution is ~41 kcal mol^{-1}, which is close to the corresponding values for secondary nitramines,[7] where the cleavage of the N—NO_2 bond is determining. This mechanism is also most probable for the $N(NO_2)_2^-$ anion. It has been proposed as the main mechanism of the thermal decomposition of dinitramide salts,[2] but should be confirmed by the independent determination of the energy of the N—NO_2 bond.

The rate of the decomposition of the $HN(NO_2)_2$ molecules in the 0—100 °C temperature range is 10^7—10^5 times higher than that for the anions. The ratio of the rates of the decomposition of HNO_3 and $HClO_4$ molecules and their anions is even higher. These acids decompose through the reversible formation of anhydrides Cl_2O_7 and N_2O_5, which decompose at the relatively weak ClO_3—$OClO_3$ and NO_2—ONO_2 bonds, and the reaction order with respect to the acid is second or even higher.[8]

It is likely that the reversible formation of the anhydride in the reaction

$$2\,HN(NO_2)_2 \rightleftharpoons H_2N(NO_2)_2^+ + N(NO_2)_2^- \rightleftharpoons$$

$$\rightleftharpoons H_2O + N_6O_7,$$

also occurs to some extent. However, an increase in the rate of the decomposition of the anhydride does not compensate for its low (compared to that of the $HN(NO_2)_2$ molecules) concentration; therefore, the contribution of the anhydride decomposition to the overall process does not play a substantial role. The decomposition of dinitramide is monomolecular, likely due to the relatively weak N—NO_2 bond, when the molecular decomposition becomes more favorable than the formation of the anhydride and its subsequent thermal decomposition.

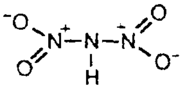
In the HNO_3-containing systems, at low temperatures, the extent of the formation of the mixed anhydride is much greater due to the high concentration of the HNO_3 molecules and their considerably easier protonation:

$$HN(NO_2)_2 + HNO_3 \rightleftharpoons$$

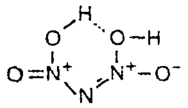
$$\rightleftharpoons H_2NO_3^+ + N(NO_2)_2^- \rightleftharpoons H_2O + N_4O_6,$$

therefore, the relative contribution of the reaction route through the decomposition of the anhydride increases strongly, and this route becomes determining.

The increase in the activation energy of the decomposition of the $N(NO_2)_2^-$ anions as compared to that of the $HN(NO_2)_2$ molecules can be explained by the greater value of the effective order of the N—N bond in the anion due to the contribution of the resonance structures with the double N=N bond. It can also be supposed that the decomposition of the $HN(NO_2)_2$ molecules proceeds through the decomposition of their nitro form, in which the main contribution to the bond order is made by the resonance structure **B**.



B



C

The protonation of the $HN(NO_2)_2$ molecules should not affect the strength of the N—N bond, and the orders of the N—N bond in $H_2N(NO_2)_2^+$ and $HN(NO_2)_2$ are close. However, when the second proton adds to $HN(NO_2)_2$, the protonated form gains the possibility of decomposing *via* the dehydration reaction. Water should be eliminated more easily from the *O*-protonated acido form of the six-membered cycle (**C**). This structure is similar to that of the acido form **A** presented above.[6]

The kinetic regularities observed and the composition of the final products of the decomposition can correspond to the following reactions:

— *in the decomposition of the* $N(NO_2)_2^-$ *anions*

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

$$NO_2 + {}^{\cdot}N(NO_2)^- \rightarrow N_2O + NO_3^-;$$

— *in the decomposition of the* $HN(NO_2)_2$ *molecules*

$$HN(NO_2)_2 \rightarrow NO_2 + HN^{\cdot}NO_2,$$

$$HN^{\cdot}NO_2 \rightarrow N_2O + OH,$$

$$NO_2 + OH \rightarrow HNO_3;$$

— *in the decomposition of the* $H_2N(NO_2)_2^+$ *cations*

$$H_2N(NO_2)_2^+ \rightarrow H_2O + N_3O_3^+;$$

$$N_3O_3^+ \rightarrow NO_2^+ + N_2O,$$

$$NO_2^+ + H_2O \xrightarrow{H_2O} HNO_3 + H_3O^+.$$

The thermal decomposition of dinitramide was studied in many media; however, autocatalysis was observed only in relatively concentrated aqueous solutions. The autocatalysis is likely related to the formation of the mixed anhydride of nitric acid and dinitramide, N_4O_6, and its subsequent decomposition. No autocatalysis is observed in dilute solutions of dinitramide in H_2O and aqueous H_2SO_4 and AcOH, since the concentration of the mixed anhydride is low because of a decrease in the content of the HNO_3 due to the ionization

$$HNO_3 + H_2O \rightleftharpoons NO_3^- + H_3O^+,$$

$$HNO_3 + 2\ H_2SO_4 \rightleftharpoons NO_2^+ + 2\ HSO_4^- + H_3O^+$$

and the formation of nitronium acetate

$$HNO_3 + AcOH \rightleftharpoons AcONO_2 + H_2O.$$

Thus, the kinetic regularities of the thermal decomposition of dinitramide fit completely the general scheme of decomposition of other oxygen-containing acids, but the quantitative ratios of the reaction rate are different.

References

1. A. I. Kazakov, Yu. I. Rubtsov, G. B. Manelis, and L. P. Andrienko, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 2129 [*Russ. Chem. Bull.*, 1997, **46**, 2015 (Engl. Transl.)].
2. G. B. Manelis, in *26th INT Annual Conference of ICT "Pyrothechnics: Basic Principles, Technology, Application,"* Karlsruhe, 1995, 15.1.
3. A. I. Kazakov, Yu. I. Rubtsov, G. B. Manelis, and L. P. Andrienko, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 395 [*Russ. Chem. Bull.*, 1998, **47**, No. 3 (Engl. Transl.)].
4. S. G. Entelis and R. P. Tiger, *Kinetika reaktsii v zhidkoi faze* [*Kinetics of Liquid-Phase Reactions*], Khimiya, Moscow, 1973, 416 pp. (in Russian).
5. C. H. Rochester, in *Acidity Functions*, Academic Press, London—New York, 1970, 300.
6. V. A. Shlyapochnikov, N. O. Cherskaya, O. A. Luk'yanov, V. P. Gorelik, and V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1610 [*Russ. Chem. Bull.*, 1994, **43**, 1522 (Engl. Transl.)].
7. B. L. Korsounskii, L. Ya. Kiseleva, V. I. Ramushev, and F. I. Dubovitskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 1778 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1974, **23** (Engl. Transl.)].
8. G. B. Manelis, G. M. Nazin, Yu. I. Rubtsov, and V. A. Strunin, *Termicheskoe razlozhenie i gorenie vzryvchatykh veshchestv i porokhov* [*Thermal Decomposition and Combustion of Explosives and Propellants*], Nauka, Moscow, 1996, 101 pp. (in Russian).

Received April 14, 1997