# Kinetics of thermal decomposition of dinitramide
## 1.* Decomposition of different forms of dinitramide

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Kinetic regularities of thermal decomposition of dinitramide in aqueous and sulfuric acid solutions were studied in a wide temperature range. The rate of the thermal decomposition of dinitramide was established to be determined by the rates of decomposition of different forms of dinitramide as the acidity of the medium increases: first, $N(NO_2)^-$ anions, then $HN(NO_2)_2$ molecules, and finally, protonated $H_2N(NO_2)_2^+$ cations. The temperature dependences of the rate constants of the decomposition of $N(NO_2)^-$ ($k_{an}$) and $HN(NO_2)_2$ ($k'_{ac}$) and the equilibrium constant of dissociation of $HN(NO_2)_2$ ($K_a$) were determined: $k_{an} = 1.7 \cdot 10^{17} \exp(-20.5 \cdot 10^3/T)$, s$^{-1}$, $k'_{ac} = 7.9 \cdot 10^{16} \exp(-16.1 \cdot 10^3/T)$, s$^{-1}$, and $K_a = 1.4 \cdot 10 \exp(-2.6 \cdot 10^3/T)$. The temperature dependences of the decomposition rate constant of $H_2N(NO_2)_2^+$ ($k_d$) and the equilibrium constant of the dissociation of $H_2N(NO_2)_2^+$ ($K_d$) were estimated: $k_d = 10^{12} \exp(-7.9 \cdot 10^3/T)$, s$^{-1}$ and $K_d = 1.1 \exp(6.4 \cdot 10^3/T)$. The kinetic and thermodynamic constants obtained make it possible to calculate the decomposition rate of dinitramide solutions in a wide range of temperatures and acidities of the medium.

**Key words:** kinetics, thermal decomposition, dinitramide.

Several works[1–4] devoted to the synthesis and study of different dinitramide salts have recently been published. The method for the preparation of dinitramide has been described,[1] and it has been established that dinitramide is a mobile liquid, which is decomposed in several minutes with self-warming and generous evolution of gaseous products. Sometimes the decomposition is accompanied by explosion.

At the same time, the available data[5,6] on the kinetics and mechanism of the thermal decomposition of the ammonium salt of dinitramide show that this salt is sufficiently stable thermally even at elevated temperatures, *i.e.*, the $N(NO_2)_2^-$ anion is considerably more stable than the dinitramide molecule. For all previously studied ammonium salts, it has been established[7] that their thermal decomposition occurs *via* the preliminary equilibrium dissociation of the salt to ammonia and the acid, and the rate of the thermal decomposition is determined by the acid concentration and the rate constants of its decomposition or interactions with other ions or molecules in the system. A reliable evaluation of the role of dinitramide in the thermal decomposition of its onium salts requires quantitative data on the rate constants of the thermal decomposition of the dinitramide anions and molecules and the rate constants of the interaction of dinitramide with other components of the reacting system.

In this report, we considered the laws governing the thermal decomposition of different forms of dinitramides, which are present in solution, in a wide range of acidities.

## Experimental

Dinitramide was synthesized by the reaction of $KN(NO_2)_2$ with dry HCl according to the previously described procedure.[1] All operations on the preparation of dinitramide and subsequent preparation of kinetic experiments were carried out in a dark room.

We attempted to study the kinetics of heat release of pure dinitramide with small weighed samples using a microcalorimeter, but even for a weight of 30 mg and less at 10—20 °C 10—15 min after the explosion occurs followed by the deformation of the aluminum ampule of the calorimeter. Thus, to perform the experiments under isothermic conditions, one should decrease sharply the rate of heat release per volume unit, which can be achieved by using rather dilute solutions. It is difficult to select an organic aprotic solvent due to the high reactivity of dinitramide; therefore, we decided to study aqueous solutions in which dinitramide molecules are ionized to a great extent, but the corresponding positions of equilibrium can be calculated with sufficient accuracy.

The concentration of the solution obtained was determined by alkalimetric titration of the acid or spectrophotometric analysis of the content of the $N(NO_2)_2^-$ ions. The coincidence was good within the accuracy of the spectrophotometric analy-

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* In this series of articles, we report the results of studies of the thermal decomposition of dinitramide performed in 1974—1978 and not published previously.

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sis, and the analytical concentration of dinitramide in the solution was determined rather reliably. Aqueous solutions with concentrations of 0.01—3.78 mol.% $HN(NO_2)_2$ were obtained.

The kinetics of the thermal decomposition of $HN(NO_2)_2$ in solutions was studied by measurements of the rate of heat release on a dynamic microcalorimeter in evacuated, sealed, and completely thermostatted glass ampules with an inner volume of ~2 $cm^3$. This made it possible to study the solutions without noticeable changes in the composition at temperatures substantially higher than their boiling point and to retain all the decomposition products in the system and study their effect. Under the experimental conditions, not more than 9% water and 0.1% dinitramide contained in the liquid phase could pass to the gas phase. Since there are no grounds to suppose than the rate of the decomposition of the $HN(NO_2)_2$ molecules increases substantially on going from the liquid to gas, the rate of the gas-phase reaction can be neglected under these conditions.

The decomposition of aqueous solutions of $NH_4N(NO_2)_2$ and $KN(NO_2)_2$ containing 0.18—40.07 mol.% $H_2SO_4$ was studied to investigate the rate of the thermal decomposition in media with a higher acidity. Since a decrease in the acidity of the medium results in a considerable increase in the reaction rate, we decreased the temperature of the experiments to retain the range of decomposition rates convenient for the measurements (temperature range 9.0—150.8 °C, concentration of salt 0.1—0.3 mol $L^{-1}$).

When the concentration of $H_2SO_4$ was lower than 25.45 mol.%, the experiments were carried out in the same way as for aqueous solutions. In the acid with a high concentration, the decomposition rate is sufficiently high at room temperature, and the preparation of the sealed ampule outside the calorimeter would lead to the cessation of a considerable part of the reaction before measurements. Therefore, the experiments were performed in ampules some of whose parts were outside the calorimeter. At first, the acid was placed in the ampule, and when the acid reached the temperature of the calorimeter, a salt pellet was introduced, and the mixture was rapidly stirred with a vertical stirrer, after which the ampule was closed from the top. This ampule is thermostatted only partially, but since the temperature of the experiments was not higher than that of the environment, no condensation of products occurred on the outside part of the ampule.

The $pK_a$ values of dinitramide in the medium of $H_2SO_4$ were determined spectrophotometrically measuring the ratios of the concentrations of the ions to neutral molecules in the solutions of $H_2SO_4$ with the exactly known value of the acidity function $H_0$.[8] The concentration of the anions was determined at $\lambda$ = 285 nm, and the concentration of dinitramide was calculated from the difference in the optical densities of an aqueous solution and a solution in aqueous $H_2SO_4$. The value $pK_a$ = $-4.85\pm0.05$ was obtained. Direct measurement of the absorption of the $HN(NO_2)_2$ molecules is difficult, because solutions with complete protonation of the $N(NO_2)_2^-$ anions are rapidly decomposed already at ~20 °C.

## Results and Discussion

In the 100—150.8 °C temperature range, we studied the reaction in aqueous solutions containing 0.01—3.79 mol.% $HN(NO_2)_2$, which corresponds to the analytical concentration of $5.5 \cdot 10^{-3}$—2.70 mol $L^{-1}$. In dilute solutions, the kinetic curves are described by the equation of the first-order reaction, and when the concentration of $HN(NO_2)_2$ is much higher than 1.5 mol.%, the autoacceleration of the process begins. In this report, we analyzed only the initial decomposition rates corresponding to the initial composition. The values of the initial rate constants $k_1$ are presented in Table 1.

**Table 1.** Rate constants ($k$) of decomposition of $HN(NO_2)_2$ in an aqueous solution

| $C$ (mol.%) | $T$/°C | $k \cdot 10^6/s^{-1}$ | $C$ (mol.%) | $T$/°C | $k \cdot 10^6/s^{-1}$ |
|---|---|---|---|---|---|
| 0.01 | 150.8 | 340 | 1.45 | 115.8 | 26 |
| 0.02 | 150.8 | 670 | 1.80 | 105.9 | 10 |
| 0.06 | 150.8 | 990 | 2.26 | 105.9 | 22 |
| 0.06 | 150.8 | 700 | 2.63 | 100 | 14 |
| 0.12 | 150.8 | 1000 | 2.63 | 103.2 | 12 |
| 0.17 | 150.8 | 1220 | 2.63 | 105.9 | 24 |
| 0.35 | 100 | 1.0 | 26.3 | 110.8 | 33 |
| 0.35 | 103 | 3.3 | 26.3 | 115.8 | 53 |
| 0.35 | 110.8 | 6.0 | 3.05 | 105.9 | 43 |
| 0.35 | 115.8 | 11 | 3.43 | 105.9 | 64 |
| 1.45 | 100 | 4.2 | 3.79 | 100 | 19 |
| 1.45 | 103.2 | 5.6 | 3.79 | 105.9 | 77 |
| 1.45 | 105.9 | 8.3 | 3.79 | 110.8 | 150 |
| 1.45 | 110.8 | 15 | 3.79 | 115.8 | 190 |

Since both nondissociated molecules and the $N(NO_2)_2^-$ anions participate in the decomposition reaction of aqueous solutions of $HN(NO_2)_2$, it was important to evaluate the contribution of each of these species. For this purpose, we obtained the kinetic curves of the decomposition of an aqueous solution of $KN(NO_2)_2$ (2.35 mol.%) at 96.5—159.8 °C. These curves are described by the equations of the first-order reaction, and the rate constants obtained are presented below.

| $T$/°C | 96.5 | 99.7 | 102.6 | 104.8 | 106.5 | 110.8 | 159.8 |
|---|---|---|---|---|---|---|---|
| $k \cdot 10^7/s^{-1}$ | 2.3 | 5.9 | 6.2 | 13 | 20 | 15 | 2600 |

In a solution of $HN(NO_2)_2$ (3.05 mol.%) at 106.2 °C, we studied the kinetics of the consumption of the $N(NO_2)_2^-$ anions and the change in the content of the $H_3O^+$ ions as compared to the depth of decomposition determined from the heat release. Up to the moment of cessation of the heat release, the content of the $H_3O^+$ ions decreased only by 10%, *i.e.*, the main decomposition product in the solution is nitric acid. The IR spectroscopic study shows that only nitrous oxide is present in the gas phase, *i.e.*, the stoichiometric equation of the decomposition mainly has the form

$$HN(NO_2)_2 = HNO_3 + N_2O.$$

Aqueous solutions of dinitramide are characterized by a high degree of ionization:

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

The starting molecules and ions that formed in the solution are hydrated by water molecules. The changes in the concentrations of both the $HN(NO_2)_2$ molecules and the $N(NO_2)_2^-$ anions contribute to the observed decomposition rate constant. Very dilute solutions (≤0.03 mol.%) almost always do not contain the $HN(NO_2)_2$ molecules, and the rate constants for the decomposition of $KN(NO_2)_2$, $NH_4N(NO_2)_2$, and $HN(NO_2)_2$ coincide.

Since in all studied solutions of dinitramide $C_{HN(NO_2)_2} \ll C_{N(NO_2)_2^-}$, the concentration of the anions is almost equal to the analytical concentration of the acid. In the general case, the initial rate of the consumption of the anions can be written as follows:[9]

$$(\mathrm{d}C/\mathrm{d}t)_{t=0} = k_{\mathrm{an,g}}(C_{\mathrm{an}}\gamma_{\mathrm{an}})^n/\gamma_{\mathrm{an}}^{\neq} + k_{\mathrm{ac,g}}(C_{\mathrm{ac}}\gamma_{\mathrm{ac}})^m/\gamma_{\mathrm{ac}}^{\neq}, \quad (1)$$

where $k_{\mathrm{an,g}}$ and $k_{\mathrm{ac,g}}$ are the rate constants of the decomposition of the anions and acid in the gas phase; $C_{\mathrm{an}}$ and $C_{\mathrm{ac}}$ are the concentrations of the anions and acid; $n$ and $m$ are the reaction orders with respect to the anions and acid; $\gamma_{\mathrm{an}}$, $\gamma_{\mathrm{ac}}$, $\gamma_{\mathrm{an}}^{\#}$, and $\gamma_{\mathrm{ac}}^{\#}$ are the activity coefficients of the anions, acid, and the corresponding activated complexes. Taking into account $k_{\mathrm{an}} = k_{\mathrm{an,g}}\ \gamma_{\mathrm{an}}^n/\gamma_{\mathrm{an}}^{\#}$ and $k_{\mathrm{ac}} = k_{\mathrm{ac,g}}\ \gamma_{\mathrm{ac}}^n/\gamma_{\mathrm{ac}}^{\#}$ ($k_{\mathrm{an}}$ and $k_{\mathrm{ac}}$ are the decomposition rate constants in the liquid phase),[9] we have

$$(\mathrm{d}C/\mathrm{d}t)_{t=0} = k_{\mathrm{an}}C_{\mathrm{an}}^n + k_{\mathrm{ac}}C_{\mathrm{ac}}^m. \quad (2)$$

The reaction order and kinetic parameters of the ion decomposition were determined from the analysis of the kinetics curves of the decomposition of dilute solutions of $KN(NO_2)_2$ and $NH_4N(NO_2)_2$. The decomposition of these solutions obeys the kinetic law of the first-order reaction, and the following temperature dependence was obtained for $k_{\mathrm{an}}$:

$$k_{\mathrm{an}} = 1.7 \cdot 10^{17} \exp(-20.5 \cdot 10^3/T),\ \mathrm{s}^{-1}.$$

The concentration of the nondissociated $HN(NO_2)_2$ molecules in aqueous solutions was estimated from the correlation

$$C_{\mathrm{ac}} = C_0/(1 + 10^{H_0 - \mathrm{p}K_a}), \quad (3)$$

where $H_0$ is the acidity function of the solution of the acid and $C_0$ is its overall initial concentration. The $H_0$ values for solutions of $HN(NO_2)_2$ were not determined, but in the concentration range studied, the acidity functions for all strong acids are close and depend mainly on the activity of the $H_3O^+$ ions. The $H_0$ values for solutions of $H_2SO_4$ with equal molar concentrations were used.[8] In all the studied concentration and temperature ranges, taking into account the rate of the decomposition of the anions, we obtained a first-order equation with respect to the concentration of the $HN(NO_2)_2$ molecules. The temperature dependence of $k_{\mathrm{ac}}$ has the form

$$k_{\mathrm{ac}} = 3.3 \cdot 10^{14} \exp(-13.7 \cdot 10^3/T),\ \mathrm{s}^{-1}.$$

When dinitramide salts are dissolved in $H_2SO_4$, their anions are protonated to form dinitramide molecules

$$N(NO_2)^- + H^+ \rightleftharpoons HN(NO_2)_2,\ K_a = a_{H^+} \cdot a_{\mathrm{an}}/a_{\mathrm{ac}}, \quad (4)$$

and the dinitramide molecules are further protonated to form their protonated form:

$$HN(NO_2)_2 + H^+ \rightleftharpoons H_2N(NO_2)_2^+,\ K_d = a_{H^+} \cdot a_{\mathrm{ac}}/a_{\mathrm{d}}. \quad (5)$$

In the general case, in these solutions the initial rate of decomposition under the assumption of a first-order reaction of the decomposition of $H_2N(NO_2)_2^+$ has the form

$$-(\mathrm{d}C/\mathrm{d}t)_{t=0} = k_{\mathrm{an}}C_{\mathrm{an}} + k'_{\mathrm{ac}}C_{\mathrm{ac}} + k_{\mathrm{d}}C_{\mathrm{d}}, \quad (6)$$

where $k'_{\mathrm{ac}}$ is the rate constant of decomposition of the dinitramide molecules in sulfuric acid solutions and $k_{\mathrm{d}}$ and $C_{\mathrm{d}}$ are the rate constant of decomposition and the concentration of the protonated $H_2N_3O_4^+$ form. In its turn,

$$k_{\mathrm{d}} = k_{\mathrm{d,g}} \cdot \gamma_{\mathrm{d}}/\gamma_{\mathrm{d}}^{\neq}, \quad (7)$$

where $k_{\mathrm{d,g}}$ is the rate constant of decomposition of the protonated form in gas and $\gamma_{\mathrm{d}}$ and $\gamma_{\mathrm{d}}^{\#}$ are the activity coefficients of the protonated form and activated complex, respectively.

The contribution of each term to the overall reaction rate is determined by the rate constant of decomposition of the corresponding form and the acidity of the medium, which determines the concentration of this form. Solving the system of equations (4) and (5) under the assumption that the initial concentration of the salt is low and does not change the activity of the hydroxonium ions and using the expression for the acidity of the medium $h_0 = a_{H^+}\gamma_B/\gamma_{BH^+}$, one can obtain expressions for the concentrations of the anions, molecules, and protonated form of dinitramide. Three regions of the acidity of solutions of $H_2SO_4$ likely should exist, where the rate of the decomposition of the dissolved dinitramide salt is determined by the rate of the decomposition of only one equilibrium form: $N(NO_2)_2^-$, $HN(NO_2)_2$, or $H_2N(NO_2)_2^+$. The decomposition rate of the anions is determining when $H_0 \ll \mathrm{p}K_a$ and dinitramide is present almost solely in the form of anions. The decomposition rate is independent of the acidity function of the solution $H_0$ and described by the first term of Eq. (6). As the acidity of the medium increases, the concentration of the $HN(NO_2)_2$ molecules increases and that of $H_2N(NO_2)_2^+$ is still infinitesimally low. Then, beginning from some $H_0$ value, the decomposition rate is determined by the rate of the decomposition of the $HN(NO_2)_2$ molecules. In this region, the concentration of $HN(NO_2)_2$ and the decomposition rate increase linearly as the acidity of the system increases:

$$-(\mathrm{d}C/\mathrm{d}t)_{t=0} = k'_{\mathrm{ac}}C_0h_0/K_a. \quad (8)$$

The concentration of the protonated dinitramide molecules increases proportionally to the square of the acidity, and the concentration of the $HN(NO_2)_2$ molecules increases proportionally to $h_0$; therefore, beginning from some $h_0$ value, the decomposition of the protonated form of dinitramide becomes rate-determining, and the expression for the initial rate has the form

$$-(dC/dt)_{t=0} = k_d C_0 h_0^2/(K_a K_d). \qquad (9)$$

In this acidity range, a second order of the reaction with respect to the acidity of the medium should be observed.

When the acidity further increases, the determining role of the decomposition of $H_2N(NO_2)_2^+$ is retained, the concentration of the $N(NO_2)_2^-$ anions becomes low, equilibrium (4) already does not play a substantial role, $C_{HN(NO_2)_2}$ is almost constant and close to $C_0$, $C_{H_2N(NO_2)_2^+}$ is determined only by equilibrium (5), and the expression for the rate has the form

$$-(dC/dt)_{t=0} = k_d \cdot C_0 \cdot h_0/K_d, \qquad (10)$$

*i.e.*, the first order with respect to the acidity of the solution should be observed again. When a high degree of protonation of the $HN(NO_2)_2$ molecules is achieved and the content of these molecules can be neglected, the concentration of the protonated form becomes constant, and the reaction rate should be independent of the acidity.

The dependences of the experimental rate constant of decomposition of the solutions on $H_0$ at different temperatures are shown in Fig. 1. The $H_0$ values for the solutions of $H_2SO_4$ at these temperatures are calculated from the corresponding dependences.[10] The transition from the decomposition of the $HN(NO_2)_2$ molecules to the decomposition of the protonated form (dependence *4*) and the change of the second order with respect to the acidity of the medium by the first order for the decomposition of the protonated form (dependence *6*) are pronounced. The region in which the $HN(NO_2)_2$ molecules are completely protonated is not achieved, because in this region the decomposition rates are too high. The linear dependence of log*k* on $H_0$ observed experimentally indicates that, first, the values of the $k_{an}$, $k_{ac}'$, and $k_d$ rate constants and, hence, the ratios of the activity coefficients, which enter these values (according to correlations (1) and (7)) remain unchanged in the whole studied range of the $H_2SO_4$ concentrations and, second, the $H_0$ function plotted from the data for primary nitroanilines is appropriate for the description of the protonation of the anion and nitramide molecule.

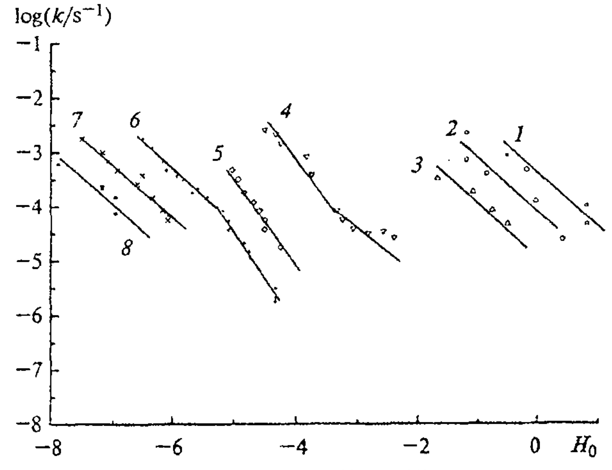

**Fig. 1.** Dependences of log*k* on $H_0$ at different temperatures, *T*/°C: 158.8 (*1*); 136 (*2*); 121.4 (*3*); 83.3 (*4*); 30.6 (*5*); 20.7 (*6*); 3.7 (*7*); and −1.1 (*8*).

The following dependences were obtained from experiments at different temperatures and correlations (8) and (9) taking into account the temperature dependence of $H_0$:

$$k'_{ac}/K_a = 5.7 \cdot 10^{15} \exp(-18.6 \cdot 10^3/T),\ s^{-1}, \qquad (11)$$

$$k_d/(K_d K_a) = 6.6 \cdot 10^{10} \exp(-16.9 \cdot 10^3/T),\ s^{-1}, \qquad (12)$$

$$k_d/K_d = 9.1 \cdot 10^{11} \exp(-14.3 \cdot 10^3/T),\ s^{-1}. \qquad (13)$$

Comparison of Eqs. (12) and (13) gives

$$K_a = 1.4 \cdot 10 \exp(2.6 \cdot 10^3), \text{ at } 20\ ^\circ C\ K_a = 10^{4.99}.$$

The latter value and the spectroscopically determined $K_a = 10^{4.35}$ coincide within the experimental and calculation accuracies. From correlation (11), using the expression obtained for $K_a$, for the solution of $H_2SO_4$ we have

$$k'_{ac} = 7.9 \cdot 10^{16} \exp(-16.1 \cdot 10^3/T),\ s^{-1}. \qquad (14)$$

These $k'_{ac}$ values are somewhat lower, and their temperature dependences are somewhat more pronounced than those for the previously obtained $k_{ac}$ values in aqueous solutions. These distinctions can be related to different degrees of solvation of the $HN(NO_2)_2$ molecules in aqueous and sulfuric acid solutions, since sulfuric acid competes with the dinitramide molecules for water molecules. In accordance with this fact, the reaction rate increases when the solution of $KN(NO_2)_2$ is diluted with water.

When the protonated $H_2N(NO_2)_2^+$ form was decomposed, values of acidity of the solutions close to or exceeding the $K_d$ value were not achieved, and this value was not determined. To obtain at least rough estimations of the rate constant of the decomposition of the protonated form $k_d$, the $K_d$ value was estimated from the comparison of the ionization constants of dihydric acids at the first and seconds steps. In the majority of cases, this difference at 20 °C is 4—5 orders of magnitude. We accepted the average value of 4.5. Then $K_d(20\ ^\circ C) = 3.3 \cdot 10^9$, and $k_d(20\ ^\circ C) = 2.0\ s^{-1}$. Based on the probable cyclic structure of the protonated form, we can assume that the pre-exponential for its transition state is equal to $10^{12}\ s^{-1}$. Then

$$k_d = 10^{12} \exp(-7.9 \cdot 10^3/T),\ s^{-1},$$

$$K_d = 1.1 \exp(6.4 \cdot 10^3/T).$$

The $k_{an}$, $k'_{ac}$, and $k_d$ values that allow one to compare the rate constants of decomposition of different forms of dinitramide at different temperatures are presented below.

| $T$/°C | $k_{an}$/s$^{-1}$ | $k'_{ac}$/s$^{-1}$ | $k_d$/s$^{-1}$ |
|---|---|---|---|
| 0 | $10^{-15.4}$ | $10^{-8.7}$ | $10^{-0.55}$ |
| 50 | $10^{-10.3}$ | $10^{-4.75}$ | $10^{1.4}$ |
| 100 | $10^{-6.6}$ | $10^{-1.85}$ | $10^{2.8}$ |
| 200 | $10^{-1.6}$ | $10^{2.1}$ | $10^{4.75}$ |
| 300 | $10^{1.7}$ | $10^{4.7}$ | $10^{6}$ |

The ratio of the real decomposition rates, except differences in rate constants, depends on the acidity of the medium and equilibrium constants of protonation $K_a$ and $K_d$ according to correlations (8)—(10).

The dependences of the overall rate constant of the decomposition of the dinitramide solutions on $H_0$ at 20 and 300 °C calculated from the above temperature dependences of the decomposition rates of its different forms are presented in Fig. 2. At 20 °C and $H_0 > 1.27$ (region I), the rate is determined by the rate of decomposition of the anions and is independent of $H_0$. In the range of $1.27 > H_0 > -1.9$ (region II), the decomposition of the $HN(NO_2)_2$ molecules is rate-determining, and the rate is proportional to the acidity of the medium. When the acidity further increases ($H_0$ decreases), in point *b* the leading role is transferred to the decomposition of the protonated form of dinitramide (region III) and, correspondingly, the second order with respect to the acidity of the medium is fulfilled. After reaching point *c* ($H_0 = -4.9$, $C_{an} = C_{ac}$), the acidity reaches the value at which $C_{ac} \gg C_{an}$, $C_{ac} >> C_d$, and the concentration of $H_2N(NO_2)_2{}^+$ is proportional to the first degree of acidity (region IV). The fact that it is proportional to the square of the acidity (region III) can be interpreted as the equilibrium interaction between two $HN(NO_2)_2$ molecules, for example, with the formation of anhydride and its subsequent decomposition. This mechanism takes place when aqueous solutions of perchloric[11] and nitric[12] acids are decomposed. However, in this case, the rate should be proportional to $C_0{}^2$, and the first order with respect to $C_0$ is observed in experiments. In addition, when $H_0 < pK_a$ (region IV), $C_{HN(NO_2)_2} \approx$ const and the rate of the bimolecular interaction of the $HN(NO_2)_2$ molecules should be constant, but in fact it increases due to the protonation of these molecules. Thus, the assumption that the reaction occurs through the interaction of two dinitramide molecules does not agree with the experimental data obtained.

When the temperature increases to 300 °C, the shape of the curve changes substantially due to the different temperature dependences of the decomposition rates and concentrations of different forms of dinitramide. Points *a* and *b* are shifted to higher acidity, because the activation energy of decomposition decreases when the anion and then the dinitramide molecule are protonated. At the same time, the position of point *c* is determined by the $K_a$ value, which decreases as the temperature increases, due to which point *c* is shifted to lower acidities. Therefore, region III narrows and at 220 °C should completely disappear. As the acidity of the medium increases, $C_{an}$ becomes substantially lower than $C_{ac}$, which is close to $C_0$, and the decomposition of the $HN(NO_2)_2$ molecules continues to determine the decomposition rate. Therefore, a plateau should appear on the dependence of log*k* on $H_0$, and in point *b* the leading role is again transferred to the decomposition of $H_2N(NO_2)_2{}^+$, and the first order with respect to the acidity is observed again. The data presented above show that at 300 °C all rate constants are very high, and under these conditions, isothermic calorimetric measurements are impossible. At the same time, these data can be important for the analysis of mechanisms of combustion and detonation of dinitramide in acidic media.

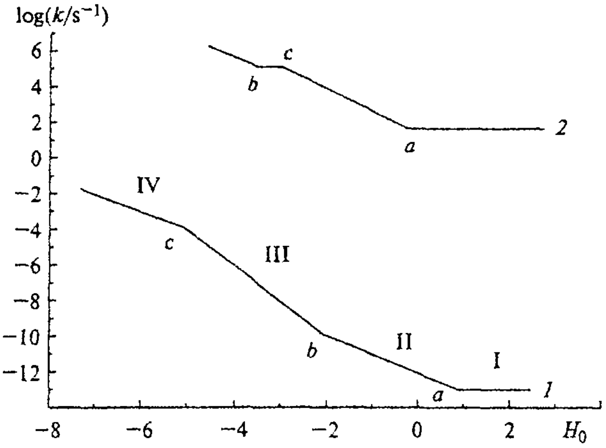

**Fig. 2.** Dependences of log*k* on $H_0$ at 20 (*1*) and 300 °C (*2*).

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