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Abstract

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A. V. RAEVSKII, G. B. MANELIS

ON THE MECHANISM OF THE DECOMPOSITION OF AMMONIUM PERCHLORATE

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There is a very extensive literature on the thermal decomposition of ammonium perchlorate ($^{1-9}$). However, the question of the development of the reaction in single crystals of the salt has not received sufficient attention. Birkamshaw (^{2}), observing partially decomposed crystals under a microscope, established that the decomposition process develops at individual centers. At the same time, he did not carry out detailed studies. A careful quantitative investigation of the kinetics of formation, growth, and development of the centers is of considerable interest from the standpoint of establishing the mechanism of the reaction in single crystals of ammonium perchlorate. In this connection, microcinematographic filming of the decomposition process of single crystals of ammonium perchlorate was carried out. In addition to the microscopic observations, kinetic curves of the thermal decomposition of single crystals of NH_4ClO_4 "in air" were recorded from weight loss.

Crystals of NH_4ClO_4 (0.5 to 5 mm in size) were grown from aqueous solution at room temperature. The ammonium perchlorate was preliminarily recrystallized twice. Decomposition of the specimens was carried out on a special heating stage under isothermal conditions (accuracy of maintaining the specimen temperature ±1°C). Observation and recording were conducted on an MKU-1 microcinematographic apparatus.

Table 1

Temp., °C	v_1	v_2	v_3	v_4
	μ/min	μ/min	μ/min	μ/min
215	11	0.8	0.9	–
220	13	1.2	1.4	–
225	17	1.6	2.0	–
230	25	2.4	2.9	–
235	34	3.3	4.0	–
250	–	–	–	5.7

Temp., °C	v_1	v_2	v_3	v_4
255	–	–	–	6.6
260	–	–	–	8.0
265	–	–	–	9.0
272	–	–	–	11.0

Note: v_1 –longitudinal velocity; v_2 –transverse velocity of growth of centers from the side of the rhombic face; v_3 –velocity of growth of centers from the side of the rectangular face; v_4 –velocity of growth of centers after the phase transition.

The kinetic curves of decomposition of single crystals of NH_4ClO_4 were recorded on microbalances with automatic recording, developed at the branch of the Institute of Chemical Physics of the Academy of Sciences of the USSR (recording accuracy ±0.05 mg).

Microscopic study of the decomposition process of ammonium perchlorate at temperatures of 210—236° (below the temperature of the phase transition) showed that the decomposition reaction begins at individual sites of the crystal and develops by growth of the centers formed. Nucleation of a center occurs near the surface of the single crystal at a depth of 20—30 μ. At sufficiently high magnifications (about 1000×), it is seen that the reaction centers of decomposition do not have a sharp boundary, but consist of a large number of spherical nuclei ($\emptyset\,1$—$2\,\mu$). Formation and growth of centers occur by coalescence of nuclei arising near the growing center. Slow microcinematography showed that, after appearing, the nuclei are in continuous motion until they merge with the main body of the center. The nuclei move mainly in forward and reverse directions parallel to the main diagonal of the rhomb at a velocity of

7-10 μ per minute at 230°. The nuclei move the faster the smaller they are, and they traverse a distance hundreds of times greater than their linear dimensions. The center appears as a stationary elongated core surrounded by a cloud of moving nuclei.

From the rhombic face of the single crystal, the centers have a cigar-like shape. Preferential growth occurs along the direction of the major diagonal of the rhombus. The growth of the centers proceeds at a constant rate, in the longitudinal direction almost 10 times greater than in the transverse direction (Table 1).

The activation energy for longitudinal growth is 31 ± 1 kcal/mole; for transverse growth, 33 ± 1 kcal/mole. The scatter of the growth-rate values, both on different crystals and on one and the same crystal, did not exceed 5%.

Decomposition centers on the rectangular face of the crystal are close in shape to a hemisphere. Cleavages of single crystals were made through the decomposition centers parallel to the rhombic face; these showed that only in very rare cases does a trace, consisting of individual nuclei, extend from the center into

Fig. 1. Decomposition centers: a—from the side of the rhombic (300×), b—from the side of the rectangular (100×) face of an NH_4ClO_4 single crystal (t = 220°)

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the depth of the crystal. The activation energy of the growth rate of centers developing at rectangular faces is 33 ± 1 kcal/mole.

In Fig. 1 growing centers are shown from the side of the rhombic and rectangular faces. Since the reaction centers develop anisotropically, one should expect an influence of the crystal habit on the overall rate of the decomposition reaction of ammonium perchlorate. The kinetics of the thermal decomposition of single crystals of equal weight but different habit was studied by the gravimetric method. From Fig. 3 it is seen that the reaction rate increases with an increase in the fraction of surface contributed by rhombic faces.

Fig. 1. Decomposition centers: *a*—from the side of the rhombic (300×), *b*—from the side of the rectangular (100×) face of an NH_4ClO_4 single crystal ($t = 220°$).

In the temperature region above the phase-transition temperature in the cubic modification of NH_4ClO_4, decomposition proceeds through centers arising throughout the entire volume of the crystal. The shape of the centers is close to spherical, with sharp contours. Nucleation occurs at one point; then the center begins to enlarge and grows until it coalesces with neighboring centers (Fig. 2). The activation energy of the growth rate of the centers in this case is 17 ± 1 kcal/mole.

In those cases where the initial crystal contained a large number of growth defects, the phase transition at $T = 238$-$240°$ proceeded indistinctly,

cracks and stresses formed in the crystal, and the reaction developed at the resulting defective sites.

It was then of interest to identify the characteristic features of the decomposition of NH_4ClO_4 single crystals under the action of a catalyst for ammonium perchlorate decomposition—carbon ([8]). Microcinematography of the decomposition process ($t = 230°$) of NH_4ClO_4 single crystals with a semitransparent carbon film deposited on them showed that the number of centers increases considerably and that the rate of growth of a center in the transverse direction increases. The mechanism of formation and growth of the centers in this case does not change appreciably. The experimentally observed regularities in the development of the reaction in ammonium perchlorate crystals can be explained on the basis of the following assumptions.

Fig. 2. Appearance of decomposition centers (100×) in a single crystal after the phase transition

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

($t = 265°$)

In the ionic lattice of NH_4ClO_4, an electron passes into the conduction band from the ClO_4^- ion with formation of a $ClO_4^{\cdot}$ particle. The electrons are partially trapped at traps with formation of a pair of uncharged particles $[NH_4^{\cdot}] \cdot [ClO_4^{\cdot}]$. The concentration of complexes of this type is thermodynamically equilibrium. The stage kinetically limiting the reaction rate is the decomposition of the complex (or of the $ClO_4^{\cdot}$ particle) with formation of intermediate products (atoms or radicals), which rapidly transform into the final products.

Fig. 3. Effect of habit on the decomposition kinetics of NH_4ClO_4 single crystals. Ratio of the areas of rhombic and rectangular faces: 2.5 : 1 for curve 1 and 1 : 1 for curve 2

The introduction of donors or acceptors of electrons and the consequent change in the semiconductor properties of the crystal increase or decrease the concentration of electrons in the conduction band and thereby change the equilibrium concentration of $[ClO_4^{\cdot}]$ particles. At the same time, the number of free traps will change, and hence the concentration of $[NH_4^{\cdot}] \cdot [ClO_4^{\cdot}]$ complexes. In this way the change in the rate of decomposition in the presence of carbon can be explained. Electron traps, as is known from solid-state physics, may be concentrated near dislocations and defects of this type. Since dislocations are distributed nonuniformly through the crystal, the reaction also nucleates only at certain sites where the defectiveness is higher.

When the reaction proceeds at certain sites, the crystal is subjected to mechanical action owing to the accumulation of products in the reaction centers. This leads to the appearance of stresses and, as a consequence, to the formation of a new network of dislocations around the growing center. Because of the anisotropy of the mechanical properties, the dislocations arise with a predominant distribution along particular axes of the crystal, which also leads to anisotropy in the growth rate of the center. The nuclei observed at temperatures below the phase transition apparently are cavities filled with decomposition products. Their motion is probably connected with the thermal motion of dislocations.

Institute of Chemical Physics
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.