Thermal decomposition of ammonium dinitramide and mechanism of anomalous decay of dinitramide salts

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Thermal decomposition of ammonium dinitramide proceeds *via* homolytic rupture of the $N-NO_2$ bond and partially by the proton transfer reaction. The monomolecular decay of the anion to N_2O and NO_3^- in the solid state at 60 °C occurs with higher rates than those in the melt. This is related to a change in the reactivity of the anion due to the violation of its symmetry on going to the solid state. The absence of hydrogen bonds between the anion and cations or water molecules is an additional condition for the fast decay.

Key words: ammonium dinitramide, decomposition, solid phase, kinetics, reaction mechanism.

Ammonium dinitramide $NH_4^+N(NO_2)_2^-$ (ADN) is a promising high-energy oxidant for ecologically pure solid rocket fuels[1,2] and, hence, data on its thermal decomposition is of great interest. Previously,[1] the practical problems of thermal stability of ADN have been considered briefly, and the unique ability of ADN has been mentioned: the pronounced anomalous decay at temperatures of ~60 °C. The term "anomalous decay" has been introduced[1] to designate unusual effects observed during decomposition of dinitramide (DN) salts: an increase in the decomposition rate on going from the melt to the solid state and a negative effective activation energy within a narrow temperature range which is close, as found later, to the melting point of the eutectic mixture of the salt with nitrate of the corresponding cation. It has been shown in the later works[3,4] that the anomalous decay is characteristic of metal dinitramidates but was never observed for onium salts. In this respect, ADN is the exception, and a detailed study of this salt can provide a key for understanding of the mechanism of anomalous decay.

Experimental

The kinetics of thermal decomposition of ADN was studied by the manometric method, whose correctness was checked by spectrophotometric determination of the content of the $N_3O_4^-$ anion in the sample during decomposition. The spectral parameters of ADN in an aqueous solution are the following: λ_{max} = 283.5 nm, extinction coefficient $\varepsilon = 5600 \pm 100$ L mol^{-1} cm^{-1}. The reaction was carried out in 0.2—10-cm^3 glass vessels with crescent-like membranes, whose sensitivity can be varied from 0.1 to 5.0 Torr. The pressure was measured by the compensation method with a relative error not higher than 1%. The maximum degree of filling the vessel with the substance, (m/V_f)/g cm^{-3} (where m is the weighed sample, and V_f is the volume free of the substance), was 1. Higher m/V_f values were required at low temperatures to observe gas release at early stages of the reaction at the conversion of 0.01—0.10% and at high temperatures to carry out the whole reaction under a high pressure of the volatile and gaseous products. In this case, installations for pressures up to 100 atm were used.

To measure the deuterium isotope effect upon ADN decomposition, we synthesized $ND_4^+N(NO_2)_2^-$ samples enriched in deuterium by 95% by the exchange reaction with D_2O during three-fold evaporation of 10% solutions of ADN in D_2O followed by drying *in vacuo* at 50 °C for 3 h.

For convenience of comparison of the results of experiments performed at different temperatures and m/V_f values, all kinetic curves were plotted in $\Delta V-t$ coordinates, where ΔV is the volume of gaseous products released from 1 g of the substance in the t moment and referred to standard conditions (0 °C, 760 Torr).

To calculate the rate constants, the kinetic curves were processed by first-order or first-order autocatalytic equations. In the cases where the process was not described by these equations or only initial regions of the kinetic curves were obtained, the first-order rate constants of the primary stage of decomposition were calculated from the time of decomposition with conversion of 0.1 or 1%.

Gaseous reaction products were analyzed by GC. The content of water in ADN was determined by the Fischer method.

Results and Discussion

Decomposition in melt. At high free volume ($m/V_f < 10^{-4}$ g cm^{-3}) and temperatures >120 °C, the decomposition of ADN obeys the first-order law, and the process rates are independent of the presence of an ammonium nitrate admixture in ADN (Fig. 1). Four moles of gaseous products consisting of N_2O (~25 vol.%), N_2

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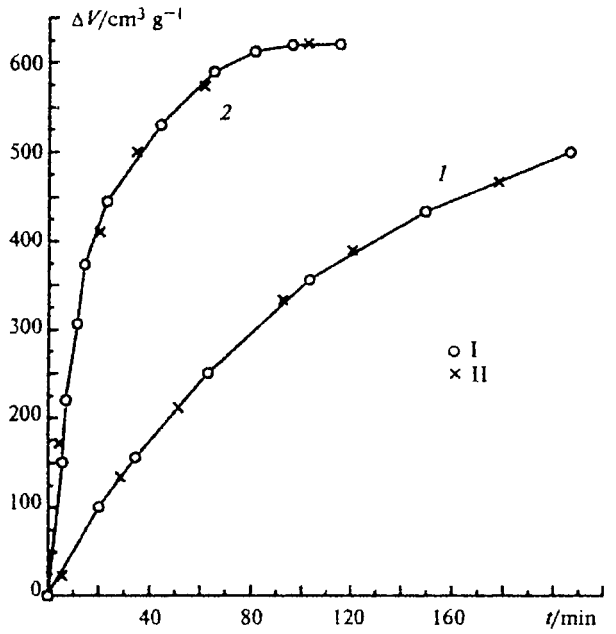

Fig. 1. Kinetic curves of ADN decomposition in melt at $m/V_f = 4 \cdot 10^{-4}$ g cm^{-3} and temperatures of 150 (*1*) and 170 °C (*2*). Content of ammonium nitrate in the samples: 0.3% (I) and 10% (II).

(~25 vol.%), and H_2O (~50%) were formed from 1 mole of the substance. NO and NO_2 were found in minor amounts. The first-order rate constant is described by the equation

$$k = 10^{14.4}\exp[-35500/(RT)]\ s^{-1}. \quad (1)$$

At 95—120 °C and $m/V_f > 0.01$ g cm^{-3}, the reaction has a pronounced autocatalytic character (Figs. 2 and 3), and gaseous or volatile products are the catalysts. This follows from two facts: first, the rates of the catalytic stage of decomposition depend on the m/V_f value (see Fig. 2); second, after evacuation of the gaseous products at the acceleration stage, the rates always decrease to the initial values. It was shown by direct methods that the decay can be accelerated by HNO_3 and NO_2. These both products, as well as water, are highly soluble in liquid ADN. The gas phase consists mainly of N_2O and N_2, and the ratio between these products changes strongly (Table 1). The character of the catalytic stage of decomposition also changes. The overall kinetic curve of the ADN decomposition at 104 °C and $m/V_f = 0.3$ g cm^{-3} is presented in Fig. 3. Before a conversion of about 10%, this curve is formally described by the first-order autocatalytic equation

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

where $\eta = \Delta V/\Delta V_\infty$ is conversion, $k_1 = 9.92 \cdot 10^{-7}$ s^{-1}, and $k_2 = 5.60 \cdot 10^{-4}$ s^{-1}. The ratio $k_2/k_1 = 564$; this implies that the rates of initial and catalytic stages are virtually equal already at 0.2% conversion. This conclusion agrees with the data in Fig. 2: at 100 °C, a linear region in the curves at different m/V_f is observed before 0.1—0.2% conversions only. After a 10% decomposition, the character of the catalytic stage changes (see Fig. 3). The curve calculated from Eq. (2) differs substantially from the experimental curve, which is described (after 15% decomposition) by the first-order equation

$$d\eta/dt = k_3(1 - \eta) \quad (3)$$

at $k_3 = 5.0 \cdot 10^{-5}$ s^{-1}. After a 15% decomposition, water, HNO_3, and N_2 stopped to form, and N_2O and NH_4NO_3 became the only products of ADN decomposition. Despite changes in the composition of the gas phase, the stoichiometric coefficient of the reaction remains unchanged and equal to 0.95—1.00 mole of products per mole of ADN, which corresponds to $\Delta V_\infty = 1.72$—1.80. The rate constants of the initial decomposition stage calculated from the time of 0.1% decay at 100, 105, and 115 °C fall well on the temperature dependence described by Eq. (1) (Fig. 4).

Autocatalysis makes it possible to stabilize ADN in the melt by binding the catalysts with chemical reagents. Experiments on ADN decomposition at 98—120 °C were carried out in the presence of different amines and salts

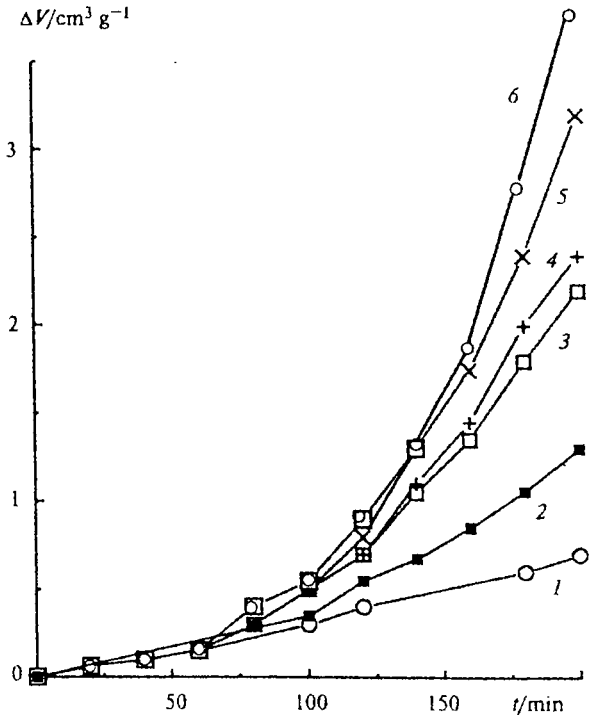

Fig. 2. Initial stages of decomposition of pure ADN samples (0.3% NH_4NO_3) at 100 °C and $m/V_f = 0.003$ (*1*), 0.024 (*3*), 0.08 (*4*), 0.24 (*5*), and 1.0 g cm^{-3} (*6*); *2*, ADN sample containing 10% NH_4NO_3 at $m/V_f = 0.1$ g cm^{-3}; experimental data are indicated by points.

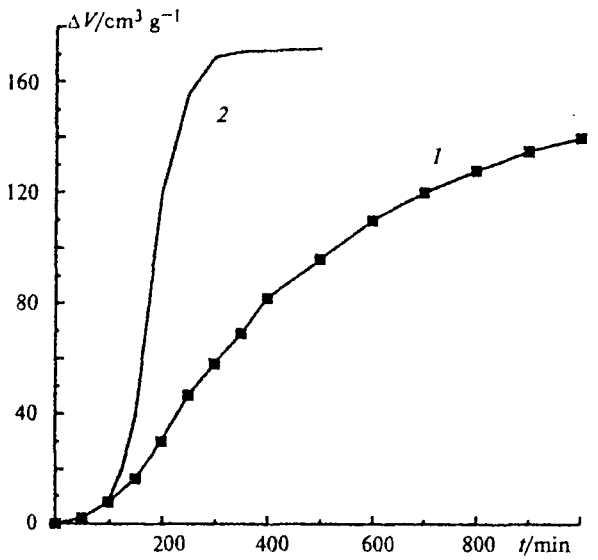

Fig. 3. Kinetic curves of ADN decomposition in the melt at 104 °C, m/V_f = 0.3 g cm^{-3}: *1*, experimental data; *2*, calculation from Eq. (2).

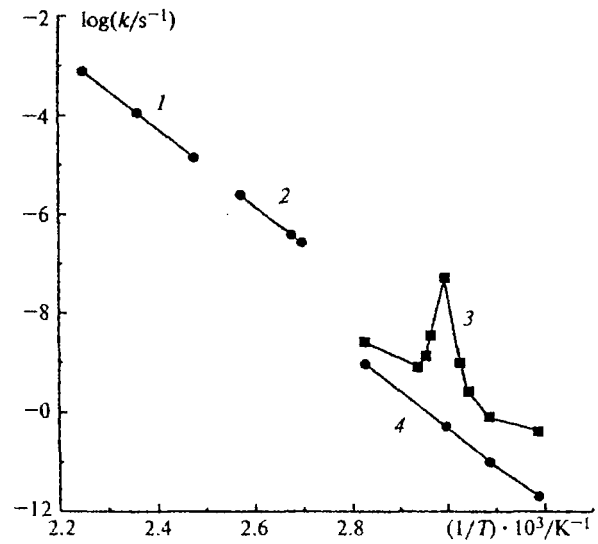

Fig. 4. Arrhenius dependences of the rate constant of the initial noncatalytic stage of ADN decomposition: *1*, melt, $m/V_f < 4 \cdot 10^{-4}$ g cm^{-3}; *2*, melt, $m/V_f > 0.1$ g cm^{-3}; *3*, solid phase, the sample contains 0.1% H_2O; and *4*, solid phase, the sample contains 0.5% H_2O.

of weak acids (NH_4F, K_3PO_4) capable of decreasing the acidity of the medium, as well as of substances of the nitrobenzene type that are readily oxidized by HNO_3 and NO_2 (the amount of an admixture is 1—3 mol.%). These compounds decrease the rates of the catalytic stage and increase the induction period by several times. In addition, strong bases (urotropin and ammonia) affect the initial stage approximately twice and decrease its rates. In experiments with deuterated ADN, the kinetic isotope effect $k_H/k_D = 1.38$ was observed for the rate constant of the initial stage.

Table 1. Composition of gaseous products of ADN decomposition in melt

T/°C	m/V_f /g cm^{-3}	η (%)	Content of product (%)			
			N_2	N_2O	H_2O	NO_2
104	0.3	2.5	43	53	Traces	Traces
104	0.3	3.8	30	66	The same	The same
104	0.3	4.8	28	68	»	»
104	0.3	100	10	90	»	»
170	10^{-4}	100	26	27	45	»

The results obtained can be explained by the reactions presented in Scheme 1.

Scheme 1

$$NH_4N(NO_2)_2 \longrightarrow NH_4^+ + NNO_2^{\cdot -} + NO_2 \quad (4)$$

$$NH_4N(NO_2)_2 \rightleftharpoons NH_3 + HN(NO_2)_2 \quad (5)$$

$$NNO_2^{\cdot -} + NO_2 \longrightarrow ONNO_2^{\cdot -} + NO \quad (6)$$

$$2\ ONNO_2^{\cdot -} \longrightarrow N_2O + NO_2^- + NO_3^- \quad (7)$$

$$NH_4^+ + NNO_2^{\cdot -} \longrightarrow NH_3 + \dot{H}NNO_2 \quad (8)$$

$$NH_4^+ + ONNO_2^{\cdot -} \longrightarrow NH_3 + \dot{H}ONNO_2 \quad (9)$$

$$HN(NO_2)_2 \longrightarrow HNO_3 + N_2O \quad (10)$$

$$\dot{H}NNO_2 \longrightarrow OH + N_2O \quad (11)$$

$$\dot{H}ONNO_2 \longrightarrow OH + 2\ NO \quad (12)$$

$$NH_3 + OH \longrightarrow NH_2 + H_2O \quad (13)$$

$$NH_3 + NO_2 \longrightarrow NH_2 + HNO_2 \quad (14)$$

$$NH_2 + NO \longrightarrow N_2 + H_2O \quad (15)$$

$$NH_2 + NO_2 \longrightarrow N_2O + H_2O \quad (16)$$

$$2\,HNO_2 \rightleftharpoons H_2O + NO + NO_2 \quad (17)$$

$$HNO_3 \longrightarrow NO_2 + 0.5\,H_2O + 0.25\,O_2 \quad (18)$$

$$2\,NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3 \quad (19)$$

$$NH_4N(NO_2)_2 + HNO_2 \rightleftharpoons NH_4NO_2 + HN(NO_2)_2 \quad (20)$$

$$NH_4N(NO_2)_2 + HNO_3 \rightleftharpoons NH_4NO_3 + HN(NO_2)_2 \quad (21)$$

$$NH_4NO_2 \rightleftharpoons N_2 + 2\,H_2O \quad (22)$$

$$2\,NO_2 \rightleftharpoons N_2O_4 \quad (23)$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \quad (24)$$

$$NO^+ + NH_4N(NO_2)_2 \rightleftharpoons NO^+N(NO_2)_2^- + NH_4^+ \quad (25)$$

$$NO^+N(NO_2)_2^- \longrightarrow N_2O + 2\,NO_2 \quad (26)$$

The initial decomposition of ADN occurs *via* two channels, which are the monomolecular decay of the anion at the N—N bond and dissociation of the salt to the base and acid. The first reaction is observed for decomposition of all DN salts with metals and strong bases.[3,4] The second channel is operative for onium salts with amines with a medium strength.[4] At least partial (not more than 50% at 100 °C) ADN decomposition through proton transfer is also favored by the kinetic isotope effect, inhibition of the initial stage by ammonia and strong acids capable of displacing ammonia from ADN, and finally, sublimation of ADN in open vessels *in vacuo*.

In the case of metal dinitramidates, reactions (6) and (7) (see Scheme 1) are the only routes of decay of primary radical anions formed after detachment of NO_2 from the anion.[5] For onium salts, proton transfer (in reactions (8) and (9)) competes successfully with these processes ($N_2O_2^{\cdot-}$ and $N_2O_3^{\cdot-}$ are stronger nucleophiles than $N_3O_4^{\cdot-}$), and NO_2 is accumulated in the system and then consumed in the oxidation of ammonia. Ion reactions proceed in the condensed phase, and the other reactions can occur in both the solution and gaseous phase.

At high m/V_f values, the products are dissolved in liquid ADN, equilibrium (19) is established (see Scheme 1), and HNO_2 and HNO_3 catalyze the decay. As NH_4NO_3 accumulates, the efficiency of catalysis decreases because of reversibility of reaction (21), and the decomposition occurs as a chain process (alternation of stages (21) and (10)) at the steady-state concentration of HNO_3. The stabilizing effect of ammonium nitrate was shown experimentally (see Fig. 2). The effect of NO_2 can be explained by the chain reaction (reactions (23)—(26)) that obeys the first-order rate equation.

Decomposition in the solid phase. The rates of decomposition in the solid phase were measured at 40—80 °C. The main data were obtained using the sample containing 0.3% NH_4NO_3 and 0.5% H_2O. The reaction proceeds with acceleration, which becomes noticeable after decomposition of 0.05% of the substance. The induction periods are long (120 h at 80 °C and ~100 days at 60 °C) and, hence, the autocatalytic stage was not studied in detail. N_2 (~10%) and N_2O are gaseous products of the decomposition. As at higher m/V_f in the liquid phase, 1 mole of ADN gives 1 mole of gaseous products (180 $cm^3\,g^{-1}$). The rate constant of decomposition in the solid phase (k_s) calculated from the rates in the linear region of the kinetic curve has the form

$$k_s = 10^{11.46}\exp[-33600/(RT)]\ s^{-1}.$$

Ammonia additives have no effect on the rates of decomposition of solid samples. The kinetic isotope effect observed at the liquid-phase decomposition of $ND_4N(NO_2)_2$ is absent in the solid phase. The channel of decomposition through the salt dissociation to the base and salt most likely is not significant in the solid phase.

Ammonium nitrate is present as an admixture in all ADN samples and forms eutectics with ADN with the composition NH_4NO_3 : ADN = 1 : 2 and m.p. 60 °C. The decomposition of ADN in the eutectic mixture occurs at 60—80 °C with the same rates as in the melt, *i.e.*, it is described by Eq. (1). Being chemically inert, ammonium nitrate affects the rates of decay *via* the melting mechanism. Due to the appearance of the liquid phase, whose fraction increases as the temperature increases (at 80 °C, the melt consists of 1 part of ammonium nitrate and 6 parts of ADN), the rates and activation energies of ADN decomposition within the 60—80 °C range should depend on the content of NH_4NO_3.

Water is the second admixture that is always present in ADN. Low amounts of water (below 0.5%) do not accelerate the decomposition. It exists, most likely, in the adsorbed state and forms no liquid phase in which ADN can be dissolved. However, already at 1% H_2O, the rates of ADN decomposition at 80 °C increases by 6 times.

The accelerating effect of water is due to dissolution of ADN. However, one more significant and anomalous phenomenon is related to the content of water in the ADN sample: the so-called anomalous decay, *i.e.*, an increase in the rates during decomposition of dry (~0.1% H_2O) samples *in vacuo* (a closed vessel, the initial pressure of 0.1 Torr) or in an inert atmosphere (N_2, dry air) higher than the decomposition rates in the liquid state.

As a whole, at 40, 50, 70, and 80 °C, an increase in the rates is low, but at 60 °C, *i.e.*, at the melting temperature of eutectics with nitrate, a very high peak of the rates was observed (see Fig. 4). The value of the peak depends on the method of drying and the degree of preliminary drying of the sample. For example, the ADN sample with the initial content of water equal to 0.65% was dried at 12, 24, or 52 h at 30 °C *in vacuo* (0.1 Torr) and then for 6 h more at 80 °C. The content of water decreased to 0.2, 0.12, 0.08, and 0.07%, and the decomposition rates at 60 °C increased by 1.4, 80, 900, and $8 \cdot 10^3$ times, respectively.

Admission of H_2O vapor (10 Torr) stops instantly the anomalous decomposition of these samples. Ammonia, methanol, acetone, NO, N_2O, and MeI act similarly but with a lower efficiency. These substances are characterized by the presence of the dipole moment and the ability to solvate charged particles.

The phenomenological description of the anomalous decay has been presented in the most complete form in Refs. 3 and 6 devoted to the study of metal dinitramidates. The properties of anomalous decay are an increase in the decomposition rates *in vacuo* to a higher level than in the liquid phase, the peak of the rates on the Arrhenius dependence in the melting point of the salt with nitrate of the corresponding metal, and instant inhibition by water vapor. Unlike metal salts, DN onium salts are not prone[4] to anomalous decay. In this respect, ADN occupies an intermediate position: it exhibits the anomalous decay only in the melting point of eutectics, and at other temperatures, the increase in the rates is low.

Based on the published data,[3,6] we can relate the appearance of the anomalous decay of DN salts with the nonsymmetrical geometric and electronic structure of the $N_3O_4^-$ anion in the crystal state.[7,8] When the nitro groups of the anion are nonequivalent, and the charge is concentrated predominantly on one of them, its reactivity increases, and a new fast channel of decay appears: elimination of NO_3^- with elimination of N_2O. The hydrogen bonds between the anion and H-containing cations or direct solvation by water molecules decrease polarization of the anion, smoothen its electronic asymmetry, and prevent intramolecular rearrangement.

Then it can be assumed that the nucleation of the eutectic phase leads to the local rearrangement of the crystalline lattice and the appearance of strains and new defects in the crystal. This can be reflected in the rates in the case where the reaction on the surface occurs much more rapidly than in the crystal bulk, which most likely takes place for the decay of metal dinitramidates noninhibited by water. The formation of eutectics for them is of greater significance if the occluded or crystallization water can be released in this process. It should be also assumed for ADN that the formation of eutectics is accompanied by the rapture of hydrogen bonds. A similar rupture of the H bonds should result at least in a minor rearrangement of the anion sublattice and, hence, can be observed by XDA. Thus, the mechanism suggested for anomalous decay can be checked by structural studies of ADN at 60 °C.

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