

Nucleation Mechanism during Low-Temperature Decomposition of Ammonium Perchlorate*

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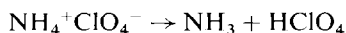
Received July 8, 1975

It is shown that proton-acceptor additions are effective inhibitors of the nucleation process of low-temperature decomposition of ammonium perchlorate (AP). In contrast to this, addition of ClO_3^- ion is a catalyst for the decomposition of AP: It increases the rate of nucleation V_n and the maximum concentration of nuclei N_{max} and decreases the induction period of nucleation τ . It is shown that impurity of ClO_3^- ion is present in the purest commercial samples of AP. It is thought that the initiator of nucleation is HClO_3 , i.e., $V_n = K[\text{H}^+] \times [\text{ClO}_3^-]$. The dependence that is demonstrated agrees very well with experimental data on the influence of addition of proton donors and acceptors and of additions of ClO_3^- ions on V_n . On the basis of this mechanism, means of regulating the temperature of initiation of AP decomposition are suggested. An explanation of the photosensitivity of AP exposed to the uv band is proposed.

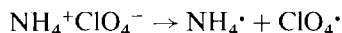
Ammonium perchlorate (AP) has been the object of intensive study during the past 20 years [see, for example, the survey of Jacobs and Whitehead (1)]. A tremendous amount of experimental material has been accumulated and effective technological methods have been found which permit the use of AP as a solid-phase oxidizer. However, an entire set of unresolved problems remain. In particular, it is not understood why AP begins to decompose with noticeable speed at temperatures of the order of 200°C, which is 300–350° lower than corresponding temperatures for perchlorates of alkali metals. Not having answered this question, it cannot be said that we have exhausted all possibilities in the search for methods of influencing the decomposition rate of AP.

In order to predict the means of controlled regulation of the rate of a chemical reaction, it is necessary to present a mechanism for it or even a rough scheme of it. At the present time, two mechanisms for thermolysis of AP are discussed in the literature. The more

widely accepted mechanism (1–7) is the so-called “proton mechanism,” which presumes that the initial elementary act of thermolysis is the transfer of a proton from the cation to the anion:



However, still in vogue is the electron mechanism, traditional in solid-state chemistry (8–9), according to which the initial elementary act of thermolysis is the transfer of an electron



with subsequent destruction of the radicals which are produced. The basic argument against this mechanism is the great (>5 eV) width of the forbidden zone. But the fact is indisputable that low-temperature decomposition of AP proceeds through formation and growth of reaction nuclei—seeds of decomposition. The reaction is autocatalytic and heterogeneous. Once begun in a crystal at a given point, it continues to develop, chiefly in the vicinity of this point (10–15). One can expect, therefore, that once we have learned the nucleation process, we will be

* Original manuscript received in Russian. A copy is available on written request to the Editor.

able to regulate the decomposition rate of AP.

Just what is the nucleation process? Although the amount of experimental data on thermolysis of AP, at times contradictory, but often repetitious, is extremely large, the process of nucleation itself has been studied very little. This is all the more surprising since, as can be concluded from the above, it is precisely in this way that a scientific solution to the problem of regulating the thermal stability of AP can be found most quickly. The present investigation has been carried out to fill this void in the area of experimental data in order to proceed in the future to a discussion of the problem indicated above.

Experimental

Single crystals of AP were grown from aqueous solution by isothermal evaporation at room temperature from commercial preparations marked "chemically pure." Additions of anions ClO_3^- , SO_4^{2-} , H_2PO_4^- , and HPO_4^{2-} were introduced into the initial aqueous solutions in the form of ammonium salts to produce corresponding solid solutions. The amount of adduct entering the crystal was determined from the results of analysis of the solutions that were obtained by dissolving the crystals studied in water. Analysis for the ClO_3^- ion was done colorimetrically with the help of *o*-tolidine. The method allows us to determine the ClO_3^- ion to 3×10^{-5} mole %. The analysis for the PO_4^{3-} ion was determined colorimetrically from the concentration of phosphomolybdenovanadic acid. The SO_4^{2-} ion was determined turbidimetrically by formation of BaSO_4 .

The decomposition process was studied microscopically, by photographing the nuclei that formed in the thermolysis process on the rhombic faces of AP crystals, and from isothermal curves of weight loss of AP powder. The grain size in the powder was 100–120 μm . Thermolysis was carried out at a temperature of $230 \pm 1^\circ\text{C}$. Since the monocrystals differ from each other in features even within the confines of one part of the preparation, 13–15 crystals were studied each time. The results were processed on "Nairi-2" computer using

a standard least-squares method. The nucleation rate was designated as V_n ; the rate of longitudinal growth of the nuclei was V_{g1} ; the rate of transverse growth of the nuclei was V_{g2} ; the maximum number of nuclei at the moment they fuse onto a surface unit was N_{max} ; and the induction period of nuclei formation was τ . Standard deviations are presented to the right of each value in the tables: The upper number is for a credibility of 95%; the lower, for a credibility of 70%.

The gross kinetics of decomposition were studied in an automatic-weight apparatus on a quartz spring balance with a sensitivity of 10^{-6} g in an air atmosphere at pressures of 30–100 Torr. At lower pressures, sublimation processes of the AP began to predominate.

Results

As suggested in (16), additions of proton acceptors should inhibit the decomposition of AP. For such additions, the ions SO_4^{2-} , H_2PO_4^- , and HPO_4^{2-} were chosen. The results of machine processing of multiple experimental data on the influence of the indicated additives on the topokinetic characteristics of the thermolysis of AP monocrystals are presented in Table I. Analysis of the results presented in this table shows that proton-acceptor additives increase τ and diminish V_n and N_{max} , but do not influence V_g ; i.e., as expected in (16), these additives are in a kinetic sense antagonistic to proton-donor additives. It is curious to note that the inhibiting effect increases not only with increase in the concentration of additive but also with increase in its proton-accepting ability: the strongest inhibitor is the HPO_4^{2-} ion; the weakest is SO_4^{2-} .

The next step was to study the influence of ClO_3^- ion on the thermolysis of AP. The choice of this additive was determined by the fact that it is, first, an efficient catalyst of gross AP decomposition (17, 18) and, second, it is known (19) that the chlorate ion is a technological impurity in AP: i.e., it unavoidably exists in all available commercial samples of AP and is already present in the AP that is used in mixture compositions.

TABLE I

RATES OF FORMATION OF NUCLEI AND THEIR GROWTH; MAXIMUM NUMBER OF NUCLEI AND INDUCTION PERIOD DURING THERMOLYSIS OF AP CRYSTALS; PURE (1) AND CONTAINING ADDITIVES (IN MOLE %)^a

Number	V_n (1/cm ² min)	V_{g1} (μm/min)	V_{g2} (μm/min)	N_{max} (1/cm ²)	τ (min)
1	45.7 ± 8.0 ± 4.0	32.3 ± 5.4 ± 2.7	4.3 ± 0.5 ± 0.2	1003 ± 284 ± 142	29 ± 2.8 ± 1.3
2	28.2 ± 9.0 ± 4.5	35.5 ± 5.0 ± 2.5	4.3 ± 0.4 ± 0.3	640 ± 120 ± 60	29 ± 2.8 ± 1.5
3	18.2 ± 8.0 ± 4.0	31.4 ± 5.4 ± 2.7	4.3 ± 0.5 ± 0.2	500 ± 80 ± 40	32 ± 2.4 ± 1.2
4	12.0 ± 3.0 ± 1.5	37.6 ± 7.0 ± 3.6	4.8 ± 0.4 ± 0.2	448 ± 61 ± 30	38 ± 5.9 ± 2.9
5	7.5 ± 2.5 ± 1.2	35.8 ± 6.0 ± 3.0	4.8 ± 0.5 ± 0.2	336 ± 59 ± 28	53 ± 5.0 ± 2.5
6	10.1 ± 3.4 ± 1.7	34.5 ± 7.9 ± 3.9	4.7 ± 1.1 ± 0.5	374 ± 64 ± 32	33 ± 2.6 ± 1.3
7	8.9 ± 2.8 ± 1.4	34.9 ± 4.3 ± 2.1	4.9 ± 0.5 ± 0.2	325 ± 60 ± 30	35 ± 3.0 ± 1.5
8	5.8 ± 3.2 ± 1.6	35.5 ± 5.0 ± 2.5	4.5 ± 1.4 ± 0.7	290 ± 57 ± 28	49 ± 3.5 ± 1.7
9	7.1 ± 1.5 ± 0.7	34.2 ± 5.7 ± 2.6	4.7 ± 0.7 ± 0.4	371 ± 92 ± 46	37 ± 4.9 ± 2.4
10	5.5 ± 0.9 ± 0.5	33.8 ± 5.0 ± 2.1	4.0 ± 0.6 ± 0.2	314 ± 44 ± 23	41 ± 7.0 ± 3.5
11	3.3 ± 1.6 ± 0.8	31.9 ± 5.9 ± 2.7	3.9 ± 0.6 ± 0.3	257 ± 94 ± 47	45 ± 5.6 ± 2.9

^a a, SO₃²⁻ ion: 3.2 × 10⁻³ (2); 8.2 × 10⁻³ (3); 4.5 × 10⁻² (4); 7.6 × 10⁻² (5). b, H₂PO₄⁻ ion: 6.1 × 10⁻³ (6); 8.8 × 10⁻³ (7); 4.3 × 10⁻² (8). c, HPO₄²⁻ ion: 3 × 10⁻⁴ (9); 5 × 10⁻³ (10); 3.1 × 10⁻² (11).

In (17, 18), it was shown that chlorate ion diminishes the induction period of decomposition of polycrystalline AP. It might be expected, therefore, that introduction of the indicated additive would lead to a decrease in the time it takes for the first seed to appear and to an increase in V_n . Nothing could be said a priori about the behaviour of V_g and N_{max} .

In Table II, the effect of addition of ClO₃⁻ ion on decomposition of AP is demonstrated. The second line of this table presents topokinetic data on thermolysis of AP monocrystals crystallized twice from a commercial reagent marked "chemically pure." As the analysis showed, even these samples (after double recrystallization) contained 1.4 × 10⁻⁴ mole % ClO₃⁻ ion. Fivefold recrystallization led to the point where within the limits of sensitivity of the analytical method used, ClO₃⁻ ion could not be detected in the AP samples.

The result of the study of such crystals is shown in the first line of Table II. As seen, fivefold crystallization leads to an increase in τ by 10 min, a decrease in V_n by half, and a significant decrease in N_{max} . On the other hand, introduction of the indicated additive leads to a decrease in the thermal stability of AP, although, within the limits of experimental error, V_g again did not change. At the indicated temperature of 230°C with additive content of greater than 10⁻¹ mole %, the nucleation process proceeded so rapidly it was impossible to register. Thus, τ at an additive content of 5 × 10⁻¹ mole % is 1.0 ± 0.3 min, i.e., comparable to the time required to heat the specimen to the temperature of the thermostat. In such specimens it was possible to measure $V_n = 160 ± 70$ cm⁻² min⁻¹ only by lowering the temperature to 220°C, at which $\tau = 2.6 ± 0.3$ min.

TABLE II

EFFECT OF CHLORATE ION ON FORMATION RATE OF REACTION NUCLEI, ON LONGITUDINAL AND TRANSVERSE RATES OF GROWTH OF THE NUCLEI, THEIR MAXIMUM NUMBER ON A UNIT OF SURFACE, AND THE INDUCTION PERIOD DURING THERMOLYSIS OF NH_4ClO_4 CRYSTALS^a

Number	V_n (1/cm ² min)	V_{g1} ($\mu\text{m}/\text{min}$)	V_{g2} ($\mu\text{m}/\text{min}$)	N_{max} (1/cm ²)	τ (min)
1	21.4 \pm 4.2 \pm 2.1	36.1 \pm 5.8 \pm 2.7	4.7 \pm 0.6 \pm 0.2	612 \pm 59 \pm 31	40.0 \pm 5.4 \pm 2.7
2	45.7 \pm 8.0 \pm 4.0	32.3 \pm 5.4 \pm 2.7	4.3 \pm 0.5 \pm 0.2	1003 \pm 284 \pm 142	29.7 \pm 2.8 \pm 1.5
3	45.7 \pm 9.0 \pm 4.5	34.8 \pm 5.8 \pm 3.0	5.8 \pm 1.2 \pm 0.6	1002 \pm 400 \pm 200	29.0 \pm 4.7 \pm 2.1
4	146 \pm 36 \pm 17	30.7 \pm 5.8 \pm 3.0	5.7 \pm 0.8 \pm 0.4	1860 \pm 155 \pm 71	23.0 \pm 4.7 \pm 2.1
5	161 \pm 26 \pm 13	32.6 \pm 2.8 \pm 1.4	4.2 \pm 0.3 \pm 0.2	2576 \pm 564 \pm 296	22.0 \pm 1.6 \pm 0.8
6	481 \pm 99 \pm 52	31.1 \pm 4.1 \pm 2.1	5.9 \pm 1.1 \pm 0.6	3632 \pm 525 \pm 275	12.0 \pm 2.7 \pm 1.4
7	615 \pm 86 \pm 43	30.6 \pm 2.9 \pm 1.6	4.6 \pm 0.5 \pm 0.3	4613 \pm 575 \pm 280	10.0 \pm 0.8 \pm 0.4

^a 1, recrystallized five times; 2, recrystallized twice; 3, with addition of 1.6×10^{-4} mol% of ClO_3^- ; 4, with addition of 8.2×10^{-4} mol% of ClO_3^- ; 5, with addition of 1.2×10^{-3} mol% of ClO_3^- ; 6, with addition of 2.0×10^{-2} mol% of ClO_3^- ; 7, with addition of 6.4×10^{-2} mol% of ClO_3^- .

Figure 1 gives time-dependence curves for the degree of gross isothermal decomposition of polycrystalline AP specimens recrystallized two and five times. As seen, decomposition of ClO_3^- -free AP begins 10–12 min later. As indicated earlier (16), even on large monocrystals of AP, the nucleation process can be followed only to the degree of decomposition $\alpha = 0.1$. At larger degrees of decomposition, the nuclei coalesce and further decomposition

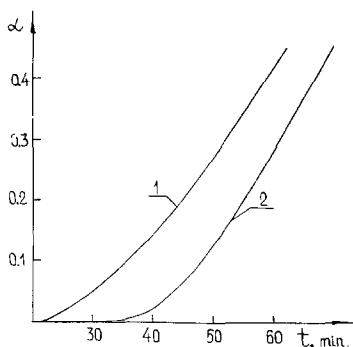


Fig. 1. Kinetic curves of thermolysis of AP powders: 1, a specimen recrystallized twice; 2, a specimen recrystallized five times.

of AP takes place because of growth in the volume of the crystal, the rate of which does not depend on the concentration of ClO_3^- ion. Actually, as was to be expected, the effect of chlorate ion is expressed only to $\alpha \leq 0.1$ and, above all, on the length of the induction period.

Discussion of the Results

In logarithmic coordinates, Fig. 2 shows the dependence of V_n on the concentration of added chlorate ion $[\text{ClO}_3^-]$ in the AP crystal. As seen in the figure, the effect of addition of

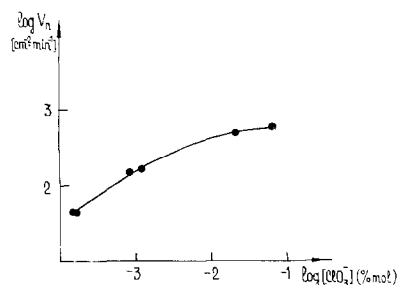


Fig. 2. Dependence of nucleation rate on concentration of added ClO_3^- ions.

the chlorate ion is maximal at small concentrations, and, at large concentrations, it gradually approaches saturation. The transition region begins at a concentration of the order of 10^{-3} mole %. It is interesting that the length of the induction period within this range of concentration does not have a tendency toward saturation and, as in the case of homogeneous autocatalytic reactions (20), can be presented by a logarithmic function of the form

$$\tau = \tau_0 - A \log [\text{ClO}_3^-] \quad (1)$$

which increases by approximately 10 min, when the concentration of the additive is decreased by an order of magnitude (see Fig. 3). It is interesting to note that the dependence (1) also describes the influence of preliminary irradiation dose on the induction period of low-temperature AP decomposition. This is a convincing argument for the mechanism set forth in (18) for the action of preliminary irradiation on the ultimate thermolysis of AP, the essence of which is that during AP irradiation, ammonium chlorate is formed and accumulated in it.

Keeping in mind the above-mentioned analogy with homogeneous autocatalytic reactions and also the fact that the effect of the additive on V_n and τ is characterized by different regularities, it can be asserted that V_n and τ reflect the nucleation process from different aspects and in different ways. This same conclusion comes from comparison of values of the activation energy for nucleation E_n and for the induction period E_τ . As established earlier (16), $E_n = 70$ kcal/mole

and $E_\tau = 20$ kcal/mole. The latter quantity, as is to be expected, coincides with the so-called "value of the activation energy for the nucleation process," which is determined by the temperature dependence of the induction period (22).

As seen in Fig. 2, at small concentrations of the additive, V_n is proportional to $[\text{ClO}_3^-]$. Taking into account the influence of proton donor additives on V_n (16) and developing the analogy with homogeneous autocatalytic reactions, it is possible to propose for V_n a dependence of the type

$$V_n = K[\text{ClO}_3^-][\text{H}^+]. \quad (2)$$

As mentioned, tendency to saturation on the curve of dependence of V_n on $[\text{ClO}_3^-]$ (Fig. 2) begins to appear when $[\text{ClO}_3^-] = 10^{-3}$ mole %. It is curious that this effect is close to the concentration of protons in pure AP at a temperature of 230°C as computed with the help of the previously determined (16) activation energy for formation of conductivity protons: $[\text{H}^+] = \exp(-20\,000/2RT) = 3 \times 10^{-3}$ mole %. Undoubtedly, this coincidence is accidental. Since the tendency toward saturation contradicts Eq. (2), to resolve the contradiction it is necessary to assume either that K is dependent on $[\text{ClO}_3^-]$ or that $[\text{ClO}_3^-]$ is distributed unevenly over the volume of the AP crystal. It is more prudent to accept the second of the two assumptions, all the more since in solid-state chemistry unequal distribution of impurity over the volume of a crystal has long been known, especially at large concentrations. Precisely in this is seen one of the phenomena of the specificity of topochemical reactions. Areas with a high concentration of impurity usually are grain boundaries, accumulations of dislocations, or individual dislocations. It is not surprising that in many studies (12, 14, 15) attention has been given to preferential formation of nuclei on the outcroppings of dislocations in AP crystals.

Consequently, the following mechanism for action of ClO_3^- ion addition on thermolysis of AP can be proposed. The proton, transferring from the ammonium ion to the perchlorate ion, becomes mobile and, moving through the AP lattice (in agreement with the

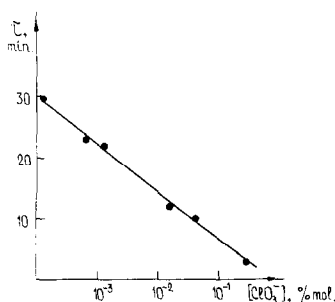
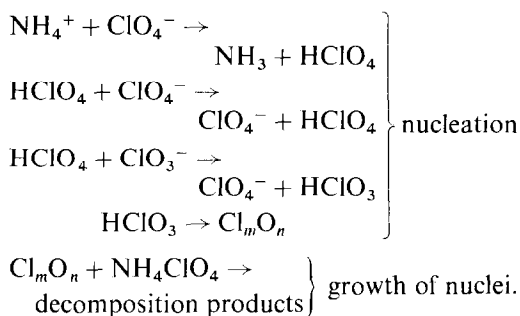


FIG. 3. Concentration dependence of induction period of nucleation on introduction of ClO_3^- ions.

conductivity mechanism suggested in (16)), is trapped by the proton acceptor, the ClO_3^- ion. The addition of the proton to the ClO_3^- ion leads to a sharp upset of its symmetry and, consequently, to destabilization of the ClO_3^- ion. It is precisely because of this (19) that ClO_3^- and ClO_4^- ions are much more stable than the corresponding acids, HClO_3 and HClO_4 . The chloric acid that is produced in this manner is less stable than the perchloric and it decomposes with formation of reactive gaseous products, basically chlorine oxides that catalyze the thermolysis of AP. The center that is formed grows, generating new gaseous products (apparently, all the same oxides of chlorine) and absorbing ClO_3^- ions randomly found in the AP matrix. The latter decompose more quickly than ClO_4^- ions but their concentration and, consequently, their accumulation in the general growth rate of the nuclei is small; therefore, the growth processes are not sensitive to presence of the indicated additive. Actually, it is assumed with all of this that the catalytic rate constant within the nuclei of the decomposition of ClO_4^- ions is significantly larger than the corresponding constant of the noncatalytic decomposition outside the nuclei.

In summary the following scheme of decomposition of AP can be described:



As seen in this scheme, the addition of ClO_3^- ion takes the role of initiator of low-temperature decomposition of AP. The linear dependence of V_n on $[\text{ClO}_3^-]$ at small concentrations of additive allows us to assert that the problem of increasing AP stability to low-temperature decomposition can be solved by maximum possible purification of the technical impurity ClO_3^- ion. An even greater effect can be

attained, as follows from Eq. (2), if there are introduced simultaneously strong proton acceptors that are stable at high temperatures. On the other hand, increasing ClO_3^- ion concentration and introducing acid additives can lower the temperature of initiation of AP decomposition substantially.

The results presented help us to understand the mechanism of thermal development of a latent image obtained during irradiation of AP crystals by light in the uv range (23). As the analysis showed, on uv irradiation, oxychloride ions (ClO_3^- , ClO_2^- , ClO^-) are formed in AP and, consequently, in agreement with the above, in places exposed to uv light nucleation on thermal development begins significantly sooner than in nonilluminated areas of the crystal, a necessary condition for realization of the photographic process (23). Just as might have been expected, the induction period of thermal development of the photographic image depends to a significant degree on the concentration of proton-acceptor additives: It decreases on introduction of proton-donor additives and increases with the introduction of proton-acceptors.

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