Decomposition mechanism of dinitramide onium salts

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Thermal decomposition of dinitramide onium salts proceeds *via* the dissociative mechanism when pK_a of the base is lower than 5.0 and *via* the monomolecular decay of the anion at $pK_a > 7.0$. On going from the melt to the solid state, the reaction mechanism does not change, and the rate decreases by 1—2 orders of magnitude. No anomalous effects inherent in dinitramide metal salts in the solid phase are observed during decomposition of onium salts.

Key words: dinitramide, onium salts, thermal decomposition, kinetics, reaction mechanism.

When salts of dinitramide, $HN(NO_2)_2$ (DNA), are thermally decomposed, two reactions can occur as the initial stage: dissociation of the salt to the base and acid (*i.e.*, the normal decomposition pattern[1] for onium salts) and monomolecular decomposition of the anion, which is large, has a complicated structure, and hence, is not very stable.[2] It is precisely the monomolecular decomposition of the anion that is of greatest interest for onium salts, because unusual characteristics of the solid-phase transformation have been previously observed[2,3] for this reaction.

We established[2] for DNA metal salts that the spontaneous decomposition of the $N(NO_2)_2^-$ anion in the liquid and solid phases proceeds *via* different mechanisms. In the first case, the N—N bond is cleaved to yield NO_2, and in the second case, the anion is decomposed to N_2O and NO_3^-. The change in the mechanism is accompanied by a sharp increase in the rate of decomposition, which occurs in the solid phase hundreds and thousands of times more rapidly than in the melt. Water vapor inhibits strongly the solid-phase reaction, decreasing its rate to a lower level than that in the liquid phase. The increase in the reactivity of the anion was explained by the change in its structure from the symmetrical one in the liquid state to the nonsymmetrical structure with the nonequivalent charge distribution on nitro groups in the solid state.

We have also shown[2] that the DNA guanidinium salt exhibits no properties of anomalous decomposition. This can be explained in two ways: either the guanidinium salt differs from metal salts in the decomposition mechanism, or the anion in the crystal of this salt is weakly polarized, and equivalence of the nitro groups in it is not distorted. Both these explanations should be checked and stimulate studying the kinetics of decomposition of onium salts and the structure of their anion in the crystalline state.

In this work, to solve the first problem, we studied several DNA salts: hydrazinium (**1**), binary ethylenediammonium (**2**), trimethylammonium (**3**), guanidinium (**4**), anilinium (**5**), binary *o*-phenylenediammonium (**6**), tetramethylammonium (**7**), and tetra(*n*-butyl)ammonium (**8**) salts. The salts were selected in such a way that the decomposition rates in the solid and liquid phases could be measured for the same object (**2**, **4**, and **8**), the solid-phase reaction could be carried out *in vacuo* and in an atmosphere of air (difficultly volatile compounds **2**, **4**, **7**, and **8**), the effect of additives of the free base on the rate could be studied for strong and weak amines (**2**, **3**, and **5**), and the rate constants could be correlated with pK_a of the base of the cation in a wide range of pK_a (**1**—**6**). Based on these data, we can make conclusions on the mechanism of decomposition and anomalies of the solid-phase reactions.

Experimental

The known[4] reactions of exchange of ammonium sulfate with DNA potassium salt, $KN(NO_2)_2$, or neutralization of aqueous or aqueous-alcoholic solutions of bases with free DNA, which was obtained by passing an aqueous solution of $KN(NO_2)_2$ through a column with KI-2-8 cation-exchange resin in the H^+-form, were used to obtain the salts. The products were twice recrystallized from ethanol or aqueous isopropanol and dried over Anhydron.

The kinetics of decomposition in the liquid phase (melt) was studied manometrically. In the majority of cases, the reactions occur according to a first-order equation (Fig. 1). Weak acceleration is observed for compounds **8** and **2** (after 50% decomposition), and very strong acceleration is observed for compound **3**. In the case of the reactions with acceleration, the first-order rate constant (k) for the initial stage was calculated from the time of achieving 1% decomposition. The volume of gaseous products at the end of the reaction (ΔV_∞/cm^3 g^{-1}) brought to normal conditions (0 °C, 700 Torr) was accepted to be 100%. For all other substances, ΔV_∞ depends

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 1951—1953, November, 1997.

Table 1. Kinetic parameters of decomposition of onium dinitramide salts

Compound	M.p. /°C	pK_a of base	State[a] (p/Torr)[b]	T /°C	E/ kcal mol^{-1}	log$A$ /s^{-1}	$k \cdot 10^5$ /s^{-1} (160 °C)	k_l/k_s (160 °C)	ΔV_∞ /cm^3 g^{-1}
1	80	8.1	l	140—180	36.0	17.70	33.0	—	820
2	126	10.1	l	130—155	35.0	14.00	21.0		500
			s (0.1)	80—105	41.6	15.60	0.4	52.5	—
			s (760)	80—120	41.6	15.60	0.4	52.5	—
3	131.5	9.86	l	135—165	34.8	14.00	25.0		350
4	144	13.6	l	150—170	36.9	15.00	23.4		450
			s (760)[c]	95—140	40.0	14.20	0.1	234	—
5	99	4.58	l	135—160	32.0	13.55	245	—	420
6	118	4.37	l	120—150	30.0	12.50	224		500
7	230	—	s (0.1)	160—205	39.6	13.80	0.06		590
			s (760)	140—170	38.6	13.70	0.16		—
8	153	—	l	160—180	38.7	14.60	1.18		—
			s (0.1)	120—140	39.6	13.80	0.06	20	306

[a] l is liquid, s is solid. [b] The air pressure in the reaction vessel is shown in parentheses. [c] Data in Ref. 2.

slightly on temperature (within 10%), and the use of average ΔV_∞ values (presented in Table 1) does not introduce substantial errors to the calculation of k. The main uncertainty in the estimation of k from the time of 1% decomposition is related to a possible dependence of the yield of gaseous products on the degree of conversion. However, the data on the composition of the products, which are presented in Table 2, suggest that these changes are not great. The ΔV_∞ value can be affected by the pressure-dependent reactions of gaseous products and dissolution of the latter in the condensed phase. To standardize these processes, all experiments were carried out at the same degree of filling the vessel with a substance, $5 \cdot 10^{-4}$ g cm^{-3}.

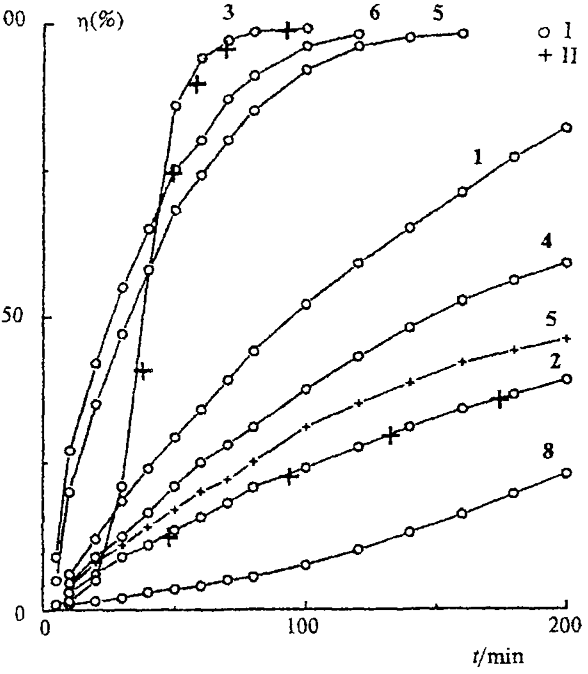

Fig. 1. Kinetic curves of decomposition of DNA onium salts in melt. Numbers of curves correspond to numbers of compounds at the temperature of the experiment of 140 (**2**, **3**, **5**, **6**), 150 (**1**, **4**), and 160 °C (**8**). I is the pure salt, II is 30 mol.% of the free base.

When solid salts were studied, the thermogravimetric procedure (a thermobalance with a sensitivity of 0.1 mg) was used along with the manometric procedure. The thermogravimetric method is convenient for reactions in a constant vacuum. The character of the solid-state decomposition is the same as that of the decomposition in the melt. Compounds **4** and **7** exhibit differences from the melt. The kinetic curves of these compounds (due to the beginning of melting) assume S-like shapes. The rate constants in manometric experiments were calculated in the same way as for the liquid phase. The ΔV_∞ values obtained in melt were used. To determine the relative mass loss $(\Delta m_t/\Delta m_\infty)$, the Δm_∞ values were determined in each experiment.

The obtained kinetic parameters of the decomposition of compounds **1**—**8** in the melt and in the solid phase are presented in Table 1.

The decomposition products of salts **2**, **4**, and **8** were analyzed. Fractionation of gases by freezing out, chromatographic determination of light gases (NO, N_2O, CO_2, and the CO + N_2 sum), and mass spectrometric analysis of products condensed at −78 °C were used for analyses. In the latter case, tubes evacuated at −78 °C and the whole injection system of the mass spectrometer were heated to 100 °C, and the quantitative (by calibrating curves) analysis of H_2O and the qualitative analysis of vapor of other products were performed. The data on the ratio of light gases are presented in Table 2. The

Table 2. Composition of light gases for decomposition of salts **2**, **4**, and **8**

Compound	State	T /°C	η (%)	Composition of light gases (%)				
				N_2+CO	NO	CO_2	N_2O	H_2O
2	l	135	15	32	—	3	56	9
	s	95	0.1	30	—	2	60	8
4	l	150	50	30	—	2	33	35
	s	120	0.1	28	—	6	20	46
8	l	160	1.0	25	5	6	38	26
	l	180	77	28	4	8	32	28
	s	140	0.4	30	12	8	26	24

condensed residue after the decomposition consists mainly of nitrate (but not nitrite) of the corresponding cation.

The products always contain noticeable quantities of the free base and products of the cleavage of cations along with light gases. For example, in the case of **4**, dicyan is formed, and Me_2NNO, MeCN, and $MeNO_2$ are formed from compound **4**. The maximum amount of organic products (less than 40%) is formed from compound **8**. At all stages, MeCN, $Bu^n{}_3N$, Bu^nOH, and butene-1 are observed.

Results and Discussion

It can be seen from Table 1 that the decomposition rates of salts **1—4** are close in the liquid phase, and their activation parameters are typical[2] of the decomposition of metal salts. Compounds **5** and **6** decompose 10 times more rapidly and compound **8** decomposes considerably more slowly than salts **1—4**. The addition of a free base does not affect the rate of decomposition of the salt of strong base **3** and decreases considerably the decomposition rate of compound **5** (pK_a of aniline is less than 5.0). The dependence of the rate constants of decomposition of **1—6** on pK_a of the base (Fig. 2) testifies that when $pK_a > 7$ the rate is independent of the basicity of amine, and when $pK_a < 5$ a sharp increase in the rate is observed. These data allow one to conclude that the mechanism of decomposition of DNA onium salts depends on pK_a of the salt-forming base. When $pK_a > 7$, the decomposition occurs, as for metal salts, *via* the cleavage of the N—N bond with the elimination of NO_2, and when $pK_a < 5$, the primary dissociation of the salt to the base and acid predominates. For the monomolecular decomposition of the anion, the difference from metal salts is only in the mechanism of secondary reactions. Instead of the disproportionation of the $O_2NN^{-\cdot}$ radical anion (which is a stronger nucleophile than $N(NO_2)^-{}_2$), the transfer of proton to this radical anion followed by the formation of the free base is possible. Instead of the oxidation of $O_2NN^{-\cdot}$ by nitrogen dioxide, in onium salts cations are oxidized. In salt **8**, at the second stage, the Hofmann reaction type cleavage of the cation occurs

$$\underset{\mathbf{8}}{Bu^n{}_3N^+(CH_2CH_2C_2H_5)\ N^{-\cdot}NO_2} \longrightarrow$$
$$\longrightarrow Bu^n{}_3N + HN^{\cdot}NO_2 + CH_2{=}CHCH_2CH_3.$$

The absolute values of the rate constants of decomposition of salts **1—4** are close to those of $KN(NO_2)_2$. Despite the large radii of organic cations, they affect the anion more strongly that Rb^+ and Cs^+ cations,[2] due likely to the mutual polarization with the anion. In tetraalkylammonium salts **7** and **8**, whose large cations are weakly polarized, their effect on the stability of the anion is very low, close to the upper stability boundary determined by the Rb^+ cation.[2]

On going from the melt to the solid state, the mechanism of the reactions remains unchanged: the composition of the products is retained, the activation energy changes slightly, and the decomposition rates in vacuum and in air are equal to one another and lower than those in the melt.

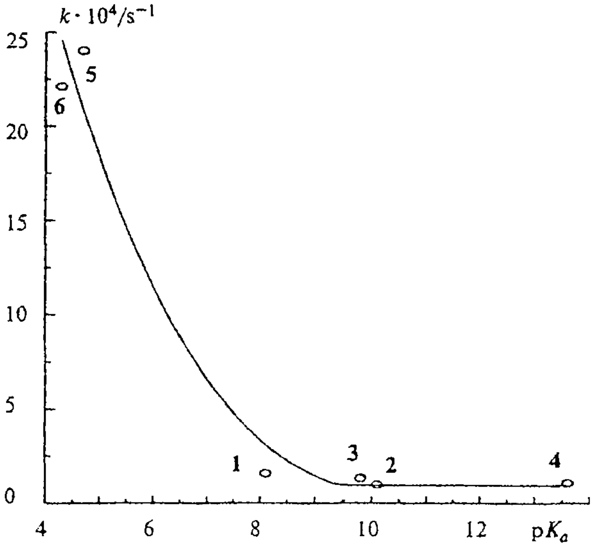

Fig. 2. Dependence of the rate constant of decomposition of DNA onium salts at 160 °C on pK_a of the base. Figures near points correspond to numbers of compounds (Table 1).

Thus, the anomalous decomposition is not inherent in onium salts. This is likely explained not by a change in the chemical mechanism of the reaction, but by the structure of the $N^-(NO_2)_2$ anion which differs (being more symmetrical) from those in metal salts. This hypothesis can be checked by X-ray diffraction studies.

This work was partially supported by the Russian Foundation for Basic Research (Project No. 95-03-09237a).

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Received April 2, 1997