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EFFECT OF AMMONIA ON THE THERMAL DECOMPOSITION OF ORTHORHOMBIC AND CUBIC AMMONIUM PERCHLORATE

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ABSTRACT

The inhibiting effect of ammonia vapours on the kinetics of the thermal decomposition of ammonium perchlorate(AP) in the temperature range 215–270°C has been investigated. An initial ammonia pressure of about 200 Torr is necessary for the practically full suppression of the decomposition of the orthorhombic crystals at temperatures close to the point of AP polymorphic transformation (240°C). With the cubic crystals, 0.5 Torr is the corresponding pressure required. In the case of complete inhibition of the decomposition in the presence of ammonia, AP crystals become yellowish. The activation energy of decomposition of the orthorhombic modification is 29 ± 0.6 kcal mole^{-1} in the absence of ammonia, and 38 ± 1.1 kcal mole^{-1} under ammonia vapour pressure of 6.5 Torr. A kinetic analysis of the traditional proton model of AP decomposition has been made showing that the increase of the activation energy in the presence of ammonia may be derived from this model.

INTRODUCTION

It has been found by many authors [1–6] that ammonia vapours have a considerable inhibiting effect on the thermal decomposition of ammonium perchlorate(AP). Recent studies [7] have shown that the ammonia inhibiting effect is sharply increased by transformation of the orthorhombic AP to the cubic modification. This finding has led to the explanation of the influence of some ammonium salt additives on the decomposition of the above two forms of AP [8].

This work represents a more detailed study of the effect of ammonia on the thermal decomposition of orthorhombic and cubic AP in the temperature range 215–270°C.

EXPERIMENTAL

Reagent grade AP was twice recrystallized in twice-distilled water. The decomposition of the polycrystalline samples of 0.4–0.6 mm particle size was followed manometrically using a glass membrane manometer. The ratio of the mass of AP to the volume of the reaction vessel was about 10^{-3} g cm^{-3} and 30 mg samples were used. After 3 h of vacuum treatment of the sample at 100°C, preliminarily dosed anhydrous ammonia vapours were condensed into a side tube of the vessel. The anhydrous ammonia was previously prepared by vacuum distillation over sodium and was stored in a glass tube in the presence of ammonium nitrate under the form of a saturated solution with relatively low vapour pressure at room temperature. The samples were heated in a thermostat with Wood's metal, and the temperature was kept constant within ± 0.5°C.

RESULTS

The kinetic curves are plotted with the coordinates: time (t) in min, and the volume of the gas products (V) in cm^3 g^{-1}, reduced to normal conditions. As the AP decomposition is carried out in the presence of the gaseous decomposition products, interruption of the process was not observed when a 30% extent of decomposition was reached [9,10]. Because of its long duration, however, the experiments were stopped before complete decomposition was present.

Figure 1 represents AP decomposition in the 237–260°C temperature range in the absence of ammonia vapours. According to Bircumshaw and Newman [1], the maximum decomposition rate (W_{max}) in the same temperature range passes through a maximum at 240°C and a minimum at 250°C. Our experiments (see also Table 1) show the same maximum at 240°C, but the minimum is observed at 242–244°C. It is seen from Table 1 that the induction period (τ)* passes through a minimum at 241°C, jumps to a higher value above this temperature, remains almost constant in the 242–246°C range, and decreases again at higher temperatures. The presence of the minimum of τ at 241°C, i.e., above the point of the phase transition, may be accounted for by the presence of a considerable amount of unchanged orthorhombic phase in the initial stage of decomposition. In the stage of acceleration, however, a considerable slowing down of decomposition is observed, the maximum rate being about three times lower than that at 240°C. Recent studies of the AP phase transition [11] support the existence of a superheated orthorhombic phase.

Figure 2 represents the orthorhombic AP decomposition at 237°C in the presence of ammonia vapours with initial pressure (P_{NH_3}) in the range 0–193 Torr. As is seen from Fig. 2, the inhibiting effect increases with

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* The induction period was arbitrarily defined as the time elapsed until 5 cm^3 g^{-1} of the gas is evolved, which corresponds to an extent of decomposition $\alpha \approx 0.7\%$. The gas evolved by complete decomposition of AP is about 720 cm^3 g^{-1} [10].

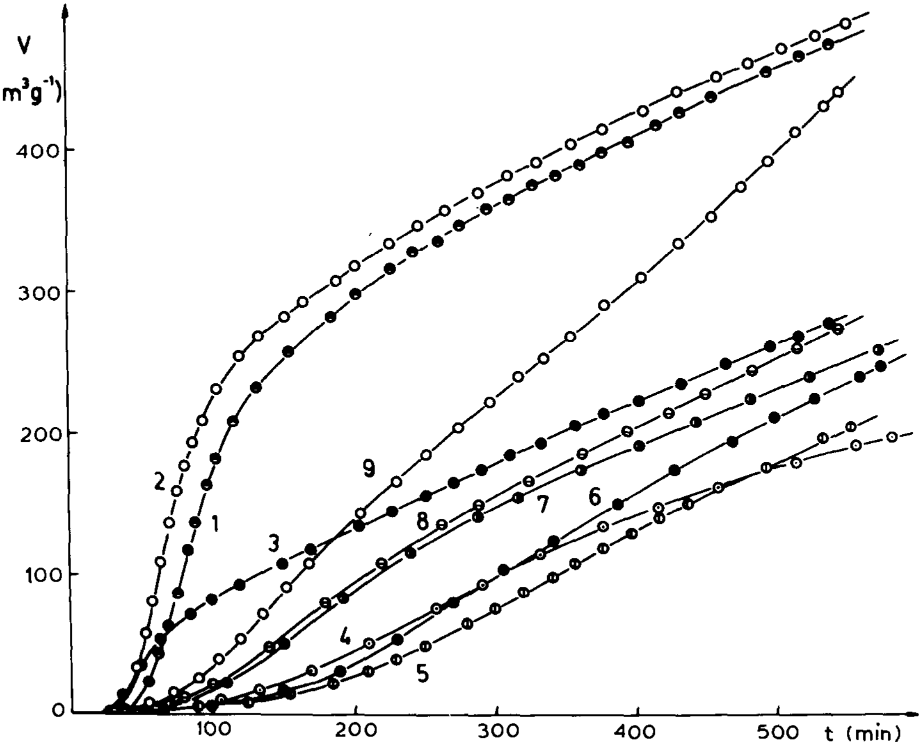

Fig. 1. Decomposition of AP at different temperatures (°C): (1) 237, (2) 240, (3) 241, (4) 242, (5) 244, (6) 246, (7) 248, (8) 250, (9) 260.

vapour pressure and gas evolution is not observed during 500 min with $P_{NH_3} \approx 200$ Torr (curve 9). Moreover, the presence of ammonia alters the character of the kinetic curves in the $0 < \alpha < 30\%(0 < V < 220$ cm^3 g$^{-1})$ range of the decomposition. In this region, the decomposition of pure AP passes through an induction period, an acceleration period, and a decay period. With ammonia pressure higher than 2 Torr (curves 4–8), two inflexions of the kinetic curves are observed corresponding to two maximum rates.

In the range of ammonia pressures $0 < P_{NH_3} < 20$ Torr (curves 1–7), it is to be pointed out that the inhibition of the process consists of a strong decrease of the maximum rates, while the induction period is only slightly affected; while W_{max} becomes about five times lower, τ is increased only 1.5 times. The latter remains practically constant up to 10 Torr, and only with ammonia pressure higher than 20 Torr is it considerably increased.

The inhibiting effect of ammonia on the decomposition of the cubic AP at 246°C (Fig. 3) is much stronger. The practically full blocking of decomposition for 600 min requires in this case an ammonia pressure of about 0.4 Torr (curve 5). The same experiment shows in its later stages (Fig. 3b, curve 5) the development of a reaction whose rate is very similar to that of pure AP

TABLE 1

Induction periods and maximum rates of AP decomposition under different temperatures and pressures of NH_3

No.	t (°C)	P_{NH_3} (Torr)	τ (min)	W_{max} ($cm^3\ g^{-1}\ min^{-1}$)
1	237	0	41	3.8
2	240	0	33	4.7
3	241	0	29	1.7
4	242	0	85	0.54
5	244	0	85	0.57
6	246	0	84	0.69
7	248	0	67	0.78
8	250	0	54	0.82
9	260	0	44	1.2
10	270	0	21	1.6
11	237	0	41	3.8
12	237	0.20	40	3.2
13	237	2.1	41	2.1
14	237	6.5	44	1.9
15	237	9.2	49	1.9
16	237	15	52	1.8
17	237	20	58	0.78
18	237	45	72	
19	246	0	84	0.69
20	246	0.02	104	0.73
21	246	0.20	170	0.83
22	246	0.30	252	0.70
23	246	0.39	700	0.65
24	260	0.67	190	1.0
25	270	0.67	88	1.4

decomposition (curve 1). This gives grounds to suppose that decomposition should begin in the experiments with high ammonia concentrations, but the respective induction periods are of very long duration. The data in Fig. 3 and Table 1 show that inhibition of cubic AP decomposition consists in a strong increase of the induction period, not in a decrease of the maximum rate, which remains practically constant with $0 < P_{NH_3} < 0.4$ Torr. It remains unknown whether with $0 < \alpha < 30\%$ two maximum rate values would be observed and whether these would be decreased with the increase of P_{NH_3}, similar to the decomposition of the orthorhombic AP (Fig. 2, curves 4–8).

The extremely strong increase in τ by raising of P_{NH_3} with the cubic crystals did not permit investigation of the decomposition in its later stages even when the temperature exceeded by 30°C the point of phase transition (see Fig. 4). Figure 4 (curves 1–4) shows the decomposition of cubic AP in the 241–270°C temperature range with an initial ammonia pressure of 2

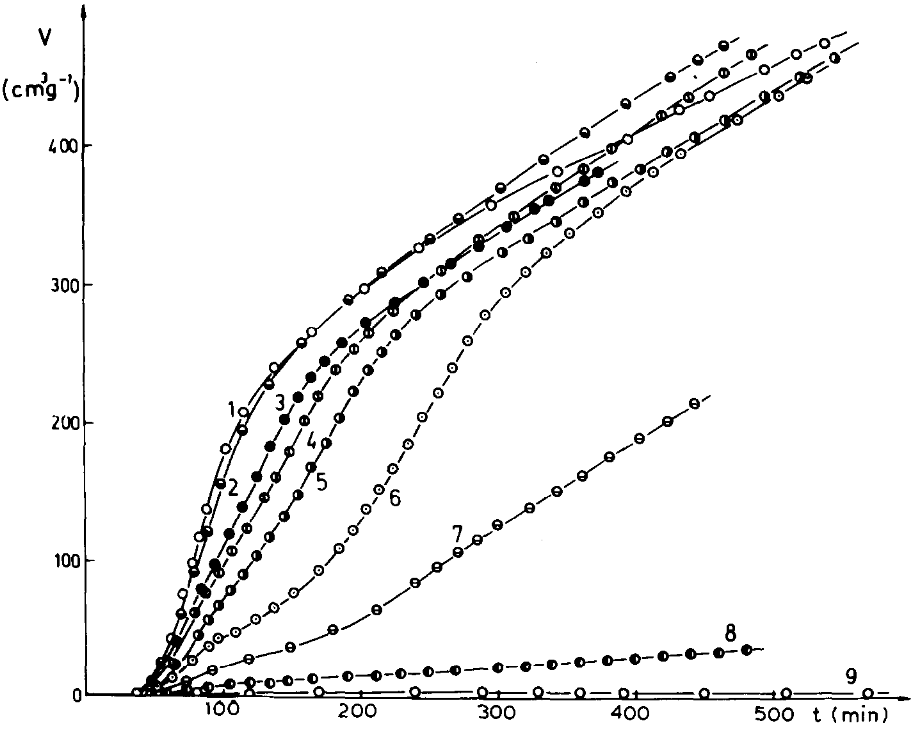

Fig. 2. Decomposition of AP at 237°C under initial NH_3 pressures (Torr): (1) 0, (2) 0.20, (3) 2.1, (4) 6.5, (5) 9.2, (6) 15, (7) 20, (8) 45, (9) 193.

Torr. This insignificant ammonia quantity effects practically full suppression in the said temperature range. As an exception, the experiment at 241°C (curve 1) produced significant rates and extents of decomposition for the time of experimentation. The possible cause is a suspected presence of small quantities of the superheated orthorhombic phase, with this close to the point of the phase transition temperature. The three-fold decrease in vapour pressure to 0.67 Torr (curves 5 and 6) produces a decrease in the inhibition and leads to significant decomposition rates at 260 and 270°C. As is seen from Table 1, these decomposition rates are very close to those observed in the absence of ammonia, and the inhibiting effect of the latter consists mainly in strong extension of τ. It is to be pointed out that the kinetic isotherms obtained in the presence of ammonia at 270°C and higher temperatures do not exhibit the decay period with $\alpha < 30\%$, which is characteristic for pure AP decomposition, and the stage of acceleration is followed by a stage of almost constant rate (see curve 6).

Considering the great differences between the ammonia inhibiting effects on orthorhombic and cubic AP decomposition, it is to be expected that the temperature decrease in the course of isothermal decomposition of cubic AP under 240°C should sharply accelerate the reaction. The opposite effect

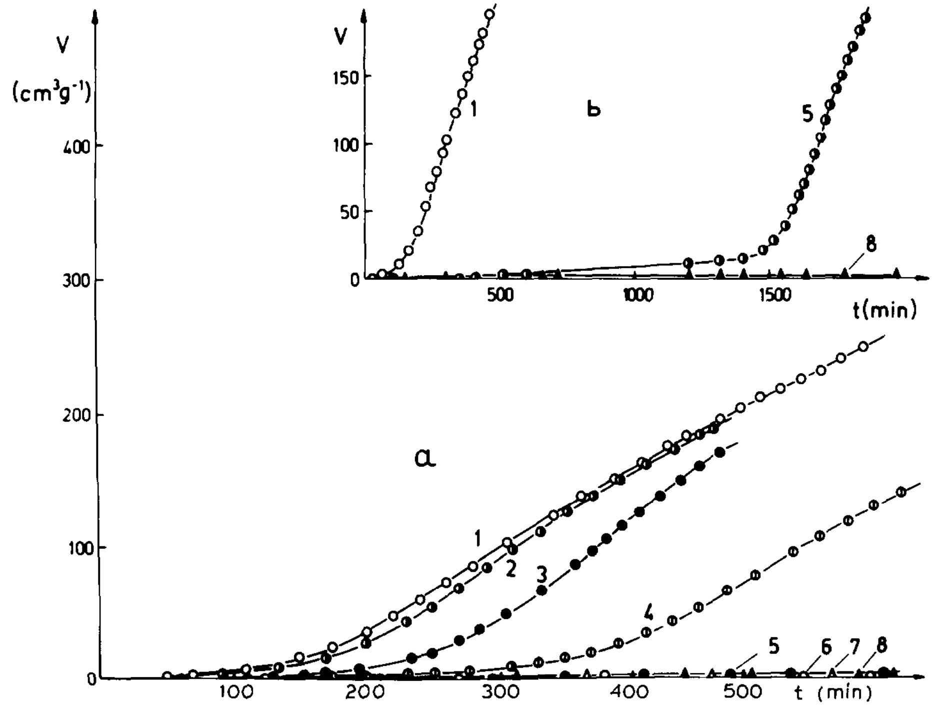

Fig. 3. Decomposition of AP at 246°C under initial NH_3 pressures (Torr): (1) 0, (2) 0.02, (3) 0.20, (4) 0.30, (5) 0.39, (6) 0.67, (7) 2.0, (8) 20.

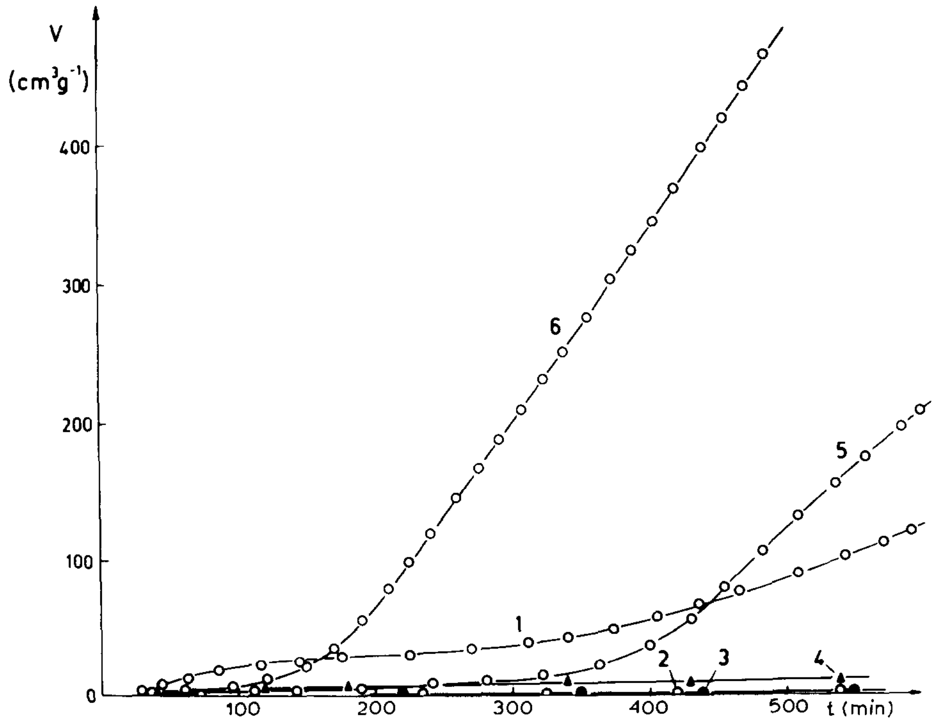

Fig. 4. AP decomposition in the presence of NH_3 (2.0 Torr) at different temperatures (°C): (1) 241, (2) 242, (3) 246, (4) 270; and in the presence of NH_3 (0.67 Torr) at temperatures: (5) 260, (6) 270.

should be observed with the orthorhombic crystals with raising of the temperature above 240°C. The data in fig. 5 justify these expectations. Curve 1′ shows the decomposition of the cubic crystals in the presence of ammonia (0.67 Torr) with initial temperature 242°C and final temperature 237°C. It is seen that about 250 min after passing under the point of phase transition (see curve 1″), decomposition takes place with a rate very close to that of pure AP decomposition at the same temperature (curve 1). On the other hand, when initial AP decomposition has taken place at 237°C (curves 2′ and 3′) with consecutive raising of the temperature to 246°C (see curves 2″ and 3″), the opposite effect has been observed: a strong retardation of the reaction results from the phase transition. In this case, however, the sharp change in the reaction rate occurs only 5 min after the temperature of the thermostat has passed above 240°C.

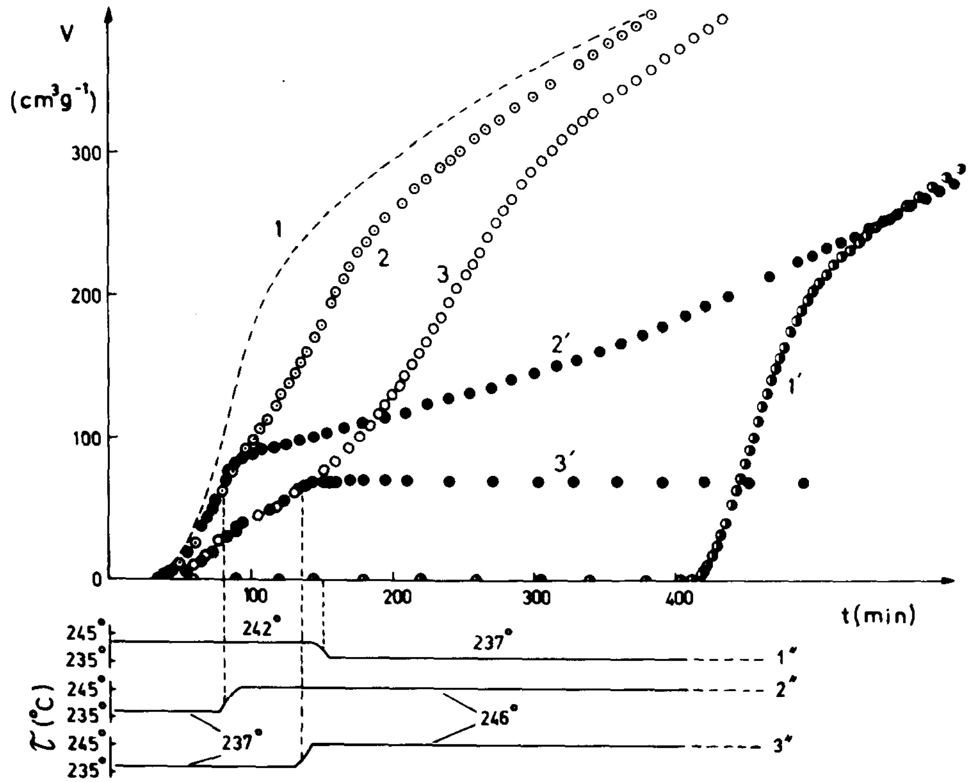

Fig. 5. (1), (2), (3) Decomposition of AP at 237°C and NH_3 pressures 0, 6.5 and 15 Torr, respectively; (1′) AP decomposition under 0.67 Torr NH_3 pressure at 242°C and (after the dotted line) 237°C; (2′) and (3′) 6.5 and 15 Torr NH_3 pressure, respectively, at 237°C and (after the dotted line) 246°C; (1″), (2″), (3″) the course of the average temperature in experiments 1′, 2′ and 3′, respectively.

Figure 6 represents the Arrhenius plots of the coefficient of coincidence(R) of the kinetic isotherms (see ref. 12) of orthorhombic AP decomposition in the 215–237°C temperature range with initial ammonia pressures of 0 Torr (curve 1) and 6.5 ± 0.03 Torr (curve 2). The coefficient of coincidence of each isotherm has been computed for the region $10 < V < 230$ cm^3 g^{-1} ($1.4 < \alpha < 32\%$). The mean root-square error of the arithmetic mean value of R in this region was found to be less than 0.5% in the experiments without NH_3 and less than 1.5% in the experiments with NH_3. The activation energy values obtained from the Arrhenius plots by the least-squares method are 29 ± 0.6 kcal mole^{-1} for the AP decomposition in the absence of NH_3 and 38 ± 1.1 kcal mole^{-1} for the AP decomposition under ammonia vapour pressure of 6.5 Torr.

The increase in the activation energy of topochemical reactions with raising of the pressure of the reversibly evolved final reaction product has been established by Zawadski and Bretsznajder [13] and theoretically explained by Pawlutschenko and Prodan [14]. According to the above results, a similar effect is valid with AP thermolysis in the presence of ammonia, one of the primary products of this reaction according to the so-called proton transfer mechanism of AP decomposition [4].

It is worth noting that a slight yellowish coloration of the AP crystals has been found after all the experiments with full blocking of the decomposition.

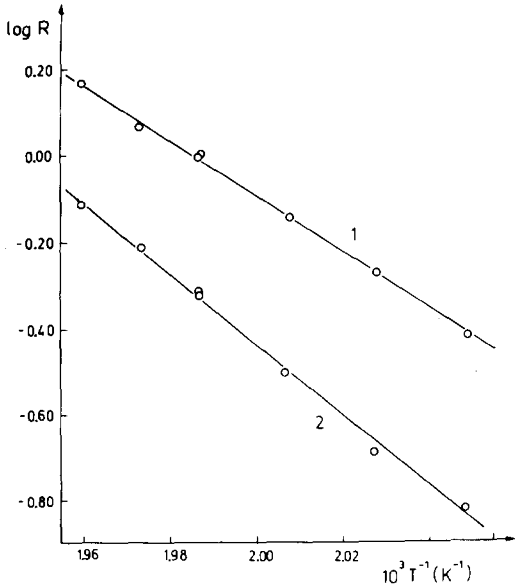

Fig. 6. Dependence of the coefficient of coincidence (R) on temperature. (1) AP+0 Torr NH_3; (2) AP+6.5 Torr NH_3. The R values of the two samples at 230°C are taken in the ratio of their maximum rates.

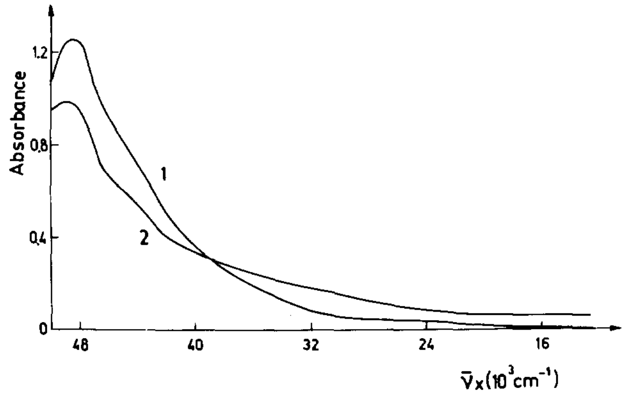

Fig. 7. Absorption spectra: (1) colourless crystals; (2) coloured crystals.

Microscopic observation showed them to be almost transparent. The coloration was visually established to appear 20 min after the start of the experiments. It did not disappear after 5 years of storage of the samples at room temperature. To verify whether the colour change was not due to interaction of the crystal surface with trace amounts of organic substances (vacuum grease vapours or ammonia contaminations), ammonia has been produced by ammonium sulphate decomposition in some experiments and its introduction in the reaction vessel has been carried out without condensation. Under these conditions, the same colour effect has been observed as with the usual experiments. The recent microscopic investigations of Raevskii and Manelis [15] on the thermal decomposition of AP single crystals have shown the formation of brown-yellow reaction nuclei, the coloration of which has been attributed to the presence of chlore and nitrogen oxides. We have recorded the EPR spectra of the coloured samples at room temperature and at liquid nitrogen temperature but paramagnetic particles which could be ClO_2 or NO_2 molecules have not been detected. That coloration is not due to NO_2 is supported by the fact that the samples did not lose their colour at $-60°C$, which should be the result of dimerization of the oxide. The IR spectra of the coloured and non-coloured samples have been found to be absolutely identical. As can be seen from Fig. 7, the UV–visual absorption spectrum of the coloured samples exhibits a tail of residual absorption at the end of the UV region, which is not present in the spectrum of the colourless samples and may account for the coloration. The spectrum of the coloured samples, however, does not exhibit additional peaks which might throw light on the nature of the coloration.

DISCUSSION

Burcumshaw and Newman [1] were the first to observe the decrease of the maximum rate of decomposition of AP as a result of its phase transition from orthorhombic to cubic form. The origins of this phenomenon have not yet been elucidated. According to Manelis et al. [16], it is due to the lower rate of multiplication of the dislocations with the growth of the reaction nuclei in the isotropic cubic lattice than in the anisotropic one. In Refs. 7, 8 and 10 two possible explanations of the phenomenon have been advanced: (1) the phase transition of AP from orthorhombic to cubic modification leads to the formation of stable dislocation groups, i.e., to polygonization, facilitating the diffusion of $HClO_4$ along the newly formed grain boundaries, which decreases the rate of ammonia oxidation by the products of acid decay [10]; (2) the decomposition of the $HClO_4$ molecules is catalyzed by the inner surfaces, whose catalytic activity decreases with the transition of the orthorhombic crystals to the cubic modification [7,8]. These suppositions are based on the assumptions that low-temperature decomposition proceeds as a result of formation and growth of reaction nuclei in the subsurface layer of the crystals [17] and that the decomposition proceeds by the so-called proton transfer mechanism advanced by Jacobs et al. [4,18]

$$
\begin{array}{lcccc}
NH_4^+ClO_4^- & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} & NH_3(a) & + & HClO_4(a) \\
 & & k_5\downarrow\uparrow k_6 & & k_7\downarrow\uparrow k_8 \\
 & & NH_3(g) & & HClO_4(g)
\end{array}
\qquad (1)
$$

$$HClO_4(a) \xrightarrow{k_3} A + \ldots.$$

$$A + NH_3(a) \xrightarrow{k_4} B + \ldots.$$

where A is an active intermediate product of the $HClO_4$ decomposition (say ClO_3, ClO_2, etc.), B is one of the final products of AP decomposition, and the indexes a and g designate adsorbed molecules and molecules in the gas phase, respectively.

In the present work, an interpretation of the effect of the phase transition on the kinetics of AP decomposition with $\alpha > 1\%$ has been attempted on the basis of the above model and the assumption [7,8] that the rate constant k_3 jumps to lower values as a result of the transition of the AP from orthorhombic to cubic form.

The application of the quasi-stationary concentrations method [19] to the above model in the case of closed space decomposition yields five algebraic equations, four of which are independent. As the quasi-stationary concentrations of the intermedite products are five, each of them is not unequivocally determined by the rate constants (k_i) at a given temperature and is a function of the concentration of each of the other products. If we choose the concentration of gaseous NH_3 to be x, we have for the $HClO_4$ concentrations on the surface and in the gas phase, respectively

$$[\mathrm{HClO_4(a)}] = \frac{k_1 k_5}{k_2 k_6 x + k_3 k_5} \tag{2}$$

$$[\mathrm{HClO_4(g)}] = \frac{k_1 k_5 k_7}{(k_2 k_6 x + k_3 k_5) k_8} \tag{3)*}$$

The decomposition rate (W) is expressed according to model (1) by

$$W = \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_4[\mathrm{NH_3(a)}][\mathrm{A}] = k_3[\mathrm{HClO_4(a)}] \tag{4}$$

By substituting (2) in (4) we obtain

$$W = \frac{k_1 k_3 k_5}{k_2 k_6 x + k_3 k_5} \tag{5}$$

Equation (5) shows that the rate of low-temperature AP decomposition must decrease with the increase of the quasi-stationary ammonia vapour concentration produced by introducing the NH_3 in the reaction vessel.

If we assume that the temperature dependence of W and of each rate constant are, respectively, $W = W^0 \exp(-E/RT)$ and $k_i = k_i^0 \exp(-E_i/RT)$, logarithmic differentiation yields

$$E = E_1 + E_3 + E_5 - \frac{k_2 k_6 (E_2 + E_6)\, x + k_3 k_5 (E_3 + E_5)}{k_2 k_6 x + k_3 k_5} \tag{6}$$

The first derivative of E as a function of x is

$$\frac{\partial E}{\partial x} = \frac{k_2 k_3 k_5 k_6 [E_3 + E_5 - (E_2 + E_6)]}{(k_2 k_6 x + k_3 k_5)^2} \tag{7}$$

As is seen from eqn. (7), the sign of the derivative will be determined by the difference in the activation energy sums. When $E_3 + E_5 > E_2 + E_6$, $\partial E/\partial x > 0$ and the activation energy increases monotonously with the increase of NH_3 concentration in the gas phase; in the alternative case, E decreases with x, and with equal sums E does not depend on x.

As we have established in the present work that the activation energy of AP decomposition increases in the presence of ammonia (Fig. 6), it is to be assumed that

$$E_3 + E_5 > E_2 + E_6 \tag{8}$$

There are no data available in the literature for the activation energy values in the inequality (8), which makes impossible its checking by an

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* In refs. 8 and 20, a kinetic analysis of the same model has been made with the wrong assumption that $[\mathrm{NH_3(g)}]:[\mathrm{HClO_4(g)}] = 1$ [20] and $[\mathrm{NH_3(g)}]:[\mathrm{HClO_4(g)}] = \mathrm{const.}$ [8], while it is seen from eqn. (3) that the concentrations of these substances are in reciprocal dependence.

independent way. (Only the E_3 value is known for the case of homogeneous decomposition of $HClO_4$ and is 47.6 kcal $mole^{-1}$ according to ref. [21].) Considering that NH_3 desorption is endothermic, the conclusion can be drawn that $E_5 > E_6$. On the other hand, the fact that E_3 represents the bond energy of Cl–O in $HClO_4$ gives grounds to assume that it exceeds considerably the activation energy of the desorption of ammonia from the AP surface. On this basis the conclusion can be made that the inequality (8) is due mainly to the inequality $E_3 > E_2$. The latter correlates well with the fact that proton equilibria in condensed phases are achieved for 10^{-7}–10^{-5} sec [6,22], while the life-time of $HClO_4$ molecules is by many orders longer.

The sharp decrease of the maximum rates of the decomposition of AP as a result of its transition from orthorhombic to cubic modification may be accounted for by the sharp decrease of k_3 in eqn. (5) due to the lowering in catalytic activity of the inner crystal surfaces [7,8]. Obviously the sharp increase in the inhibiting effect of ammonia with the phase transition may be elucidated by the same reasons.

The above kinetic analysis of the proton model of AP decomposition shows that the rise in activation energy of this process with the increase of P_{NH_3} may be deduced from the model, and hence serves as indirect evidence for its validity. However, this model is to be considered only as an approximative scheme of the chemical processes involved in the low-temperature AP decomposition. It does not describe the topochemical character of the decomposition and the participation of many intermediate and final products in the process. For example, the participation of water vapours deserves mentioning with their capacity to form $HClO_4$ hydrates, which are more stable than the anhydrous acid [23,24]. Khairetdinov and Boldyrev [6] have recently proposed a modified proton model of AP decomposition describing the nucleation with the participation of ClO_3^- ions. As established by the authors, these ions, which are unavoidable impurities in AP crystals, increase considerably the nucleation rate, but do not affect the rate of nuclei growth. The latter gives grounds to use the original proton model of Jacobs et al. [4,18] for the description of AP decomposition in the stages with $\alpha > 1\%$ because the reaction proceeds by the growth of nuclei in these stages.

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