Stabilization of ammonium dinitramide in the liquid phase

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The kinetics of accumulation of the main products of thermal decomposition of ammonium dinitramide in the melt was investigated. The isotope composition of nitrogen-containing gases evolved by the decomposition of $^{15}NH_4N(NO_2)_2$ and $NH_4{}^{15}N(NO_2)_2$ was found. Easily oxidized salts, amines, amides, iodides, and other compounds soluble in the melt interfere with the liquid-phase decomposition of ammonium dinitramide.

Key words: ammonium dinitramide, thermal decomposition, kinetics, stabilization, isotope composition.

Ammonium dinitramide (ADNA) is a new high-energy oxidant for environmentally safe rocket fuels.[1—3] However, it ranks below traditional oxidants, *viz.*, octogen and ammonium perchlorate, in thermal stability. The temperature of the beginning of intense decomposition (T_{bid}) of ADNA is equal[3] to 135 °C, and slow decomposition observed by the evolution of gas bubbles from the melt begins immediately after melting.[4] Therefore, ADNA stabilization is an urgent problem.

Target search for inhibitors of ADNA liquid-phase decomposition requires the elucidation of the chemical nature of the processes that occur during its decomposition. With this purpose we studied the kinetics of ADNA catalytic decomposition from the accumulation of the main decomposition products.

To reveal the main routes of formation of nitrogen-containing gases, we synthesized two ADNA samples labeled with the ^{15}N isotope. In the first sample, the label was in the NH_4^+ cation, and the second sample contained the label in the central nitrogen atom in the $N(NO_2)_2^-$ anion.

Experimental

ADNA with the ^{15}N label in the cation was prepared by neutralization of a 2% solution of dinitramide (DNA) in diethyl ether with liquid ammonia $^{15}NH_3$ at −40 °C. Ammonia enriched in ^{15}N (97%) was used. The sample was washed with diethyl ether, recrystallized from isopropyl alcohol, and dried in a vacuum desiccator. ADNA with the label at the central N atom was synthesized from iminodipropionitrile $(NCCH_2CH_2)_2{}^{15}NH$, which was obtained by the reaction of acrylonitrile with $^{15}NH_3$. The sample was recrystallized from isopropyl alcohol and thoroughly dried. The content of the main substance with respect to the anion was at least 99.5% (spectrophotometric analysis).

Isotope analysis of nitrogen-containing gases evolved during the decomposition of the labeled samples at 120 °C (duration of the experiment was from 20 min (first probe) to 10 h) was carried out on an MS-10 mass spectrometer. The kinetics of N_2 and N_2O evolution was studied by the ampoule method. Weighed samples of ADNA (~0.5 g) were placed in ~5-cm^3 ampoules, which were evacuated, sealed, and stored at a specified temperature for a specified time. After the ampoules were unsealed, the gas phase was analyzed on an LKhM-80 chromatograph (column 3 m × 3 mm, active carbon modified with $NiSO_4$, helium as the carrier gas, 40 mL min^{-1}, heat transfer detector).

The kinetics of nitrate ion accumulation was studied by spectrophotometry after complete ADNA decomposition (first with lead ions in an alkaline medium and then with sulfaminic acid). The absorbance was measured in a maximum of the absorption band at λ = 206 nm, from which the background absorbance at λ = 284 nm was subtracted, and the nitrate ion

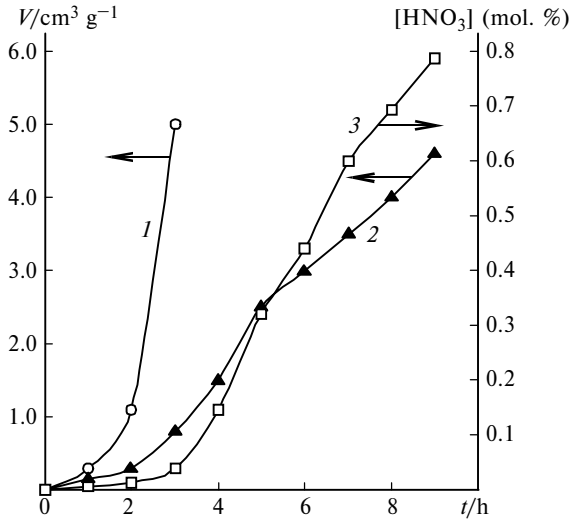

Fig. 1. Kinetic curves for evolution of N_2O (*1*) and N_2 (*2*) and accumulation of the acid (*3*) during ADNA decomposition (T = 100 °C, m/v = 0.1 g cm^{-3}).

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Table 1. Kinetics of ammonium nitrate (AN) accumulation and N_2O evolution during ADNA thermal decomposition (T = 100 °C)

Time/h	Volume of N_2O/cm^3 g^{-1}	Content of AN (wt.%)
0.5	0.11	0.4
1.0	0.27	0.7
1.5	0.62	1.0
2.0	1.11	1.5
2.5	2.50	2.1
3.0	4.50	2.6
3.5	5.50	3.0
4.0	12.10	6.8
4.5	20.20	8.1
5.0	24.00	8.5
5.5	27.50	11.0
6.0	28.60	12.0
6.5	32.40	15.8
7.0	35.10	17.3
7.5	35.60	19.4
8.0	45.90	20.5
8.5	44.20	21.2
9.0	47.50	21.4

content was determined from the calibration plot.[5] The relative error of determination was 10%.

The acidity of the residue after thermal decomposition was monitored with a pH-meter. The acid concentration was determined from the calibration plot pH *vs.* HNO_3 concentration in ADNA.

The results of analysis of the gas and condensed phases are presented in Fig. 1 and Table 1.

The thermal decomposition of ADNA mixtures with additives was studied by the manometric method using Bourdon glass-membrane gauges. The efficiency of stabilizers was evaluated from the induction period at 120 °C (Fig. 2) and the initial decomposition rate with a content of additives of 1 mol.% and 1 wt.% (Table 2).

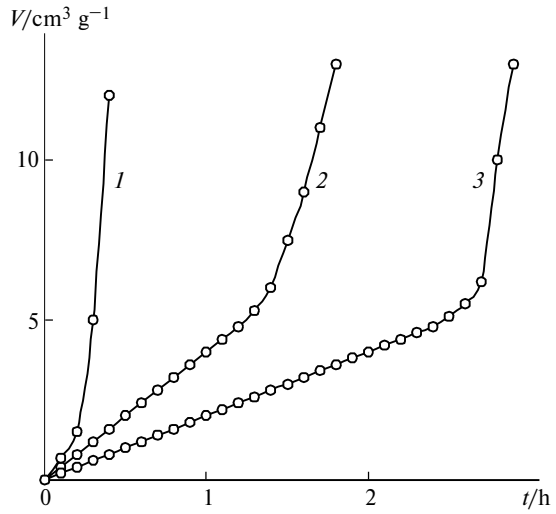
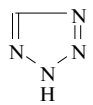
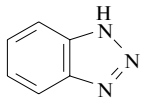
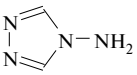


Fig. 2. Influence of stabilizers on ADNA thermal decomposition at T = 120 °C, m/v = 0.02 g cm^{-3}: starting sample (*1*) and samples containing 0.78 mol.% KBr (*2*) and 0.58 mol.% KI (*3*) additives.

Results and Discussion

Isotope analysis of the nitrogen-containing gaseous decomposition products of ADNA labeled with ^{15}N from the NH_4^+ cation showed the absence of the ^{15}N label in NO and N_2O. Therefore, these gases are formed upon the decomposition of the anion. The ^{15}N label was found in N_2 in the form of $^{15}N^{14}N$, and its fraction increased during the experiment from 40% at low conversions to 90% at complete ADNA decomposition. It can be assumed that N_2 is formed by the decomposition

Table 2. Influence of stabilizers on the thermal decomposition of the ADNA melt containing the additive of 1 mol.% (*A*) and 1 wt.% (*B*) (T = 120 °C, m/v = 0.02 g cm^{-3})

Stabilizer	W_0* /cm^3 g^{-1} h^{-1}	t**/min	
		A	*B*
No additives	6.0	5	5
Amines			
Ph_2NH	2.2	20	—
$(CH_2)_6N_4$ (urotropine)	1.8	240	210
m-$NO_2C_6H_4NH_2$	2.1	180	160
$NH_2C(=NH)NHNO_2$	6	5	—
Amides			
NH_2CONH_2	4.1	190	390
$NH_2CONHNH_2$	1.8	420	700
$NH_2NHCOCONHNH_2$	1.8	420	440
$MeCONH_2$	4.4	40	—
$NH_2C(=NH)NHCN$	2.5	160	240
Dinitramide salts			
$(CH_2)_6N_4 \cdot HN_3O_4$	3.0	140	75
$NH_2NHCOCONHNH_2 \cdot HN_3O_4$	2.5	270	150
$NH_2CONHNH_2 \cdot HN_3O_4$	4.5	150	100
$[Pb(NH_2CONHNH_2)_2](N_3O_4)_2$	1.9	300	75
$[Zn(NH_3)_4](N_3O_4)_2$	198	440	160
Other salts			
KI	2.3	250	190
$K_2Cr_2O_7$	2.5	110	—
KBr	4.0	240	250
$(CH_2)_6N_4 \cdot HI$	2.3	430	200
$(NH_4)_2SO_4$	2.3	180	180
Acids			
PhCOOH	3.5	16	—
p-$NH_2C_6H_4COOH$	199	270	240
Other additives			
PhOH	2.1	110	150
	5.0	30	—
	1.8	160	160
	2.1	330	480

* Initial decomposition rate.
** Induction period.

of the NH_4^+ cation in such a way that one N atom originates from the NH_4^+ cation, and the $N(NO_2)_2^-$ anion produces the second N atom.

In the decomposition of ADNA with a labeled central N atom, the ^{15}N label was found in N_2O, which evolved only in the form of $^{15}N^{14}NO$, and partially in N_2 and NO. The content of labeled N_2 and NO was only ~10% of the total content of these gases. These results can be explained within the framework of a scheme that agrees with the published data[6,7] on the mechanism of ADNA decomposition

$$^{15}NH_4N(NO_2)_2 \longrightarrow {}^{15}NN + NO + N_2O,$$

$$NH_4{}^{15}N(NO_2)_2 \longrightarrow N_2 + {}^{15}NNO + NO.$$

The ratio between N_2O and N_2 changes during decomposition. In the initial step their amounts are approximately the same. Then the rate of N_2O decomposition increases, and that of N_2 evolution remains unchanged for some time (see Fig. 1). The data on the kinetics of accumulation of the main decomposition products (see Table 1 and Fig. 1) and the results of isotope analysis suggest that the oxidation of the ammonium cation is responsible for the formation of N_2 and an autocatalyst, whereas N_2O and NH_4NO_3 are the products of the acid decomposition of the $N(NO_2)_2^-$ anion. Autocatalysis can also be eliminated by the introduction of readily oxidized compounds, which prevent the oxidation of the NH_4^+ cation. Based on these prerequisites, we tested different readily oxidized compounds: amines (both in the free state and in the composition of complex and onium DNA salts), amides, ammonium salts, iodides, and others (see Table 2). At the same molar content, compounds containing amino groups and iodides are the most efficient stabilizers. They decrease the initial decomposition rate 2—3-fold rather than increase considerably the induction period. The solubility of an assumed stabilizer in the ADNA melt plays an important role. For example, diphenylamine is insoluble in the melted oxidants and does not inhibit autocatalysis.

At the same weight content, semicarbazide, oxalyldihydrazide, aminotriazole, and urea are the most efficient stabilizers. According to the published data,[4,6,7] the stabilizing effect of amines is due to the suppression of ADNA decomposition *via* a dissociative mechanism. In our opinion, the stabilizing effect of amines and other additives is based on their ability to be oxidized by intermediate products of ADNA decomposition. Since amines can be oxidized by nitrogen oxides, their stabilizing effect can be related to the reduction ability of the amino groups rather than their basicity. Indeed, the experimental results show that when pK_a of amines changes by 5 units from urotropine (4.9) to dicyanodiamide (−0.4), the initial decomposition rate remains unchanged and amounts to ~2.0 $cm^3\ g^{-1}\ h^{-1}$ at 120 °C. Thus, the stabilization of the ADNA melt due to the oxidation of additives makes it possible to explain the influence of both amines and other readily oxidized compounds on the decomposition of the liquid oxidant.

The stabilizing effect of some readily oxidized compounds on the decomposition of the ADNA melt does not ensure their chemical compatibility with a solid oxidant. This is due to the fact that the decomposition rate of the solid ADNA sample is lower by two orders of magnitude than that of the liquid sample.

Therefore, the interaction of an additive with ADNA, which is imperceptible against the background of fast gas evolution from the melt, can become significant as compared to the low decomposition rate of the solid salt.

The stability of solid ADNA can be worsened due to the existence of low-melting eutectics with some compounds[5] because of the indicated difference between the rates of the solid and melted oxidant along with direct chemical interaction.

The results of the study of the interaction of some of the most efficient stabilizers with the solid oxidant at low temperatures will be published elsewhere.

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