Anomalous decomposition of dinitramide metal salts in the solid phase

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Unusual regularities are observed for decomposition of dinitramide metal salts in the solid phase: the solid-phase reaction is 10—10^3 times faster than that in the melt, its rate has a sharp peak in the region of eutectics melting with the decomposition product (metal nitrate), and it is instantly inhibited by water vapor. In the inhibited regime, the rate in the solid phase is lower than that in the liquid phase. No indications of this anomalous behavior are observed for the decomposition of the dinitramide guanidinium salt.

Key words: dinitramide, metal salts, thermal decomposition, solid-phase reactions.

It was found in the work[1] devoted to the study of the thermal decomposition of potassium dinitramide ($KN(NO_2)_2$) that on going from the melt to the solid state, the reaction rate does not decrease, as usually takes place for inorganic salts,[2] but, on the contrary, increases sharply. Water vapor inhibits the solid-phase reaction, and the decomposition of solid $KN(NO_2)_2$ in the inhibited regime is considerably slower than in the melt. The study of the mechanism of this unusual reaction, which was named the anomalous decomposition,[1] can be facilitated by a detailed phenomenological description and establishment of its scope and limitations among dinitramide (DNA) salts. Therefore, in this work, we studied the liquid- and solid-phase decomposition of several metal DNA metal salts and one onium salt, dinitramide guanidinium.

Experimental

DNA salts with Li^+, Na^+, Rb^+, Cs^+, Ba^{2+}, and $(NH_2)_3C^+$ cations were synthesized according to described procedures.[3,4] The products were twice recrystallized from ethanol or aqueous isopropanol and dried over Anhydron in a vacuum desiccator. These procedures rapidly decreased the water content to 0.2—0.4%, after which the drying process was sharply retarded. More drastic drying conditions down to 0.05% H_2O (60—70 °C, vacuum) are accompanied, as a rule, by the partial decomposition of the substance. Lithium and barium salts were synthesized as low-melting crystal hydrates. They were dehydrated to 0.5% H_2O by drying over P_2O_5 at ~20 °C in vacuum (0.01 Torr).

The decomposition rate was measured by manometric or gravimetric methods. The products were analyzed by GLC and mass spectrometry.

Like $KN(NO_2)_2$,[1,5] the composition of metal salts was simple and constant at different temperatures and degrees of conversion: solid salts yield 1 mole of N_2O, and liquid salts give 1 mole of NO + 0.5 mole of N_2O. This fact allows one to obtain rate constants from the initial regions of kinetic gas evolution curves with a high accuracy.

Decomposition of solid salts in a vacuum of 0.1 Torr (permanent pumping out) in an atmosphere of moist air or at a pressure of neat water vapor of 10—15 Torr was monitored by a thermobalance. In the last two cases, the reactions are slow, and the manometric procedure, which is more sensitive than weighing, was used to study the reaction. Due to the fast escape of residual water vapor, the conditions of decomposition in closed vessels correspond to the decomposition in an atmosphere of moist air.[1]

Rate constants of the liquid-phase decomposition at 100 °C were estimated to compare decomposition rate constants in the solid phase and in the melt. The extrapolation of data on decomposition[5,6] in the melt was used for alkaline salts (for $RbN(NO_2)_2$, these data were also obtained experimentally). In addition, the decomposition rates of $RbN(NO_2)_2$ in a low-melting eutectic mixture with rubidium nitrate were measured directly at 100 °C. For the barium salt, the parameters of the liquid-phase decomposition were determined from the decomposition of 10—25 mol.% solutions of Ba^{2+} in liquid $KN(NO_2)_2$. Ba^{2+} ions were introduced into $KN(NO_2)_2$ as barium nitrate. The observed rate constant of the decomposition of this mixture is described by the equation

$$k_{obs} = k(K^+)/[(1 + m_2M_1/m_1M_2)] + k(Ba^{2+})/[1 + (m_1M_2/m_2M_1)],$$

where m is the weighed sample and M is the molecular weight; index 1 refers to $KN(NO_2)_2$ and index 2 refers to $Ba(NO_3)_2$. The $k(K^+)$ value taken from Ref. 5 was used for the calculation of $k(Ba^{2+})$ from k_{obs}.

The formation of eutectics of DNA salts and the corresponding nitrates was studied by differential scanning calorimetry. Rubidium, cesium, and guanidinium salts give these eutectics with m.p. 84.5, 81.5, and 128 °C, respectively. The composition of the eutectic mixtures is the following: $RbN(NO_2)_2/RbNO_3 = 9/1$, $CsN(NO_2)_2/CsNO_3 = 9.5/0.5$.

Results and Discussion

The complete kinetic curves and initial regions of the mass loss curves for the decomposition of $RbN(NO_2)_2$

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and $CsN(NO_2)_2$ in a vacuum of 0.1 Torr at different temperatures are presented in Figs. 1—4. The reactions are characterized by a pronounced acceleration, which is typical of topochemical processes, and a very strong retention (this phenomenon appears as follows: after the process is complete, a considerable portion of the starting compound remains unconsumed). The rate peaks are observed in points of eutectic melting on the Arrhenius dependences of the rate constants (Fig. 5). All other metal salts have the same character of decomposition as $RbN(NO_2)_2$ and $CsN(NO_2)_2$, but they do not give eutectic mixtures with products and have no breaks on the temperature dependences of the rate constants (see Fig. 5).

The retention effect and rate peaks can be explained by one reason: localization of the reaction on the surface

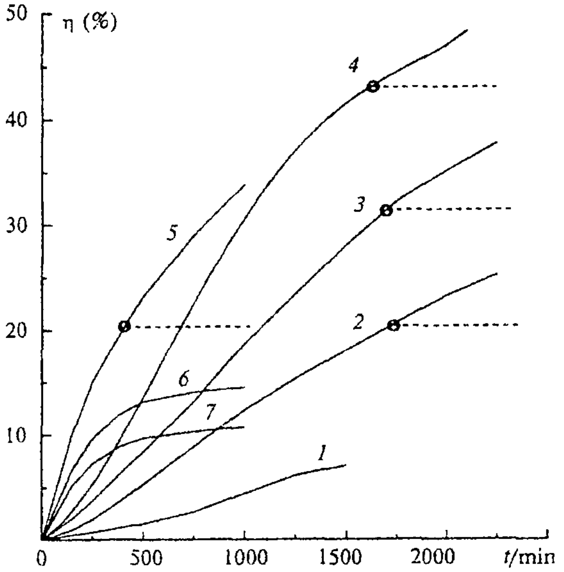

Fig. 1. Decomposition of $RbN(NO_2)_2$ *in vacuo*. T/°C: *1*, 50; *2*, 60; *3*, 70; *4*, 80; *5*, 82; *6*, 84.5; and *7*, 90. Moments of injection of moist air are marked by circles. Dotted lines show the continuation of kinetic curves after injection of air.

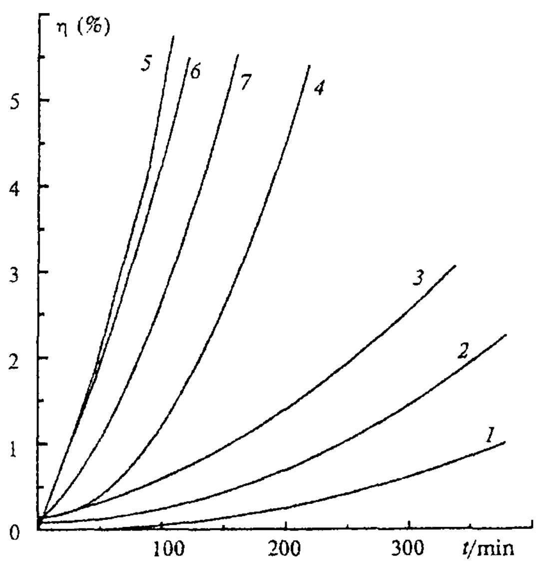

Fig. 2. Initial regions of kinetic curves presented in Fig. 1. Numbers of curves coincide.

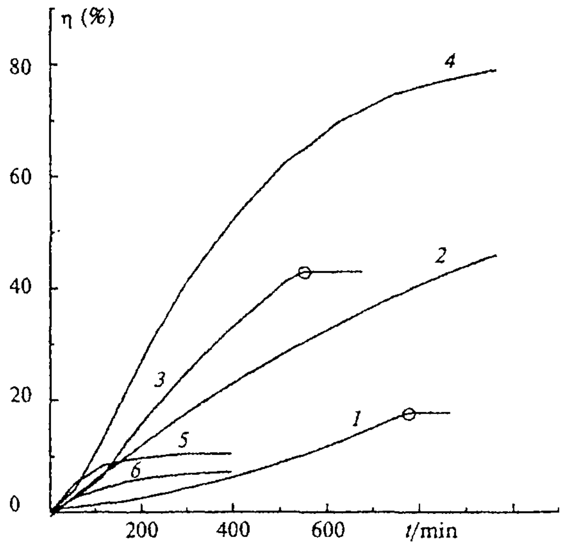

Fig. 3. Kinetic curves of decomposition of $CsN(NO_2)_2$ *in vacuo*. T/°C: *1*, 60.7; *2*, 70; *3*, 75; *4*, 80.3; *5*, 81.5; and *6*, 84.5. The moment of injection of 10 Torr of H_2O is marked by the circle.

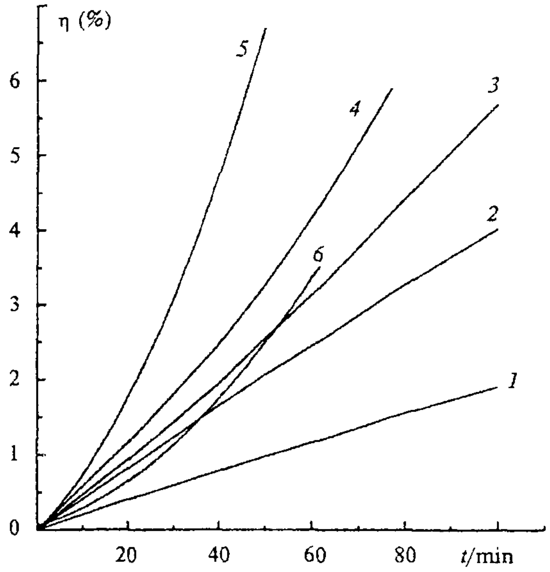

Fig. 4. Initial regions of curves presented in Fig. 3. Numbers of curves coincide.

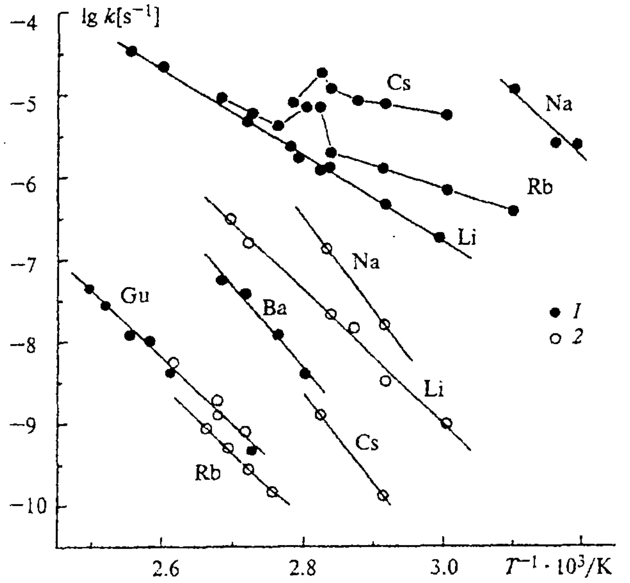

Fig. 5. Temperature dependences of rate constants of decomposition of DNA salts in the solid phase. Symbols near curves correspond to cations; Gu is guanidinium, *1*, reaction *in vacuo*; *2*, decomposition inhibited by water vapor.

and nonequilibrium defects of the crystal lattice. After "working out" or "recovering" of defect regions by covering them with the product layer, the reaction is stopped. It can be reinitiated by simple grinding of partially decomposed crystals. This effect has been previously observed for $KN(NO_2)_2$ and described in detail.[1] The concentration of defects in crystal (and, hence, the rate as well) increases when the eutectic is formed, especially near its melting point. The reaction is stopped at the early stages at temperatures higher than the eutectic melting point, because the reaction centers begin to melt.

The last fact reflects the main specific feature of decomposition of metal dinitramide salts: under conditions of removing gaseous products, the rate in the solid phase is higher than in the liquid phase.

It can be seen from Table 1 that the ratio of decomposition rate constants in the solid and liquid phases, k_s/k_l, varies (at 100 °C) from 10 ($LiN(NO_2)_2$, $Ba(N(NO_2)_2)_2$) to 10^4 ($NaN(NO_2)_2$).

The second specific feature of all metal salts (which has been previously observed for $KN(NO_2)_2$ [1]) is the inhibition of the solid-phase reaction by water vapor (Figs. 1 and 3, Table 1). The addition of 10—15 Torr of water vapor at any stage of decomposition immediately stops the reaction. The injection of moist air acts in the same manner. Ammonia, NO, N_2O, and acetone or methanol vapor also retard the decomposition, but considerably more weakly than water vapor. In closed vessels at an initial pressure of 0.1 Torr, the reaction occurs rapidly at first as in vacuum but is stopped as N_2O is accumulated and residual water vapor escapes.

Table 1. Kinetic parameters of decomposition of dinitramide salts in different states

Cation	M.p. of salt/°C	State	ΔT /°C	E /kcal mol^{-1}	lg$A$ /s^{-1}	$k \cdot 10^5$/s^{-1} (160 °C)	k/s^{-1} (100 °C)
Li^+	158	Melt	—	(36.0)[a]	(15.0)	67[b]	$8.1 \cdot 10^{-7}$
		Solid (0.1)[c]	62—120	26.0	10.0	—	$5.7 \cdot 10^{-6}$
		Solid (760)	60—98	40.6	17.3	—	$3.2 \cdot 10^{-7}$
Na^+	111	Melt	—	(38.0)	(15.0)	6.4[b]	$5.4 \cdot 10^{-7}$
		Solid (0.1)	30—50	40.0	22.0	—	$3.6 \cdot 10^{-2}$
		Solid (760)	70—80	46.0	21.4	—	$2.7 \cdot 10^{-6}$
K^+[d]	127	Melt	130—190	39.5	15.1	1.4	$8.9 \cdot 10^{-9}$
		Solid (0.1)	80—100	26.6	10.3	—	$5.1 \cdot 10^{-6}$
		Solid (760)	80—120	41.0	15.6	—	$3.7 \cdot 10^{-9}$
Rb^+	108	Melt	—	(39.6)	(15.0)	1.0[b]	$6.2 \cdot 10^{-9}$
		Melt	130—170	40.1	15.3	1.1	$6.3 \cdot 10^{-9}$
		Eutect. with $RbNO_3$	100	—	—	—	$6.1 \cdot 10^{-9}$
		Solid (0.1)	50—100	20.0	6.6	—	$7.6 \cdot 10^{-6}$
		Solid (760)	70—102	38.0	12.8	—	$3.4 \cdot 10^{-10}$
Cs^+	88	Melt	—	(39.2)	(15.0)	1.62[b]	$1.0 \cdot 10^{-8}$
		Solid (0.1)	60—85	13.0	3.0	—	$2.4 \cdot 10^{-5}$
		Solid (760)	70—80	39.0	14.7	—	$6.9 \cdot 10^{-9}$
Ba^{2+}		Solution in $KN(NO_2)_2$	160—180	50.0	20.8	3.2	$2.8 \cdot 10^{-9}$
		Solid (0.1)	80—100	47.3	20.5	—	$5.6 \cdot 10^{-8}$
$(NH_2)_3C^+$		Melt	150	—	—	—	$1.1 \cdot 10^{-4}$[e]
	144	Solid (0.1)	95—138	40.0	14.2	—	$3.4 \cdot 10^{-7}$[e]
		Solid (760)	95—110	40.0	14.2	—	$3.4 \cdot 10^{-7}$[e]

Note. [a] Calculated from the k values at 160 °C presented in Ref. 6 assuming that log$A$/s^{-1} has the value 15.0 typical of alkaline salts. [b] Data in Ref. 6. [c] Air pressure (Torr) above the sample. [d] Data of Refs. 1 and 3. [e] At 150 °C.

The strong effect of water vapor suggests that decomposition is possible only in dry layers of the substance, and its rate depends on the degree of preliminary drying and conditions of removing residues of the solvent and gaseous products. The lithium and barium DNA salts, which have the smallest k_s/k_l ratios, were obtained from crystal hydrates and, perhaps, the residual moisture retards their decomposition *in vacuo* at the initial stages. These compounds have the maximum degree of acceleration (which can be related to the water loss), and at the acceleration stage, their k_s/k_l values become equal to those of other salts.

The water vapor-inhibited decomposition of metal salts in the solid phase has a lower rate than that in the melt. Its parameters are presented in Table 1.

The results obtained testify that all the described[1] properties of the anomalous decomposition (a great k_s/k_l ratio, the rate peak at the point of eutectic melting with the product, and inhibition by water vapor) are retained for all DNS metal salts.

Unlike DNA metal salts, the DNA guanidinium salt manifests no specific features of solid-phase decomposition. The rates in vacuum and in air are equal (see Table 1), and no increase in the rate is observed (Fig. 5) at the point of eutectic melting with guanidinium nitrate (128 °C). The rate in the solid state is 400 times lower than in the liquid phase (point at 150 °C, see Table 1).

Similarly to the conclusions in Ref. 1, it can be assumed that the phenomenon of anomalous decomposition is related to changes in the structure of the DNA anion on going from the melt to the solid state. The anion in the crystal can have a structure with a nonsymmetric charge distribution and nonequivalent nitro groups. It is reasonable to expect that these anions have an increased reactivity, in particular, their thermal stability can change. The observed difference in the kinetic behavior of metal and guanidinium dinitramides makes it possible to check this hypothesis by structural studies.

The data presented in Table 1 allow one to draw an important conclusion concerning the liquid-phase decomposition of DNA salts. The comparison of k_l with the cation radius of the alkaline salts shows that this dependence is not monotonic: the minimum of the rate is observed for $RbN(NO_2)_2$. The nonmonotonic character of the dependence of the stability of large anions on the electronegativity of the cations was theoretically predicted.[7] Probably, it is not the minimum, but the lower limit (Rb = Cs) of the cation effect on the stability of the $N_3O_4^-$ anion. In both cases, it can be expected that at any polarizing strength of the cation, the stability of the DNA salt cannot be higher than that of $RbN(NO_2)_2$.

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