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Authors: G.B. Manelis
Ju. I. Rubtsov

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OF AMMONIUM PERCHLORATE

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KINETICS OF THE THERMAL DECOMPOSITION
OF AMMONIUM PERCHLORATE

by

G.B. Manelis
Ju. I. Rubtsov

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MICHESKOGO RASPADA PERKHLORATA AMMONIYA
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KINETICS OF THE THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE.

G.B. Manelis, Ju.I. Rubtsov.

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Ammonium perchlorate is one of the most convenient agents for investigating the kinetics of the thermal decomposition reaction in the solid phase. In NH_4ClO_4 phase transition takes place in an area of sufficiently intense thermal decomposition, therefore it is possible to investigate the kinetics of the reaction in two crystalline modifications.

Regardless of the significant number of works dedicated to the study of the thermal decomposition of NH_4ClO_4 /1-10/, many details of the mechanism of this reaction have not yet been disclosed. The kinetic parameters of the reaction were determined in many works /3-6,10/, but, due to the absence of a theoretically based kinetic equation of the reaction, calculation of the speed constant was made on the basis of various empirical and semiempirical equations, different equations being used for different parts of the same kinetic curve. In many cases the results differ substantially from one another. For example, values of the activation energy for the 200 - 330°C temperature range fluctuate from 20,6 to 32 kcal/mole. Most of the authors confined themselves to determination of the temperature dependence of the process speed and do not cite absolute values of the speed (values of the pre-exponential factors are lacking).

Experimental part.

Technical ammonium perchlorate was preliminarily purified by twofold recrystallization from distilled water, was dried at 90 - 100°C, was pulverized in an agate mortar, and, after dispersion,

a fraction with a particle size of 50 to 100 μ was removed. Investigation of the kinetics of thermal decomposition was carried out by means of two methods in stainless steel, aluminum, and glass ampoules. The kinetics of the reaction of mass loss in air were investigated in stainless steel ampoules on ATV-2 automatic thermal scales /11/. The kinetics of heat release during the thermal decomposition of NH_4ClO_4 , and the heat effect of the reaction, were studied in aluminum and glass ampoules on an automatic dual calorimeter /12/. A weighed portion of 100 mg. was taken during work with the ATV-2 scales, and one of 50 mg to 1 g was taken during work with the calorimeter, depending on the temperature.

Kinetic curves obtained for NH_4ClO_4 by the weighing method within the temperature range of 200 to 280°C, are shown in Figures 1 - 3; from these it can be seen that the thermal decomposition reaction of ammonium perchlorate possesses two characteristic features: 1) within the temperature range of 200 to 280°C the decomposition reaction slows down sharply after decomposition of 30 to 35% of the taken weighed portion, although complete cessation of reaction does not occur; it continues with a relatively slow speed; 2) at temperatures over 236°C ammonium perchlorate changes its crystalline modification, passing from an orthorhombic lattice into a cubic one: this transition is accompanied by a substantial decrease of the reaction speed of the thermal decomposition, since the decomposition reaction develops more slowly in a cubic lattice.

The kinetics of heat release during thermal decomposition of

3.

NH_4ClO_4 were investigated within the temperature range of 196,5 to 234,5°C, because at higher temperatures the reaction succeeds already in reaching a substantial depth during heating of the ampoule outside of the calorimeter. The reaction was produced in aluminum and glass ampoules. The heating time of the weighed portion in an aluminum ampoule is substantially shorter than in glass; however, aluminum influences the decomposition reaction of ammonium perchlorate, somewhat decreasing its speed. The obtained curves of the heat release rate are shown on Figures 4,5.

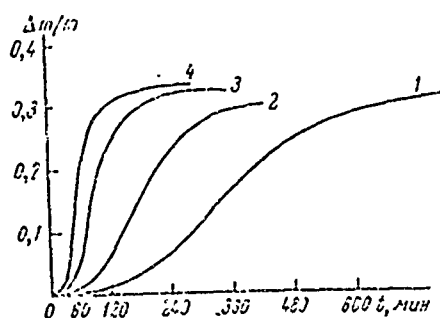


Figure 1. Kinetic curves of the thermal decomposition reaction of NH_4ClO_4 within the temperature range of 200 to 230°C; 1 : 200; 2 : 210; 3 : 220; 4 : 230°C.

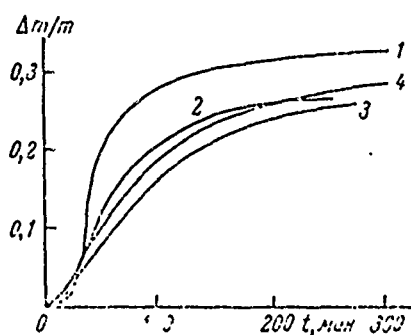


Figure 2. Kinetic curves of the thermal decomposition reaction of NH_4ClO_4 within the temperature range of 236 to 255°C; 1:236; 2:240; 3:245; 4:255°C.

Since a well-founded kinetic equation for the reaction of thermal decomposition in the solid phase is lacking at the present time, use was made of an empirical equation of the following type to obtain quantitative data on the speed of the thermal decomposition reaction:

$$\frac{d\eta}{dt} = k_1(1-\eta)^{1/2} + k_2\eta(1-\eta)^{1/2} \quad (1)$$

(in the temperature range of 196,5 to 236°C)

$$\frac{d\eta}{dt} = k_1(1-\eta)^2 + k_2\eta(1-\eta)^2 \quad (2)$$

within the temperature range of 240 to 280°C, where $\eta = \Delta m / \Delta m_{\text{const}}$ is the depth of decomposition of the substance, $\eta = 1$ corresponds to 30 - 35% decomposition of NH_4ClO_4 .

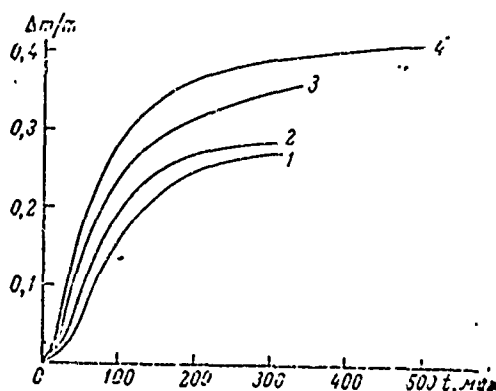


Figure 3. Kinetic curves of the thermal decomposition reaction of NH_4ClO_4 within the temperature range of 245 to 280°C; 1:245; 2:255; 3:265; 4:280°C.

The value k_2 was determined from alignment of the speed curve in the corresponding coordinates. Speed curves for the weighing experiments were found by graphical differentiation of the obtained kinetic curves. Since the value k_1 is small in comparison to k_2 , it is more convenient to find it after integrating equations (1) and (2) with an initial condition of $\eta = 0$ when $t = 0$. The obtained integral relationships have the following form:

$$k_2 t = \frac{2(1 - \gamma\sqrt{1 - \eta})}{(1 + \eta_0)\sqrt{1 - \eta}} + \frac{1}{(1 + \eta_0)^{3/2}} \ln \frac{(\sqrt{1 - \eta} - \gamma\sqrt{1 - \eta_0})(1 + \gamma\sqrt{1 + \eta_0})}{(\sqrt{1 - \eta} + \gamma\sqrt{1 + \eta_0})(1 - \gamma\sqrt{1 + \eta_0})}, \quad (3)$$

$$k_2 t = \frac{1}{1 + \eta_0} \frac{\eta}{1 - \eta} + \frac{1}{(1 + \eta_0)^2} \ln \frac{\eta + \eta_0}{\eta_0(1 - \eta)}, \quad (4)$$

where $\gamma = k_1/k_2$. Knowing k_2 and taking from the kinetic curve the time for the obtaining some percentage of decomposition η (usually $\eta = 0,3$ was used), it is possible to find η_0 , and, consequently, also k_1 .

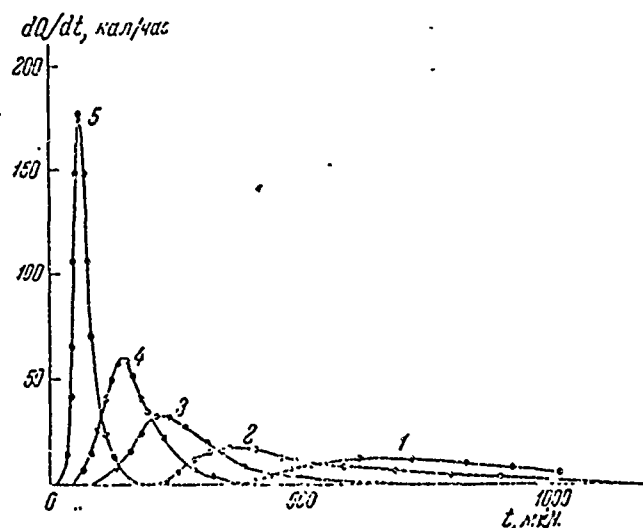


Figure 4. Curves of the rate of heat release during the thermal decomposition of KClO_3 at different temperatures: 1:196,7; 2:204; 3:210; 4:227; 5:234,5°C.

Table 1 shows the values of k_1 and k_2 obtained from weighing experiments in steel ampoules. Table 2 shows values of the thermal reaction effects and the values of k_1 and k_2 for the experiments on the kinetics of heat release. The relationships of values k_1 and k_2 to the temperature have the following form:

$$k_1 = 10^{8,0} \cdot \exp(-30\,000/RT), \text{sec}^{-1} \text{ (steel ampoules),}$$

$$k_1 = 10^{7,5} \cdot \exp(-30\,000/RT), \text{sec}^{-1} \text{ (glass and aluminum ampoules).}$$

Within the temperature range of 196 to 236°C:

$$k_2 = 10^{10,2} \cdot \exp(-30\,000/RT), \text{sec}^{-1} \text{ (in steel and glass ampoules),}$$

$$k_2 = 10^{10,05} \cdot \exp(-30\,000/RT), \text{sec}^{-1} \text{ (in aluminum ampoules).}$$

Discussion of the results.

At the present time we assume, for the reaction of the thermal decomposition of NH_4ClO_4 , the mechanism connected with the passage of an electron from the anion ClO_4^- to the cation NH_4^+ /10/, the concentration of forming complexes $\text{NH}_4^+ \cdot \text{ClO}_4^-$ being in thermodynamic equilibrium, and the decomposition reaction of this complex limiting the speed of the whole reaction. The concentration of complexes is determined by the number of electron traps in the crystal, due to which a change of the electronic state brings about a change in the speed of thermal decomposition. The reaction products deform the crystalline lattice surrounding them, creating new defects in it, which can be electron traps. Thus, a center of reaction development starts to grow within the volume of the crystal.

G,

t, °C	Q (exp) cal/g	% decomposi- tion by weight	Q per g de- composition NH ₄ ClO ₄ , cal	10 ⁴ k ₂ , sec ⁻¹	10 ⁸ k ₁ , sec ⁻¹
In glass					
199,5	130,5	38	344	2,78	0,64
214	123,4	36,2	341	7,5	1,5
217,5	140	39	359	9,0	1,8
229	164	46,6	352	16,2	3,25
233,5	125,2	36,2	346	23	4,6
Q average = 348 ± 11					
In aluminum					
196,5	43,1	12,95	333	1,62	0,51
204	106,1	32,2	330	2,5	0,79
210	115,2	33,2	346	3,36	1,15
222	120,5	36,9	327	7,7	2,4
222	113,5	33,8	336	7,4	2,3
234,5	123,6	37	334	20,8	6,0
Q average = 334 ± 12					

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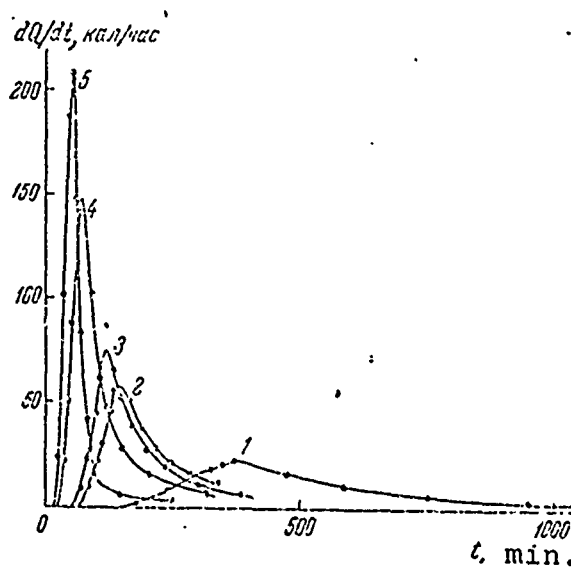
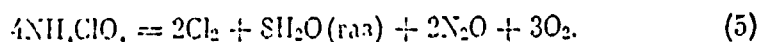


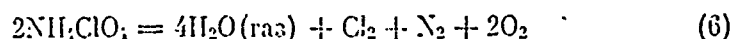
Figure 5. Speed curves of heat release during thermal decomposition of NH₄ClO₄ in glass ampoules: 1:199,5; 2:214; 3:217,5; 4:229; 5:233,5°C.

In the kinetic equation of the reaction assumed by us the value k_1 characterizes the initial speed, i.e. the number of electronic traps, and the value k_2 characterizes the speed of development of the reaction centers. It is characteristic that the same dependence of value k_1 on the temperature is retained in the cubic lattice of NH_4ClO_4 after the phase transfer, as in the orthorhombic lattice. Consequently, in the case of a phase transition not only the number of electronic traps is retained, but also the distance between the edge of the valence zone and the electronic levels of traps. At the same time, the phase of transition is accompanied by heat absorption (the heat of transition is 2,3 kcal/mole /13/) and an increase in the volume of the crystal, consequently, the binding energy of the ions in the cubic lattice decreases somewhat, and the inter-ion distances increase. The change of lattice parameters brings about a change in the speed of reaction development, and the value k_2 decreases during the phase transfer. The values of k_1 in stainless steel ampoules become somewhat larger because of the catalytic effect of iron oxides and chromium /14/ on the reaction of the thermal decomposition of NH_4ClO_4 . Determination of the heat effects of the thermal decomposition of ammonium perchlorate permits some assumptions to be made with regard to the course of this reaction. /174

Dodé /1,2/ cites the following equation of the decomposition within the temperature range of 200 - 300°C.



In this reaction, ~ 310 cal/g of decomposed NH_4ClO_4 should separate out. Values of the heat effect determined experimentally at temperatures of up to 236°C comprise $348 + 11$ cal/g in glass and $334 + 12$ cal/g in aluminum. A mass-spectrometric analysis of the decomposition products of ammonium perchlorate has shown that, along with nitrogen oxides, there is also a substantial quantity of free N_2 , which leads to the high value of the heat effect. For the reaction



the heat effect is equal to 390 cal/g.

Thus, in the thermal decomposition of NH_4ClO_4 along with reaction (5) there also takes place reaction (6). In the presence of aluminum, the contribution of reaction (6) into the general balance decreases.

Conclusions

1. The kinetics of the reaction of the thermal decomposition of NH_4ClO_4 have been investigated at $196,5$ to 280°C . The kinetic constants and the heat effect of the reaction were found.
2. At the phase-transition point of NH_4ClO_4 only k_2 , the constant connected with the acceleration of the process, changes, whereas the value k_1 continues to increase monotonously.

Institute of Chemical Physics
Academy of Sciences U.S.S.R.

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