THE MECHANISM OF THE LOW-TEMPERATURE DECOMPOSITION OF NH_4ClO_4

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ABSTRACT

The topokinetical aspects of the low-temperature decomposition (LTD) of ammonium perchlorate (AP) crystals, i.e. the nucleation rate (V_n), the rate of nuclei growth (V_g) and their dependence on the concentration of some additives and the temperature, have been investigated. On the basis of experimental data obtained, it is inferred that the nucleation rate of the LTD for chemically pure AP is determined by the content of free protons and unavoidable ClO_3^- ion impurity

$$V_n = k[ClO_3^-][H^+]$$

and has the activation energy $E_n = 70 \pm 4$ kcal mole^{-1}. The length of the induction period of nucleation (τ_n) is a function of ClO_3^-

$$\tau_n = \tau_0 - A \log [ClO_3^-]$$

The corresponding value of the effective activation energy is $E_T = 22 \pm 5$ kcal mole^{-1}. Addition of proton donors catalyzes the nucleation process; proton acceptors inhibit it, but all the proton active additives insignificantly influence the value of V_g. A mechanism of the nucleation process is suggested. Based on this mechanism it is possible to explain in a consistent way all the experimental data obtained and the well-known phenomenon of incomplete (30%) decomposition of AP characteristic of LTD.

During UV irradiation of AP crystals through an opaque stencil, a latent photographic image of the stencil arises within the bulk of the AP. In the early stages of the LTD, this image may be developed. It is supposed that the latent image arises due to the generation of photo-induced ClO_3^- ions in the course of UV irradiation.

On the basis of all available experimental data as well as the proposed mechanism of LTD, a means of nonempirical regulation of AP stability is suggested. In conclusion, the unresolved problems concerning the LTD of AP are reviewed.

INTRODUCTION

Ammonium perchlorate (AP) has been the subject of intensive study for the last 30 years (see, for example, the surveys of Schumacher [1], Jacobs and Whitehead [2] and Hall and Pearson [3]). This interest is undoubtedly due to the use of AP as an oxidizer in solid state propellents. It is therefore quite natural that most of the publications in this field deal with the deflagration and thermal decomposition of AP at both low (up to $T \leqslant 300°C$) (LTD) and high ($T > 380°C$) temperatures (HTD) [2]. Despite the intensive investi-

gations of the physical and chemical properties of AP, some unresolved problems still remain. One of them is the unusually low thermal stability of AP. The characteristic temperature of its marked thermal decomposition is nearly 200°C, which is 300—350°C lower than the corresponding temperatures for alkali metal perchlorates. What is the mechanism of the LTD? Not answering this question, it cannot be said we have exhausted all the possibilities in regulating the thermal stability of AP. For most applications [1,4] extremely stable AP samples are required.

At the present time, two mechanisms for the thermolysis of AP are discussed in the literature. The more widely accepted is the so-called proton mechanism [2—9], which presumes that the initial elementary act of thermolysis is the transfer of a proton from a cation to an anion to give ammonia and unstable perchloric acid

$$NH_4^+ClO_4^- \rightarrow NH_3 + HClO_4$$

The less accepted mechanism is the electron mechanism [10—14], according to which the initial elementary act of AP thermolysis is the transfer of an electron

$$NH_4^+ClO_4^- \rightarrow NH_4^0 + ClO_4^0$$
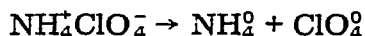
with the subsequent destruction of the radicals produced. The basic argument against this mechanism is the size of the forbidden gap. As mentioned by Maycock and Pay Verneker [10], optical spectroscopy measurements give the value $E_{opt} = 5$ eV.

However, it is indisputable that the LTD proceeds through the 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. One can expect, therefore, that once we have learned the nucleation process we will be able to regulate the decomposition rate of AP.

Although there is a large amount of experimental data on the thermolysis of AP, the process of nucleation itself has scarely been studied [15—21]. This is all the more surprising since, as can be concluded from the above, it is precisely in this way that the nonempirical solution to the problem of regulating the thermal stability of AP can be found. Undoubtedly, this is a consequence of enormous experimental difficulties associated with such investigations.

The present work has been carried out to fill this gap in the area of experimental data in order to proceed later to a discussion of the problem indicated above. We planned to analyze the temperature and concentration dependence of some topokinetical characters of the LTD: nucleation rate (V_n); induction period of nucleation (τ_n); the rate of nuclei growth (V_g); the maximum number of nuclei at the moment they fuse onto a surface unit (N_{max}); activation energies for nucleation (E_n), nuclei growth (E_g), and the energy associated with the induction period (E_τ).

2. EXPERIMENTAL

Single crystals of AP were grown from aqueous solutions by isothermal evaporation at room temperature. Only visually perfect and transparent crystals with well developed rhombic faces were chosen. All the reagents used were the purest available commercially. The concentration of additives introduced into the AP crystals was determined from the results of analysis of the solutions that were obtained by dissolving the crystals in water. The analysis of the PO_4^{3-} ion was performed calorimetrically from the concentration of phosphomolybdenovanadic acid [22]. The SO_4^{2-} ion was determined turbidimetrically by formation of $BaSO_4$. The content of ClO_3^{-} ions was analyzed by the techniques suggested in ref. 23.

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 atmosphere of ammonia or air at a pressure of 10—100 Torr. At lower pressures, the sublimation process of the AP began to predominate. The weight of the sample probe was 3 mg; the grain size in the probe was 100—120 μm. The thermal decomposition of the monocrystals was carried out under a MBB — IA microscope objective. Since the monocrystals differ from each other in features even within the confines of one part of preparation, 13—15 crystals were studied each time. The results were processed on a computer using a standard least-squares method.

3. EXPERIMENTAL RESULTS

3.1 Proton donor additives

It may be expected that, based on the proton mechanism of LTD, proton-active additives will markedly affect the decomposition rate of AP. To check this suggestion, the effect of proton donor and proton acceptor additives was investigated. In the role of proton donating impurity, we used the HSO_4^{-} ion, which has the same charge, size and geometry as the ClO_4^{-} ion and which therefore co-crystallizes well with AP. According to electrical conductivity measurements, HSO_4^{-} ions may be incorporated into AP crystals [24].

The results of computer processing of multiple experimental data are presented in Fig. 1 in Arrhenius coordinates. As can be seen, the nucleation rate (V_n) is increased with dopant concentration, whereas the rate of nuclei growth (V_g) is practically unchanged. The activation energy of the nucleation process corresponds to 70 ± 4 and 50 ± 4 kcal mole^{-1} for pure and doped specimens, respectively. The activation energy for the process of nuclei growth as computed from these data amounts to 35 ± 5 kcal mole^{-1}. Needless to say, these numbers are effective values of the activation energy since the processes of formation and growth of nuclei are certainly multistepped.

Some remarks concerning the terms. As is well known [15—21], the LTD process takes place through the formation and growth within the AP of cigar-like aggregates elongated along the crystallographic axis b (i.e. in the
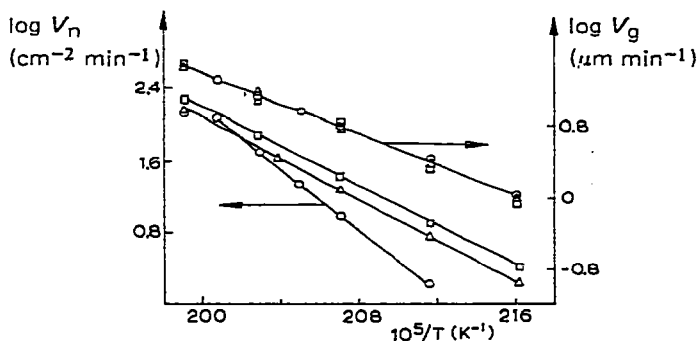
Fig. 1. Temperature dependence of V_g and V_n values for pure AP ($\circ$) and AP containing $\triangle$, 5×10^{-3} mole % HSO_4^- and $\square$, 5.1×10^{-2} mole % HSO_4^-.

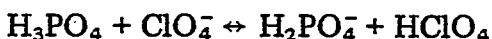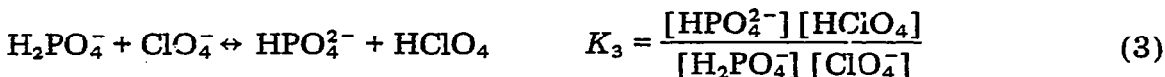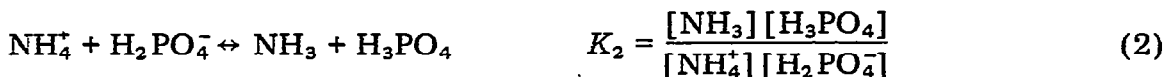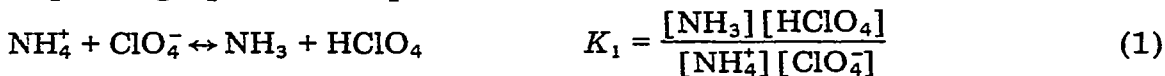[010] direction) which consist of a great number of small (1—2 μm) germs. These are formed in the vicinity of the aggregate mainly in the [010] direction and grow up to 2 μm and then stop. New germs arise in the nearest neighbour, and so the aggregate increases in size. Some authors [2,16,19,20] call such germs nuclei, but we believe that it is more correct to call a compact aggregate a nucleus, and the process of generation of new germs nucleus growth. In a recent work, Jacobs and Ng [25] also recognize the preference of such terminology.

The induction period of nucleation is decreased by the addition of HSO_4^-, but its activation energy is not changed; both the pure and doped samples have equal values, $E_\tau = 22 \pm 5$ kcal mole^{-1}.

3.2 Proton acceptor additives

To determine the effect of the proton donor action of HSO_4^- ion in the pure state, the effect of SO_4^{2-} ion additive on AP decomposition was investigated. In parallel, some other proton acceptor additives (PAA) ($H_2PO_4^-$ and HPO_4^{2-}) were also investigated.

To demonstrate the principle of the possibility of the proton acceptor action of the PAA chosen (e.g. in the case of AP + $NH_4H_2PO_4$), we will present all the possible protolytic reactions in this system, as well as the corresponding equilibrium equations

$$NH_4^+ + ClO_4^- \leftrightarrow NH_3 + HClO_4 \qquad K_1 = \frac{[NH_3][HClO_4]}{[NH_4^+][ClO_4^-]} \qquad (1)$$

$$NH_4^+ + H_2PO_4^- \leftrightarrow NH_3 + H_3PO_4 \qquad K_2 = \frac{[NH_3][H_3PO_4]}{[NH_4^+][H_2PO_4^-]} \qquad (2)$$

$$H_2PO_4^- + ClO_4^- \leftrightarrow HPO_4^{2-} + HClO_4 \qquad K_3 = \frac{[HPO_4^{2-}][HClO_4]}{[H_2PO_4^-][ClO_4^-]} \qquad (3)$$

$$2\,H_2PO_4^- \leftrightarrow H_3PO_4 + HPO_4^{2-}$$

$$H_3PO_4 + ClO_4^- \leftrightarrow H_2PO_4^- + HClO_4$$

As can be seen, only three of the five reactions are really independent, so the last two equations must be eliminated from any subsequent consideration.

The material balance equation and charge neutrality relation may be presented as

$$[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] = [H_2PO_4^-]_0 \tag{4}$$

$$[HClO_4] + [H_3PO_4] = [NH_3] + [HPO_4^{2-}] \tag{5}$$

where $[H_2PO_4]_0$ is the total concentration of the $NH_4H_2PO_4$ additive introduced into the AP crystals. Taking into consideration eqns. (1)—(3) and eqn. (5), the material balance equation may be presented as

$$\frac{[H^+](K_1 - [H^+]^2)\,K_2}{K_2[H^+]^2 - K_1K_3} + \frac{K_1(K_1 - [H^+]^2)}{K_2[H^+]^2 - K_1K_3} + \frac{(K_1 - [H^+]^2)\,K_1K_3}{[H^+](K_2[H^+]^2 - K_1K_3)}$$

$$= [H_2PO_4^-]_0 \tag{6}$$

where $[H^+] \equiv [HClO_4]$, $[NH_4^+] = [ClO_4^-] = 1$.

The right-hand side of eqn. (6) is positive, so the numerators and denominators of each component on the left-hand side must be of the same sign. If relation (7) is fulfilled

$$K_2[H^+]^2 > K_1K_3 \tag{7}$$

then

$$K_1 > [H^+]^2 \tag{8}$$

and the additive may be treated as a proton acceptor. In the opposite case, $K_1 < [H^+]^2$ and the additive must be a proton donor since, according to eqn. (1), when $K_1 = [H^+]^2$ the additive must be neutral in the proton active action. To verify eqn. (7) we rewrite it in the form

$$\frac{K_2}{K_3} > \frac{K_1}{[H^+]} \tag{9}$$

and estimate the constants K_2 and K_3. According to ref. 26

$$\frac{[NH_3][H_3O^+]}{[NH_4^+][H_2O]} = 10^{-10} \tag{10}$$

$$\frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4][H_2O]} = 10^{-2} \tag{11}$$

$$\frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-][H_2O]} = 10^{-7} \tag{12}$$

$$\frac{[ClO_4^-][H_3O^+]}{[HClO_4][H_2O]} = 10^{10} \tag{13}$$

Dividing eqn. (10) by eqn. (11) and eqn. (12) by eqn. (13) one can obtain $K_2 = 10^{-8}$, $K_3 = 10^{-17}$, i.e. $K_2/K_3 = 10^9$. Using the compatibility condition for eqns. (7) and (8), we get

$$\sqrt{K_1} \geqslant [H^+] \geqslant 10^{-4}\sqrt{K_1}$$

i.e. addition of $NH_4H_2PO_4$ to AP may only decrease the $[H^+]$ value, but no more than by 10^4 times. It must be remembered that these estimates are of

TABLE 1

Rates of formation of nuclei and their longitudinal, V_{g1}, and transverse, V_{g2}, growth; maximum number of nuclei and induction period of nucleation for pure AP and AP containing PAA

	V_n (cm^{-2} min^{-1})	V_{g1} (μ min^{-1})	V_{g2} (μ min^{-1})	N_{max} (cm^{-2})	τ_n (min)
1	45.7 ±8.0 ±4.0	32.3 ±5.4 ±2.7	4.3 ±0.48 ±0.21	1003 ±284 ±142	29 ±2.8 ±1.3
2	28.2 ±9.0 ±4.5	35.5 ±5.0 ±2.5	4.3 ±0.58 ±0.28	640 ±120 ±60	29 ±2.8 ±1.5
3	18.2 ±8.0 ±4.0	31.4 ±5.4 ±2.7	4.3 ±0.50 ±0.25	500 ±80 ±40	32 ±2.4 ±1.2
4	12.0 ±3.0 ±1.5	37.6 ±7.0 ±3.6	4.8 ±0.40 ±0.20	448 ±61 ±30	38 ±5.9 ±2.9
5	7.5 ±2.5 ±1.2	35.8 ±6.0 ±3.0	4.8 ±0.50 ±0.25	336 ±59 ±28	53 ±5.0 ±2.5
6	10.1 ±3.4 ±1.7	34.5 ±7.9 ±3.9	4.7 ±1.10 ±0.50	374 ±64 ±32	33 ±2.6 ±1.3
7	8.9 ±2.8 ±1.4	34.9 ±4.3 ±2.1	4.9 ±0.50 ±0.25	325 ±60 ±30	35 ±3.0 ±1.5
8	5.8 ±3.2 ±1.6	35.5 ±5.0 ±2.5	4.5 ±1.40 ±0.70	290 ±57 ±28	49 ±3.5 ±1.7
9	7.1 ±1.5 ±0.7	34.2 ±5.7 ±2.6	4.7 ±0.70 ±0.36	371 ±92 ±46	37 ±4.9 ±2.4
10	5.5 ±0.9 ±0.5	33.3 ±5.0 ±2.1	4.0 ±0.55 ±0.24	314 ±44 ±23	41 ±7.0 ±3.5
11	3.3 ±1.6 ±0.8	31.9 ±5.9 ±2.7	3.9 ±0.60 ±0.30	257 ±94 ±47	45 ±5.6 ±2.9

(1) Pure AP, AP containing PAA (mole %) — SO_4^{2-} ion: (2) 3.2×10^{-3}. (3) 8.2×10^{-3}. (4) 4.5×10^{-2}; (5) 7.6×10^{-2}. $H_2PO_4^-$ ion: (6) 6.1×10^{-3}; (7) 8.8×10^{-3}; (8) 4.3×10^{-2}. HPO_4^{2-} ion: (9) 3×10^{-4}; (10) 5×10^{-3}; (11) 3.1×10^{-2}.

semiquantitative character only: the exact values of the constants in eqns. (10)—(13) may differ substantially from that in the surrounding AP lattice, although the interrelation between them must be changed insignificantly.

It is clear from the above that $(NH_4)_2HPO_4$ in the AP crystal is a stronger acceptor. As for SO_4^{2-} ion evidently it may be only a proton acceptor, but the weakest of all three analyzed.

The data of Table 1 demonstrate the influence of PAA on the topokinetical parameters of the LTD. Standard deviations are presented to the right of each value in the table. The upper value is for 95% credibility, the lower is for a credibility of 70%. Analysis of the results presented in Table 1 shows that PAA increase τ_n and diminish V_n and N_{max}, but insignificantly influence V_g. It is curious to note that the inhibiting effect increases not only with increase of PAA concentration, but also with increase in its proton acceptor ability: the strongest inhibitor is HPO_4^{2-} ion; the weakest is SO_4^{2-}.

As may be expected, PAA also influence the gross kinetics of the LTD, especially its initial steps. Figure 2 demonstrates the kinetics of the isothermal decomposition of a polycrystalline sample of AP containing HPO_4^{2-} impurity. DTA curves of the same samples are presented in Fig. 3. It is seen
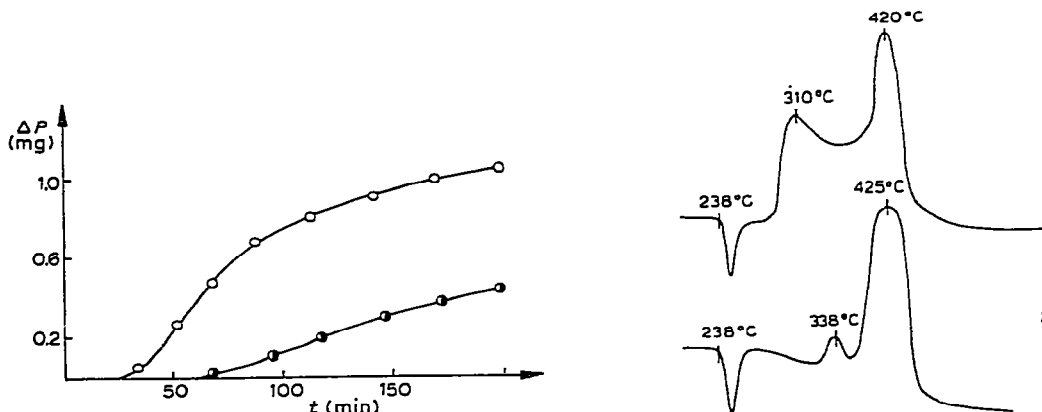
Fig. 2. Kinetic curves of LTD for different polycrystalline AP samples: $\circ$, pure AP; $\bullet$, AP containing 3.1×10^{-2} mole % HPO_4^{2-}. $T = 235°C$.

Fig. 3. Thermal analysis curves for pure AP (1) and AP containing 3.1×10^{-2} mole % HPO_4^{2-} (2).

that even the smallest quantities of the additive substantially influence the AP stability: the induction period of the LTD is doubled; the decomposition temperature is increased by 25—30°C; and the height of the LTD exothermic peak is substantially decreased. Therefore, the proton acceptor and proton donor additives are antagonistic to the LTD process of AP. The effect is undoubtedly due to the proton active properties of the additives. This is proved first of all by the dissimilar action of HSO_4^- and SO_4^{2-} ions, as well as by a strong correlation between the magnitude of the effect and the proton acceptor ability of the additives.

3.3 ClO_3^- ion additive

The next step was to study the influence of homogeneous ClO_3^- ion additive on the LTD process of AP. The choice of this additive was determined by the fact that it is an efficient catalyst of gross AP decomposition [27—29]; also it is known [1] that 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 used in mixture compositions.

As mentioned in previous studies [27—29], chlorate ion diminishes the induction period of the decomposition of polycrystalline AP. It might be expected, therefore, that introduction of the indicated impurity would lead to a decrease in the time it takes for the first nucleus to appear. Nothing could be said a priori about the behaviour of V_n, V_g, and N_{max}.

The effect of ClO_3^- ion doping on topokinetical features of the LTD is demonstrated in Table 2. It is observed that introduction of chlorate ion in the AP crystals really leads to a decrease of τ_n and simultaneously, to an increase of V_n and N_{max}, although V_g values are almost constant. At the indicated temperature (230°C), with the additive content greater than 10^{-1} mole %, the nucleation process proceeds so rapidly that it was impossible to record. Thus, τ_n at an additive concentration of $5 \cdot 10^{-1}$ mole % is 1.0 ± 0.3 min, i.e. comparable to the time required to heat the sample to the tempera-

TABLE 2

Effect of ClO_3^- ion on nucleation rate, longitudinal and transverse rates of growth of nuclei, their maximum number on a surface unit, and the induction period during the LTD of AP crystals

AP crystals	V_n (cm^{-2} min^{-1})		V_{g1} (μ min^{-1})		V_{g2} (μ min^{-1})		N_{max} (cm^{-2})		τ_n (min)	
NH_4ClO_4 Recryst. 5 times	21.4	±4.2 ±2.1	36.1	±5.8 ±2.7	4.7	±0.6 ±0.2	612	±59 ±31	40.0	±5.4 ±2.7
NH_4ClO_4 Recryst. twice	45.7	±8.0 ±4.0	32.3	±5.4 ±2.7	4.3	±0.5 ±0.2	1003	±284 ±142	29.7	±2.8 ±1.5
NH_4ClO_4 + 1.6×10^{-4} mole% ClO_3^-	45.7	±9.0 ±4.5	34.8	±5.8 ±3.0	5.8	±1.2 ±0.6	1002	±400 ±200	29.0	±4.7 ±2.1
NH_4ClO_4 + 8.2×10^{-4} mole% ClO_3^-	146	±35.8 ±16.8	30.7	±5.8 ±3.0	5.7	±0.8 ±0.4	1860	±155 ±71	23.0	±4.7 ±2.1
NH_4ClO_4 + 1.2×10^{-3} mole% ClO_3^-	161	±25.7 ±12.8	32.6	±2.8 ±1.4	4.2	±0.3 ±0.2	2576	±564 ±296	22.0	±1.6 ±0.8
NH_4ClO_4 + 2.1×10^{-2} mole% ClO_3^-	481	±98.7 ±51.7	31.1	±4.1 ±2.1	5.9	±1.1 ±0.6	3632	±525 ±275	12.0	±2.7 ±1.4
NH_4ClO_4 + 6.4×10^{-2} mole% ClO_3^-	615	±86.0 ±43.0	30.6	±2.9 ±1.6	4.6	±0.5 ±0.3	4613	±575 ±280	10.0	±0.8 ±0.4

ture 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 τ_n = 2.6 ± 0.3 min.
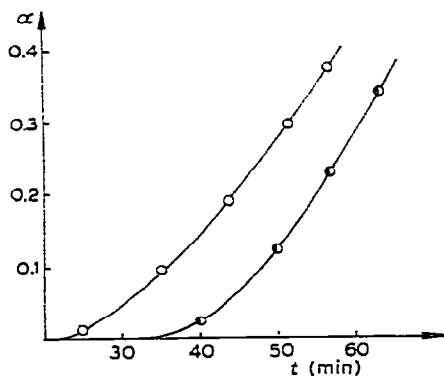

Fig. 4. Kinetic curves of LTD at T = 238°C. o, AP recrystallized twice; ●, AP recrystallized five times.

As may be expected, so-called "pure" AP crystals also contained ClO_3^- impurity, although no more than 1.4×10^{-4} mole %. Five-fold recrystallization led to the point where, within the limits of sensitivity of the analytical method used, ClO_3^- ion could not be detected in the AP samples. This corresponds to the impurity concentration $[ClO_3^-] \leqslant 5 \times 10^{-5}$ mole %. As seen, the LTD of such AP crystals is characterized by an increase in τ_n by 10 min, a decrease of V_n by a half, and a significant decrease in N_{max}. The gross kinetic data as presented in Fig. 4 also demonstrate the increase in AP stability and most of all τ_{LTD} values. So it may be concluded that the second rate-determining factor of the LTD process of "pure" AP is the concentration of unavoidable ClO_3^- ion impurity.

3.4 Thermolysis of matrix-isolated ClO_3^- ions

The topokinetical data presented in the previous sections do not allow an unambiguous treatment. The most probable mechanism of ClO_3^- ion action in AP crystals is its protonation and subsequent decomposition of $HClO_3$ acid formed. One must not exclude, however, the fact that ClO_3^- ion may decompose independently, without formation of the protonated form.

To check such a proposal we investigated the thermal decomposition of a matrix-isolated chlorate ion in the presence of different concentrations of a proton donor additive. It was shown previously [30] that the standard leophyl technique of matrix isolation is inconsistent in such cases, which is why we used the co-crystallization of $KClO_3$ with $KClO_4$ for matrix isolation. We used NH_4^+ ion as a proton donor additive, which is able, at high temperatures, to give a proton in accord with the reaction: $NH_4^+ \rightarrow NH_3 + H^+$. After crystallization from water solutions, mixed crystals as large as $2 \times 3 \times 2$ mm^3 were formed, of composition $K_{1-x}(NH_4)_x(ClO_4)_{1-y}(ClO_3)_y$, where x and y values were analyzed by standard procedures. Isothermal decomposition of the powdered crystals was performed in an atmosphere of air at $p = 300$ Torr, since at lower pressures intensive sublimation took place. Some experiments were performed on a time-of-flight mass spectrometer MSH-4 in a polythermic regime. The rate of linear increase in temperature was $100°C$ min^{-1} [31]. The reaction initiation was assumed to be at the temperatures when O_2 and/or HCl (if any) evolution was detectable.

Figure 5 demonstrates the typical mass spectra. As can be seen, the gases evolved under such conditions are NH_3 [16,17], H_2O [17,18], NO[29], O_2[31] and HCl[35]. Table 3 summarizes the data for some systems. It may be concluded that the stability of ClO_3^- ion is exactly correlated with the concentration of proton donors, i.e. the most probable reactions in these systems are

$$NH_4^+ + ClO_3^- \rightarrow NH_3 + HClO_3$$
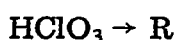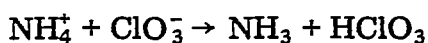
$$HClO_3 \rightarrow R$$

where R is all the products of $HClO_3$ thermal decomposition, including O_2 and HCl. This conclusion is supported by the results of isothermal experiments. As is seen from Fig. 6, the thermolysis is not achieved at $T = 320°C$ when ClO_3^- or NH_4^+ ions are present separately, but is readily achieved when
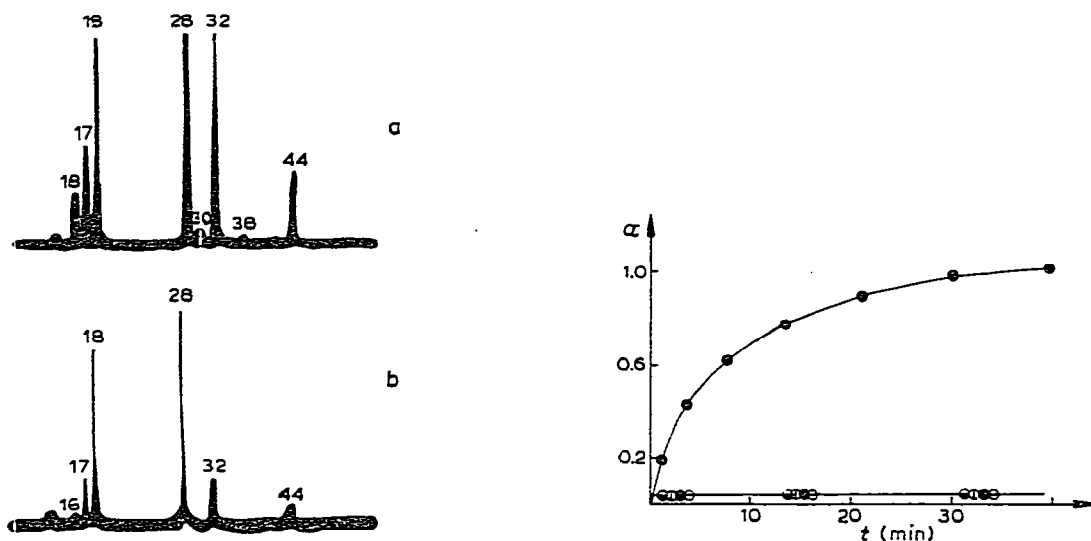
Fig. 5. (a) Mass-spectra of the thermal decomposition products of matrix-isolated ClO_3^- ion in the presence of proton donor additives; (b) background spectra.

Fig. 6. Kinetic curves of the thermal decomposition of matrix-isolated ClO_3^- ion. The concentrations are presented in mole %: ●, 1.7×10^{-2} ClO_3^- + 1.0 NH_4^+; ⊜, 3.1×10^{-1} ClO_3^-; ⊕, 2.5 NH_4^+; ◉, pure $KClO_4$; ⊖, pure $KClO_3$.

both of them are co-present in a $KClO_4$ matrix (the concentration of the reagents being less when co-present as compared to the case when they are present separately). No doubt this is due to the high solubility of NH_4ClO_3 in water compared to $KClO_4$.

One can anticipate that the formation of protonated ClO_3^- ion favours its decomposition in an inert matrix. Evidently the thermolysis of ClO_3^- ion in an AP matrix where the concentration of NH_4^+ is equal to 1 proceeds solely through the formation of its protonated form.

TABLE 3

Decomposition temperatures of matrix-isolated ClO_3^- ion in the presence of NH_4^+ ion

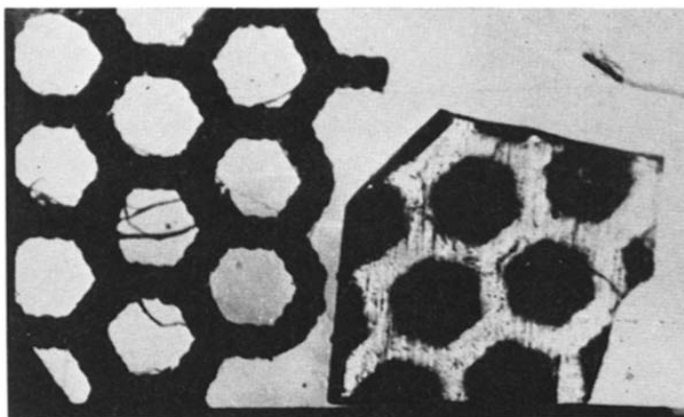| Content of additives in $KClO_4$ matrix		T_D (°C)
ClO_3^- (mole%)	NH_4^+ (mole%)	
0	0	610 ± 15
100	0	500 ± 10
3.1×10^{-1}	0	500 ± 10
3.3×10^{-1}	6.0×10^{-3}	490 ± 10
5.5×10^{-2}	1.5×10^{-2}	470 ± 10
5.2×10^{-2}	1.5×10^{-2}	380 ± 15
4.8×10^{-2}	1.0	265 ± 15

Fig. 7. Optical microscopy photograph of a developed photo-image. The photograph on the left-hand side is the stencil picture. ×40.

3.5 Influence of UV irradiation

During UV irradiation of AP crystals through an opaque stencil, a latent photographic image of the stencil arises within the bulk of the AP. This image can be thermally developed when heating pre-irradiated crystals under LTD conditions. Figure 7 demonstrates an example of the stencil and its thermally developed image. The image can be developed only on the surface of the crystal and not in its volume, even though the latent image arises throughout the bulk of the AP. This can be demonstrated as follows. If a previously irradiated crystal is cleaved along a plane parallel to its irradiated surface, the images can also be thermally developed on the newly formed surfaces and are clearly mirror-symmetrical for the two surfaces. As the analysis showed after UV irradiation as well as after more hard irradiation (X-rays, γ-rays, electrons [32]), in AP crystals ClO_3^- ions are formed and accumulated.

3.6 Effect of chlorine dioxide

ClO_2 vapours, as mentioned in ref. 33, accelerate the LTD of AP. Our investigations proved that even after 10 min exposure of AP in ClO_2 vapours of partial pressure $P = 2.5$ Torr, the induction period of the LTD is reduced to 3—5 min. Moreover, such treatment even influences the thermal decomposition of partially decomposed AP (see Fig. 8), and only 30% decomposed samples are not influenced by such a treatment. It is of interest to know whether anion or cation sublattices react with ClO_2. To check all the possibilities we investigated interactions of ClO_2 with NH_3, NH_4Cl and $KClO_4$. Schematically it may be presented as

$$ClO_2 + NH_3 \rightarrow \text{products I} \qquad (14)$$

$$ClO_2 + NH_4^+ \rightarrow \text{products II} \qquad (15)$$

$$ClO_2 + ClO_4^- \rightarrow \text{products III} \qquad (16)$$

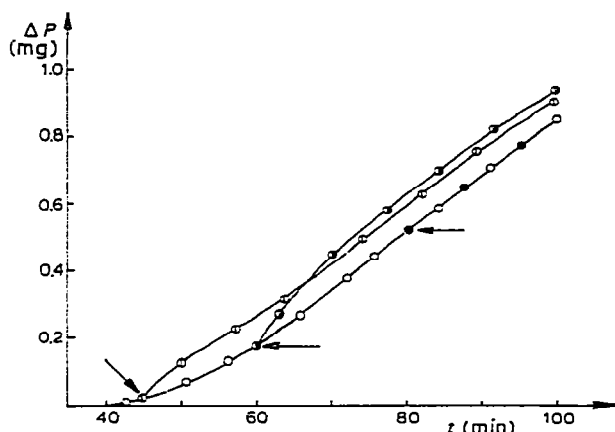Mass-spectrometric analysis indicates that interactions in accord with eqn.

Fig. 8. Kinetic curves of LTD at $T = 230°C$ for control AP sample, $\circ$, and for samples exposed for 30 min in ClO_2 vapours after partial LTD: $\oplus$, after 45 min; $\circledcirc$, after 60 min; $\bullet$, after 80 min.

(14) proceed very rapidly, even at room temperature; that described by e·jn. (15) proceeds at a comparable rate at $T = 70—80°C$. The last process did not occur at all. It may be deduced therefore, that chlorine dioxide may react with the cationic sublattice of AP or with ammonia, but not with perchlorate ion.

3.7 Effect of ammonia

In accord with data in the literature [2,7], ammonia inhibits the LTD process of AP. We also investigated this effect, but from a slightly different viewpoint. As was demonstrated by Garner and Bircumshaw [34], after the phase transition of AP at $T = 240°C$, its LTD rate decreases, and at $T = 252°C$ reaches a minimum. As was supposed by Kaidymov and Gavazova [35], this effect is due to the catalytic effect of the rhombic modification of AP on its own LTD. The high-temperature cubic modification of AP is quite a poor catalyst of the LTD, which is why its rate decreases after phase transition. The slight difference between the corresponding temperatures (240 and 252°C) was associated with the hysteresis characteristic for phase transitions. In this case the difference will tend to be quite small when hysteresis is eliminated. To check this we investigated the LTD at 238, 242 and 252°C, the decomposition temperature being approached from a higher temperature. To prevent AP decomposition at high temperatures we used an atmosphere of ammonia at $P = 105$ Torr and slowly (within 2 h) decreased the AP temperature from 260°C to the decomposition temperature. To initiate decomposition, the atmosphere of ammonia was replaced by air.

As can be seen from data presented in Fig. 9, in this case the kinetic curves take their "normal" positions: the smallest is the AP reactivity at $T = 242°C$. These data explain in a consistent way the distinction between the proposal of Kaidymov and Gavazova [35] and experimental results [34]. At the same time we have confirmed their data [35] concerning the more efficient action of LTD inhibitors in the cubic phase compared to rhombic.
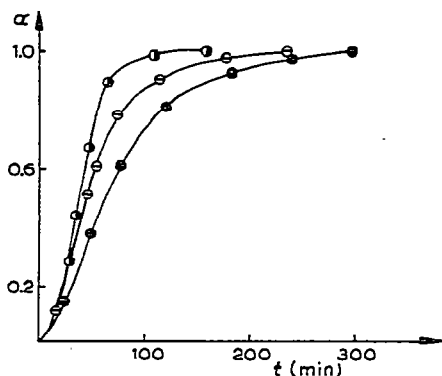
Fig. 9. Kinetic curves of the LTD of ÀP preheated for 3 h in an atmosphere of ammonia. LTD temperatures: ⊕, 238°C; ⊜, 242°C; ⊖, 252°C.
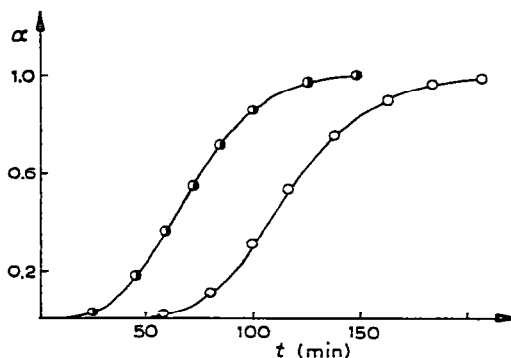
Fig. 10. Kinetic curves of LTD at $T = 225°C$ for AP exposed to an atmosphere of ammonia for 2 h, ⊕, and without exposure, O.

Therefore, at an ammonia pressure of $P = 2$ Torr, the LTD of AP in the cubic modification was entirely supressed, but no effect was observed in the rhombic phase.

It is worth mentioning that exposing AP in an atmosphere of ammonia for 2 h substantially increases its subsequent LTD rate in an atmosphere of air, and most of all decreases the induction period of the LTD. A comparative analysis of the data in Figs. 9 and 10 shows that the effect is peculiar both to cubic and rhombic phases. This unexpected result will be treated in Sect. 4.6.

DISCUSSION

4.1 Preliminary remarks concerning the LTD Mechanism

As mentioned previously, two mechanisms of LTD are now discussed in the literature: the electron mechanism and the proton mechanism. Energetically, the proton mechanism is much more probable, so the following discussion will be restricted to this mechanism. We emphasize, however, that there is no direct experimental evidence in favour of it!

The classical proton mechanism was first proposed by Jacobs [36]. The first step of LTD proceeds in accord with eqn. (1). Ammonia and perchloric acid produced in this way diffuse to the AP surface where the acid is decomposed and then the decomposition products may oxidize ammonia. Such a process is possible in principle and no doubt takes place. The question is what are its interconnections with LTD? Indeed, all "direct experimental evidence" of the proton mechanism are based on mass-spectroscopic investigations of AP heated in high vacuum [8, 36—41]: in vacuum, one may in some way exclude the secondary(e.g. gas phase) reactions. One must have in mind however, that the higher the vacuum in the system, the greater is the

probability of a sublimation by-process. Usually investigators of LTD take precautions to avoid sublimation (e.g., Sect. 2).

When heating AP, two independent processes take place: an exothermic LTD process and an endothermic sublimation process. By increasing the ambient air pressure to 100 Torr, we tried to suppress the sublimation. However, it is possible, in principle, to organize such an experimental situation when almost 100% AP will sublime by heating [2]. As is well known, sublimation of AP proceeds through its dissociation to ammonia and perchloric acid. The process is reversible: NH_3 and $HClO_4$ react on the cold walls of the system to reform AP. The activation energy of high vacuum sublimation is 20 kcal mole^{-1} [42].

Moreover, even if it were possible to suppress (hypothetical) sublimation in high vacuum experiments [8, 36—41] it would not be possible to measure the primary products of LTD. In accord with electron microscopy [19—21] as well as optical microscopy data [15—16, 18], the LTD takes place in a germ on the crystal subsurface at a depth of no less than 2 μm. This means that even in this hypothetical case, mass spectrometrically one is able to record only the secondary products of LTD. It is now evident that investigation of the mechanism of LTD is possible only by indirect experimental methods.

4.2 Interrelation between different topokinetical parameters of LTD

What is the nucleation process? First of all, one must note the difference between the mechanisms of nucleation and nuclei growth processes. It may be seen first from a comparison of the corresponding activation energy values: $E_n = 70 \pm 4$; $E_g = 35 \pm 5$ kcal mole^{-1}. This conclusion is strengthened by the dissimilar character of the influence of the additives investigated on the rate of formation and growth of the nuclei. The processes determining the length of the induction period of nucleation and the rate of nucleation, since $E_n \gg E_\tau = 22 \pm 5$ kcal mole^{-1}, are also different.

Its value, as expected, is close to the so-called "value of the activation energy for the nucleation process", which in ref. 43 is determined by the temperature dependence of the induction period. However, it is evident that the method proposed in ref. 43 is inconsistent. Actually, according to ref. 43 $E_n = 20$ and $E_g = 30$ kcal mole^{-1}, one must expect a decrease in the N_{max} value with increase of temperature, since for the condition $E_g > E_n$ the contribution to the overall decomposition of the process that has less activation energy will decrease. Indeed, for temperatures 190 and 210°C N_{max} values are 390 and 790 cm^{-2}, respectively, in accord with the relation $E_n = 70$ kcal mole$^{-1} > E_g = 35$ kcal mole^{-1}.

4.3 The chemistry of the nucleation process

From the experimental results presented in Sects 3.1 and 3.2 the process of the rate of nucleation may be proposed as

$$V_n = K_1[H^+] \tag{17}$$

However, the presence of free protons i.e. $HClO_4$ acid, is an insufficient condition for the beginning of the LTD process. Actually, $HClO_4$ acid generated in the AP sublimation process, as mentioned previously, is stable enough to avoid decomposition and, together with ammonia, reforms AP on the cold surface of the vessel. So, one must propose the existence of an additional necessary condition to initiate the LTD process. We suppose such a condition to be the presence of unavoidable ClO_3^- ion impurity.

This is proved by the data of Fig. 11, where the nucleation rate is a function of ClO_3^- ion content. It is seen that for small concentrations of ClO_3^- ion additive, the following relation is fulfilled

$$V_n = K_2[ClO_3^-] \tag{18}$$

Combining eqns. (17) and (18) it is possible to present the nucleation rate as

$$V_n = K[H^+][ClO_3^-] \tag{19}$$

i.e. the nucleation rate is proportional to the concentration of chlorate acid in the AP crystals.

As seen in Fig. 11, the effect of ClO_3^- ion additive is maximal at small concentrations and gradually tends to saturation at high concentrations. The transition region begins at a concentration of the order of 3×10^{-3} mole %. It is curious that this is close to the concentration of "free protons" in pure AP at a temperature of 230°C, as computed with the help ,- f the previously determined [45] activation energy for the formation of conductivity protons: $[H^+] = \exp(-20000/2RT) = 3 \times 10^{-3}$ mole %; perhaps it is accidental coincidence. The tendency toward saturation, however, is contradictory to eqn. (19). To resolve this it is necessary to assume either that the K value is dependent on $[ClO_3^-]$ or that ClO_3^- ion is distributed unevenly over the AP crystal volume. It is more prudent to accept the second of the two assumptions, all the more since in solid state chemistry unequal distribution of an impurity over the volume of a crystal has long been known, especially at large concentrations [45]. Areas with a high concentration of impurity are grain boundaries, accumulations of dislocations, etc.
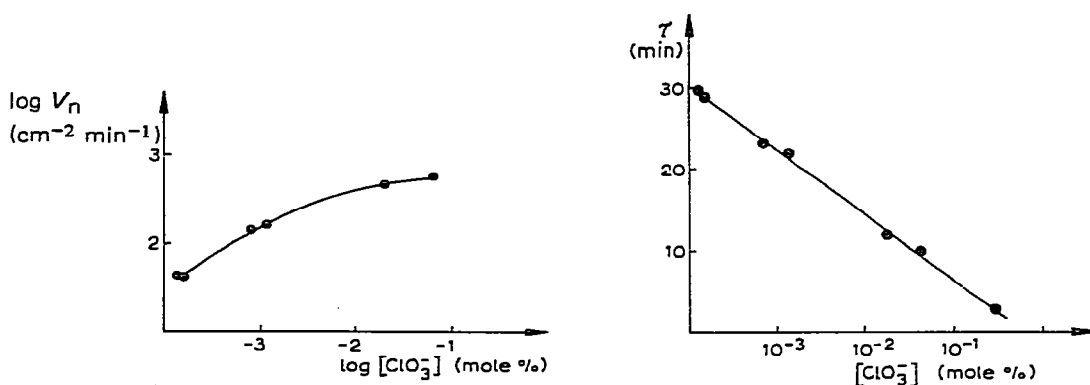

Fig. 11. Dependence of nucleation rate on concentration of added ClO_3^- ions.

Fig. 12. Concentration dependence of τ_n on introduction of ClO_3^- ions.

It is interesting that the length of the induction period within the concentration range investigated does not have a tendency toward saturation and, as illustrated by the data of Fig. 12, may be presented by a logarithmic function of the form

$$\tau_n = \tau_0 - A\log[ClO_3^-] \qquad (20)$$

increasing by approximately 10 min, when the concentration of the additive is decreased by an order of magnitude. This is an additional argument in favour of the statement that V_n and τ_n reflect the nucleation process from different aspects and in different ways.

In such a way the impurity of ClO_3^- ion may be treated as a potential centre of the nucleation process. The results of the matrix-isolated decomposition of ClO_3^- ion indicate that acceptance of a proton by the chlorate ion leads to its destabilization. Undoubtedly it is due to the asymmetry of the protonated anions that the thermal stability of acids such as $HClO_3$, $HClO_4$, $HMnO_4$, and HNO_3 is lower than that of anions ClO_3^-, ClO_4^- MnO_4^- and NO_3^- say in alkali metal salts. $HClO_3$ acid under LTD conditions destructs, with the formation of active intermediate products catalyzing the subsequent LTD process. One such product is ClO_2 which, as shown in ref. 46, may even be treated as one of final products of the LTD, with output as large as 5% of all gaseous products. Chlorine dioxide, as demonstrated in sect. 3.6, may oxidize the ammonia of AP. This leads to an accumulation of $HClO_4$ acid which catalytically decomposes on the AP surface generating new portions of ClO_2, etc. Nothing will change in our discussion if we assume (after Jacobs [41]) that ClO_2 first transforms to ClO and oxidizes ammonia in a germ. The mechanism presented above can easily explain the effect of additives on the nucleation rate.

Let us now discuss the validity of the assertion about the rate-determining character of ClO_3^- content on the nucleation process of nominally pure AP. As stated in ref. 4, the LTD process of commercially available AP is induced due to impurity content: either of transition metals or chlorate ions or extra $HClO_4$ acid. After "burning out" of impurities the LTD process is finished and AP is only able to decompose at high temperatures (HTD). Undoubtedly such a preposition is incorrect and first of all due to the fact that the LTD process lasts up to $\alpha = 30\%$ and this quantity is almost insensitive to an impurity content [2—3]. But the useful point of the assertion stated in ref. 4 (the authors call it wide-spread without, however, giving a reference) is in the emphasis of the role of all sorts of impurities in the LTD process. In our case it is of interest to know whether some other impurity besides the ClO_3^- may determine AP stability. As may be seen in Fig. 11, the commercially available sample has the same stability as the five-times recrystallized sample containing the same amount of ClO_3^- ion additive. This means that ClO_3^- ion is the stability-determining impurity in the native AP samples investigated.

4.4 Crystal chemistry of nucleation

As mentioned previously nucleus formation takes place under the surface of the AP crystal. The germ formed first grows up to 2 μm and then stops.

New germs arise mainly in the nearest neighbour (4—6 μm), in the [010] direction, and so on. Raevsky et al. [16,43] observed the germs to move mainly along the [010] direction, i.e. the direction of dislocation slip. They measured the gas pressure in a germ and found it to be nearly 2×10^6 Pa. Sometimes, as observed in refs. 18—20 the gases in a germ break the walls and get out of the AP crystal. In this case the germ ceases to grow, even though it is less than 2 μm.

After 30% decomposition, the LTD process comes to an end. As shown in optical and electron microscopy investigations [2, 14—21, 48], the residue consists of sponge-like AP with a highly developed surface. The characteristic thickness of the walls of this sponge-like structure was 3—5 μm. The residue, being exposed for some hours in vapours of AP solvents (water, ammonia, etc.) is able to undergo LTD and again no more than 30% of the total weight may decompose, and so on. In accord with Garner and Bircumshaw's proposition [15,34], this rejuvenation effect is due to partial recrystallization of sponge-like AP residue.

The following interpretation of the observed experimental data can be proposed. The potential centres of nucleation are $HClO_3$ acid molecules or even ClO_3^- ions since they have proton donor species NH_4^+ with concentration $[NH_4^+] = 1$. If the nucleation takes place on the AP surface it will cease immediately since the catalysts of LTD — intermediate products of $HClO_4$ decomposition — will escape out of the crystal. The nucleation process cannot take place deep in the volume of the AP crystal due to the cell effect, i.e. steric difficulties for $HClO_3$ decomposition (see ref. 59). It is on the subsurface where the nucleation process proceeds most readily.

Chlorine oxides which are generated in a germ oxidize ammonia, producing $HClO_4$ acid and water. In the early stages when the water content is small, $HClO_4$ acid decomposes easily, generating new portions of catalyst, i.e. chlorine oxides. Later, with increase of water content, the AP decomposition in the germ is inhibited due to the formation of $HClO_4$ acid hydrates. According to data in the literature, hydrates such as $H_2O \cdot HClO_4$, $2H_2O \cdot HClO_4$, etc., are stable enough under LTD conditions [5,9]. Undoubtedly this is due to the proton acceptor action of H_2O molecules [54] so it is more correct to represent these hydrates in the form $H_3O^+ClO_4^-$, $H_5O_2^+ClO_4^-$, etc. Therefore, the main reason for the germ to stop growing, as we suppose, is LTD inhibition due to accumulation of water molecules in a germ.
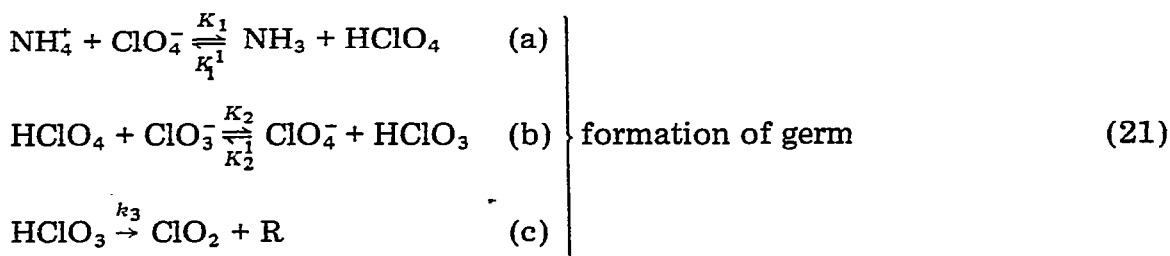
The high gas pressure in a germ results in high mechanical tensions in its vicinity, which favours the high diffusibility of the lattice near a germ. This may explain the germ movement in the nucleus zone as well as the high diffusibility of chlorine oxides. These oxides may initiate the formation of a new germ 3—5 μm from the old one. The new germ cannot arise at a shorter distance for the same reasons as an old germ ceases to grow, i.e. due to H_2O accumulation. In a hidden way this speculation implies a higher diffusibility of chlorine oxides compared to H_2O molecules. Undoubtedly it is due to the higher polarity of the H_2O molecule compared to ClO_2 or ClO.

The mechanism presented above may explain qualitatively all the known topokinetical features of LTD: incomplete decomposition, sponge-like structure of the residue, rejuvenation effect, etc. Therefore, highly dispersed
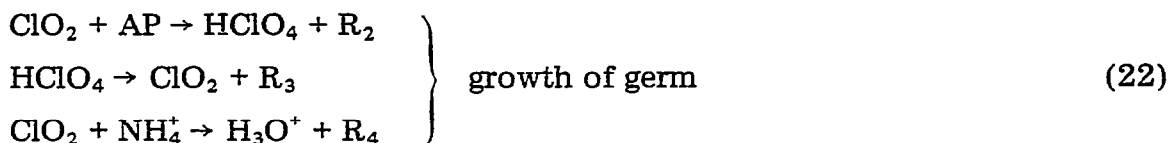
specimens of AP ($d < 4$ μm) are stable under LTD conditions [11] since the nucleation process can only take place on no less than 3—4 μm depth of an AP crystal. A decrease of the LTD temperature must result in an increase of the fraction of AP decomposed due to the higher mechanical strength of the AP crystal, as well as to the decrease of diffusibility of H_2O. Really, as was demonstrated by Schmidt [29], at $T = 190°C$ the maximum extent of decomposition is as high as $\alpha = 60\%$ instead of $\alpha = 30\%$ at $T = 230°C$. In the same manner one can also explain an increase in the maximum α value with increase of ambient gas pressure [29,49].

4.5 The scheme of the nucleation process

Using the results presented earlier, a rough scheme of the nucleation process may be presented as follows

$$
\begin{aligned}
&NH_4^+ + ClO_4^- \underset{K_1^1}{\overset{K_1}{\rightleftharpoons}} NH_3 + HClO_4 \quad\text{(a)} \\
&HClO_4 + ClO_3^- \underset{K_2^{-1}}{\overset{K_2}{\rightleftharpoons}} ClO_4^- + HClO_3 \quad\text{(b)} \\
&HClO_3 \overset{k_3}{\rightarrow} ClO_2 + R \quad\text{(c)}
\end{aligned}
\left.\rule{0cm}{1.8cm}\right\} \text{formation of germ}
\tag{21}
$$

The process of germ growth may be presented as a sequence of the following chemical reactions

$$
\begin{aligned}
&ClO_2 + AP \rightarrow HClO_4 + R_2 \\
&HClO_4 \rightarrow ClO_2 + R_3 \\
&ClO_2 + NH_4^+ \rightarrow H_3O^+ + R_4
\end{aligned}
\left.\rule{0cm}{1.5cm}\right\} \text{growth of germ}
\tag{22}
$$

Induced formation of the neighbour germ may be presented as

$$
\begin{aligned}
&m\ ClO_2 \xrightarrow{\text{diffusion}} n\ ClO_2 \\
&n\ ClO_2 + AP \rightarrow H_2O + R_5
\end{aligned}
\left.\rule{0cm}{1.1cm}\right\}
\tag{23}
$$

Inhibition and stop in growth of the germ is due to reactions

$$
\begin{aligned}
&H_2O + HClO_4 \rightarrow H_3OClO_4 \\
&H_2O + H_3OClO_4 \rightarrow H_5O_2ClO_4
\end{aligned}
\left.\rule{0cm}{1.1cm}\right\}
\tag{24}
$$

Analysis of these reactions demonstrates the poor applicability of early traditional mechanisms for describing the LTD process. The initial LTD process, i.e. nucleation, can best be presented in terms of a modified proton mechanism; but this corresponds to no more than $\alpha = 1\%$ of the entire LTD process. The basic LTD process cannot be adequately described by either the proton or electron mechanism. Our presentation of the LTD process is much closer to the proton mechanism than to the electron mechanism.

4.6 The ammonia effect

As mentioned in Sect. 3.7, exposure of AP to an atmosphere of ammonia at LTD temperatures for some hours results in an increase of subsequent AP reactivity. Starting with our conception of the LTD mechanism, one can suppose that ammonia must insignificantly influence the nucleation process since it is localized on the subsurface of the AP crystal. Most probably, ammonia preferentially inhibits decomposition of the surface regions of the AP crystals, so allowing the gaseous products of the LTD to escape out of the germ. In fact, as proved by direct optical microscopy observations after heating in an atmosphere of ammonia, an initially transparent AP single crystal becomes milky, obviously due to subsurface nucleation, but without any change in weight. When the atmosphere of ammonia is replaced by one of air, the nuclei formed can already start growth, which is probably why the subsequent LTD process takes place without any detectable induction period.

4.7 Activation energy of LTD

A comparison of the activation energies for nuclei growth, $E_g = 35 \pm 5$ kcal mole^{-1}, and for the gross kinetics of the LTD process, as derived in ref. 2 from the temperature dependence of the LTD maximal rate $E_{LTD} = 33 \pm 1.6$ kcal mole^{-1}, shows that $E_g \approx E_{LTD}$. One can assert, therefore, that the maximum rate of LTD of AP is determined mainly by the processes of the growth of nuclei. Indeed, it appears that even at the extent of decomposition $\alpha = 0.1$, practically the whole crystal is covered with nuclei that run into each other and further decomposition proceeds only at the expense of their intergrowth into the volume of the crystal [44,50]. It is not yet possible to give any reasonable interpretation of the physical meaning of the value $E_g = 35 \pm 5$ kcal mole^{-1}. Undoubtedly this is an effective value since the process of nuclei growth is complicated and multistepped.

In this respect it is easier to analyze the nucleation process. Having in mind eqn. (21b), the nuclei formation rate may be presented as

$$V_n = K_3[HClO_3] \tag{25}$$

Two different cases must be analyzed:

(1) let the reaction in accord with eqn. (21b) be irreversible, i.e. for some reason the proton cannot transfer back from ClO_3^- to ClO_4^- ion. In this case, in accord with the quasi-stationary concentrations method [55] the [HClO$_3$] value must be presented as

$$[HClO_3] = \frac{K_2}{K_3}[HClO_4][ClO_3^-]$$

and eqn. (25) will have the form

$$V_n = K_2[HClO_4][ClO_3^-]$$

(2) in the second case when the reaction in accord with eqn. (21b) is reversible, setting $[ClO_4^-] = 1$ in the quasi-stationary approximation, one ob-

82

tains

$$[HClO_3] = \frac{K_2}{K_2^i}[HClO_4][ClO_3] \tag{27}$$

combination of eqns. (24) and (27) gives

$$V_n = \frac{K_2}{K_2^i}K_3[HClO_4][ClO_3^-]$$

Using standard approximations $[NH_4ClO_4] = 1$ and $[NH_3] = [HClO_4]$, the $[HClO_4]$ value can be presented as

$$[HClO_4] = (K_1/K_1^i)^{1/2} \tag{29}$$

Designating the corresponding rate constants ratio as equilibrium constant K_E for the first case one obtains

$$V_n = (K_{1E})^{1/2} K_2[ClO_3^-] \tag{30}$$

and for the second

$$V_n = (K_{1E})^{1/2} K_{2E} K_3[ClO_3^-] \tag{31}$$

Activation energies derived from eqns. (30) and (31) may be presented in the first case as

$$E_n = H_1/2 + E_2 \tag{32}$$

and in the second as

$$E_n = H_1/2 + H_2 + E_3 \tag{33}$$

Let us estimate all the items in eqns. (32) and (33). In accord with ref. 44, as used already in Sect 4.3, $H_1 = 20$ kcal mole^{-1} E_2 cannot exceed 0.5 eV, i.e. ca 10 kcal mole^{-1} [51—53]. The E_3 value may be taken as 50 kcal mole^{-1}, i.e. the middle Cl—O bond energy between 47.6 kcal mole^{-1} in $HClO_4$ [41] and 59.1 kcal mole^{-1} in HOCl [53]. From these data, in the first case one gets $E_n = 20$ kcal mole^{-1} and in the second case $E_n = 70$ kcal mole^{-1}. The latter value is in very good agreement with the experimentally observed one. However, the basic assumption of the presupposition is reasonable enough. Indeed, proton equilibria in condensed phases are achieved for 10^{-7}—10^{-5} sec [51—55], the life-time of $HClO_3$ molecules being 6—7 orders of magnitude greater. This means that the proton exchange reaction presented in eqn. (21b) proceeds under equilibrium conditions.

The marked decrease of E_n after incorporation of the proton donor additive is in agreement with eqn. (33), since in this case extrinsic protons are produced without expenditure of energy.

The E_r value cannot be treated adequately yet, even in the case of homogeneous autocatalytic reactions [55]. All the more, it concerns the heterogeneous processes.

4.8 Irradiation influence

The length of the induction period of the LTD process of AP depends upon the logarithm of a dose of preliminary irradiation as [56]

TABLE 4

Length of induction period of thermal development, τ_D, for pure AP and AP containing proton-active additives ($T = 230°C$)

Sample	τ_D (min)
Pure	15
AP + 5.1 × 10^{-2} mole% HSO_4^-	9
AP + 5.0 × 10^{-2} mole% $CS(NH_2)_2$	20
AP + 5.0 × 10^{-3} mole% HPO_4^{2-}	25

$$\tau_{LTD} = \tau_0 - B \log \Phi$$

Almost the same regularity is characteristic for concentration dependence of the induction period of the nuclei formation process, as is demonstrated by eqn. (20). This coincidence may be treated as an additional argument in favour of the mechanism given in refs 29 and 33 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. A similar generation of ClO_3^- ions was observed in UV irradiated AP samples [57]. Accumulation of ClO_3^- ions in UV irradiated AP crystals results in the local increase in reactivity, i.e. in places irradiated by UV light nucleation on thermal development begins sooner that in non-illuminated areas of the crystal, a necessary condition for realization of the photographic process [58].

As expected, the induction period of the thermal development of the photographic image depends to a significant degree on the concentration of proton-active additives. The data of Table 4 demonstrate that PAA increase the induction period of thermal development and proton donors decrease it.

The latent image is generated in the total volume of the AP single crystal, but visualization of this image can only be observed on the by-surface regions. This additionally demonstrates the hindrance to the nucleation process in the volume of the AP crystal.

4.9 Stabilization of AP crystals

On the basis of the presented mechanism of the LTD it is possible to propose a means of regulating AP stability. The actual problem is the maximal stabilization of AP crystals [4,61], so we will restrict the following discussion to this.

The simplest way of stabilization is chemical, i.e. the utmost purification of commercially available samples; of course it is an expensive way. ClO_3^- ion is an almost unavoidable impurity in AP. In may possibly be extracted by selective oxidation of ClO_3^- or by reduction to Cl^- ion. It this way we slightly increased the AP stability by selective reduction of ClO_3^- by addition of $SnCl_2$ in ethanol solution. In water solution the effect is less, perhaps due to the hydrolytic acidity of $SnCl_2$ solutions.

Another chemical way is the introduction of PAA into AP crystals. Un-

doubtedly it is due to the proton acceptor action of ions such as HPO_4^{2-}, SO_4^{2-}, PF_6^-[4,29,61] that they are used as practical stabilizers of AP used in solid propellent compositions. Figures 2 and 3 can partially illustrate this for the case of HPO_4^{2-} ion.

An alternative approach can be offered from the analysis of the crystal chemistry of the LTD process. In fact, data in the literature demonstrate that 30 μm AP crystals are the most reactive [11,15]. Such an extremum is in agreement with the crystal chemical features of AP decomposition: the large crystals have a relatively low surface area so the specific rate of decomposition (divided by the mass of AP crystals) is small. On the contrary, for quite small crystals the nucleation process is hindered since it takes place at a depth of no less than 2—3 μm, which is why the LTD rate tends to be zero for crystals less than 4—5 μm [11,15].

It is easy to obtain large AP crystals (1 mm or more) but this way is hardly acceptable in practice. In this respect it is more reasonable to recommend a decrease in the dimensions of the AP crystals to a minimum. The best effect may be achieved by the joint action of all methods proposed, i.e. synthesis of submicron AP crystals purified from ClO_3^- and other impurities and containing PAA.

5. CONCLUDING REMARKS

In previous sections, we have described what we suppose to be the most probable LTD mechanism. Accordingly, the main factor determining AP stability is the content of ClO_3^- impurity. It is impossible, however, to entirely prevent the LTD of even ideally pure AP since it is a thermodynamically unstable compound. It is only possible to kinetically retard the reaction by, for example, blocking the easiest LTD mechanism. For our AP samples, such a way is the "chlorate ion way". However, it is possible, in principle, to realize other ways; for example, refs. 29 and 62 demonstrate the "permanganate ion way", i.e. MnO_4^- ion induced LTD. As to our contribution, it concerns the mechanism of "pure", commercially available AP.

In conclusion, we must consider some problems that require additional investigation. It is desirable to estimate more exactly the distance from the surface where the first germ is formed in AP. According to Raevsky et al., it is 20 μm, but from the data of refs. 19 and 20 one can conclude (if the electron microscopy photographs presented there really refer to LTD nuclei, and not to sublimation etch pits) that this distance is 3—5 μm.

Another interesting problem is the role of dislocations in the LTD process. It is widely stated in the literature [16—20,25] that dislocation outcrops are the potential centres of nucleation. However, there is no one direct experimental proof of this point. From the data of refs. 19 and 20 (again if they are not photographs of the sublimation etch pits), the generation of the new germs in front of growing nuclei may certainly be connected with dislocations. Two objections arise: first, as mentioned in Sect. 3.1 such a process would be more properly termed nucleus growth, and not nucleus formation; second, the known experimental data are insufficient to distinguish the rea-

son-sequence relations existing in the nuclei growth process described in refs. 19 and 20.

Having in mind the subsurface nature of the nucleation process, the question arises: why does an ambient gas atmosphere influence the LTD of AP? We must assume that at least under LTD conditions gas diffusibility in AP is abnormally high.

All this demonstrates that, in spite of the great progress in AP investigations, unresolved problems still exist. No doubt these problems, now formulated and realized, will be solved in the near future. In turn, new methods of regulating the rate of this interesting process will be found.

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