

THE THERMAL DECOMPOSITION OF DOPED AMMONIUM PERCHLORATE

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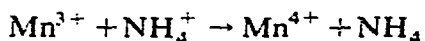
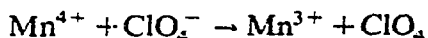
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ABSTRACT

The thermal decomposition of ammonium perchlorate doped with Cu^{2+} , Mn^{2+} , Co^{2+} and Fe^{3+} (with and without H^+) was studied using DTA and TG. Small concentrations of these ions inhibit the decomposition by eliminating the first exothermic peak. At higher concentrations, a catalyzed decomposition is observed. Either the influence of the doping ions on the mechanism of the thermal decomposition is different from that of added oxides or a modification of the electron transfer mechanism is needed.

INTRODUCTION

Low temperature decomposition, high temperature decomposition and sublimation were observed during the thermal decomposition of ammonium perchlorate (APC). Several mechanisms were suggested [1] to explain the various phenomena observed. Electron transfer was suggested to account for the low temperature decomposition, a proton transfer for the high temperature decomposition and a unified proton transfer mechanism to account for both high and low temperature decompositions and sublimation. Because of its use as a propellant, a number of studies were done to determine the influence of additives (at relatively high concentrations) on the thermal decomposition of APC (e.g. refs. 2–9). These studies used gasometric measurements of the reaction products to evaluate the kinetics and activation energies. The additives were mostly metallic oxides but several studies investigated the effect of p and n doped oxides or metallic chlorides or perchlorates [9–11]. Where an effect was found, it was the lowering of the reaction temperature and the completion of the reaction at low temperatures, in cases where electron transfer was enhanced. These catalyzed reactions were considered to support the suggested electron transfer mechanism for the decomposition of pure APC. This is not necessarily so, since there could be two mechanisms, one for pure APC and one for the catalyzed reaction with the oxide. It also seems that in several cases an initial oxidation–reduction reaction with the additive can liberate heat to catalyze the decomposition. It was suggested that the catalyst acts as a bridge for electron transfer [6]. As an example (for the addition of MnO_2) they suggested the equations



(see also ref. 11 for Cu^{2+} and ref. 5 for Fe^{3+} . It was also suggested [9] that sensitizing of the reaction is related to alteration of band characteristics of colored additives. Doping of APC with Ca^{2+} , [9] greatly increased the sublimation and the first exothermic peak of APC was eliminated. The authors concluded that the colorless multivalent cationic impurities reduce the first APC peak. In a following paper [12], another explanation was suggested. The authors claim that the decomposition is very dependent on the lattice defects (anion and cation vacancies) within the solid.

The aim of this study was to find out if doping APC with ions would change the decomposition characteristics and to check whether doping at the atomic level would give the same results as the mixtures with oxides. Also studied were the effects of the mode of crystallization on the regulation of dopant concentration and the decomposition of APC. The results of the first part of the study (APC doped with Cu^{2+} and Mn^{2+}) have already been reported [13] and the main points will be given later for the sake of comparison.

EXPERIMENTAL

Varian-Techtron atomic absorption spectrophotometers (models AA-5 and AA-6) were used for quantitative analysis of the doping ions. For the thermogravimetric analysis a Stanton-Redcroft model HT-D thermobalance was used. For DTA runs a Stanton-Redcroft model 674 instrument was used. Experimental techniques, recrystallization procedures and sample treatment have already been described [13]. Metallic perchlorates were used to dope the APC, thus avoiding the effects of added anions. APC was recrystallized with the dopant in slow, medium and fast modes, each mode with a pure APC sample for comparison. Solutions and crystals of APC doped with relatively high amounts of iron were brown. To avoid possible doping with colloidal ferric hydrous oxide, another set of APC doped with Fe^{3+} was crystallized from solutions containing a little perchloric acid. Transparent solutions and crystals were obtained.

All samples of the same mode of crystallization were prepared together, dried in a vacuum dessicator for several hours and all DTA runs of the same series were finished within 48 h to minimize ageing effects. About 80 DTA curves were recorded (Co^{2+} and Fe^{3+}), of which only a few diagrams representing the general trends are given here.

RESULTS AND DISCUSSION

Crystals grown in the slow mode were square plates (about 3 mm). In the medium mode they were needles (1–2 mm long) and in the fast mode they were powder.

In all cases there is a great difference (10^2 – 10^3) between the nominal percentage

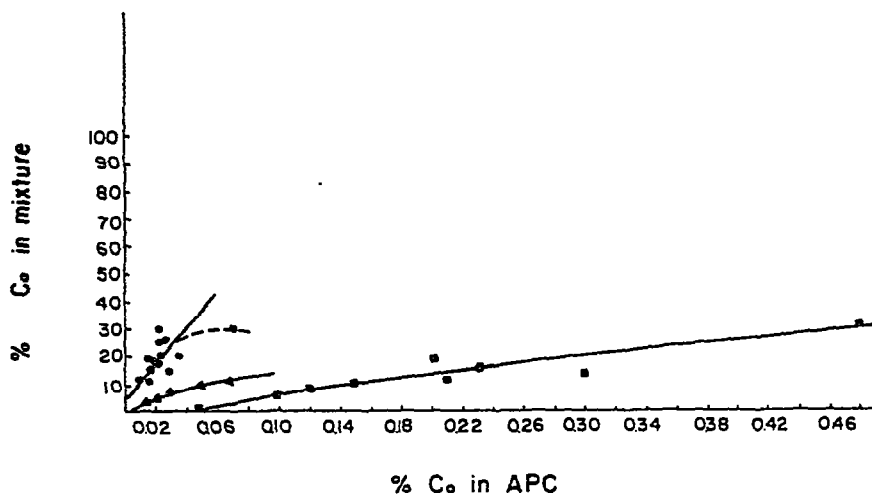


Fig. 1. Co^{2+} in the crystal as a function of Co^{2+} in the initial mixture. \odot , Slow crystallization; \blacktriangle , medium crystallization; and \blacksquare , fast crystallization.

of doping ion added to the mixture and the amount actually entering the crystal. This is in contrast to the assumption [9] that the total amount added entered the crystals.

In cases of equal amounts of dopant for the three crystallization modes it is seen

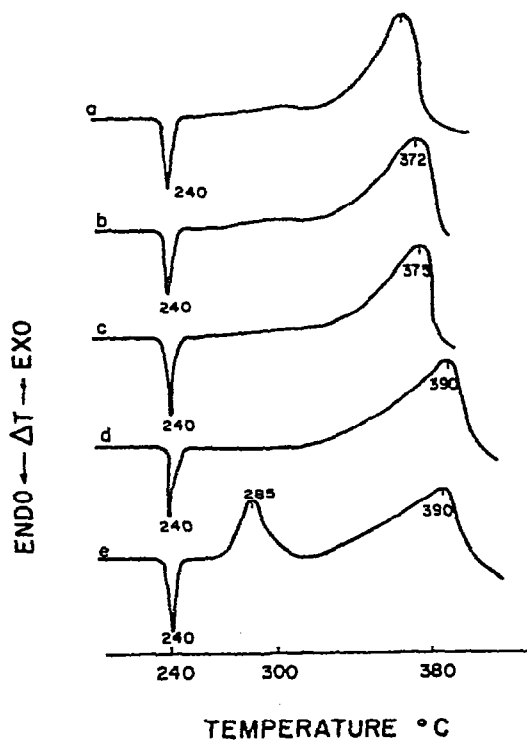


Fig. 2. DTA curves of ammonium perchlorate (crystals grown from a solution containing HClO_4) doped with Fe^{3+} (weight %): a, $260 \times 10^{-3}\%$; b, $84 \times 10^{-3}\%$; c, $62 \times 10^{-3}\%$; d, $5.2 \times 10^{-3}\%$; e, pure.

[13] that for Cu^{2+} and Mn^{2+} the highest amounts of dopant entered the crystals in slow crystallization. In the cases of Co^{2+} and Fe^{3+} the amounts of dopant in the crystals are in the order fast > medium > slow. It is not clear why Cu^{2+} and Mn^{2+} behave differently. In a former paper [13], the explanation suggested was that in the slow mode water was evaporated by evacuation so that the real dopant concentration was much higher. But, the concentrations are given as weight percentages of the APC and those do not change during evaporation. In addition, this does not explain why Cu^{2+} and Mn^{2+} do not behave in the same way as Co^{2+} and Fe^{3+} . As an example, Fig. 1 shows the concentration of Co^{2+} in the crystal as a function of its initial concentration for the three crystallization modes.

For the same initial dopant concentration of the slow mode, the final dopant concentrations in the crystal are in the order $\text{Mn}^{2+} \gg \text{Cu}^{2+}$. For the fast mode $\text{Co}^{2+} \approx \text{Fe}^{3+}$ and both are a little lower than that of Mn^{2+} in the slow mode.

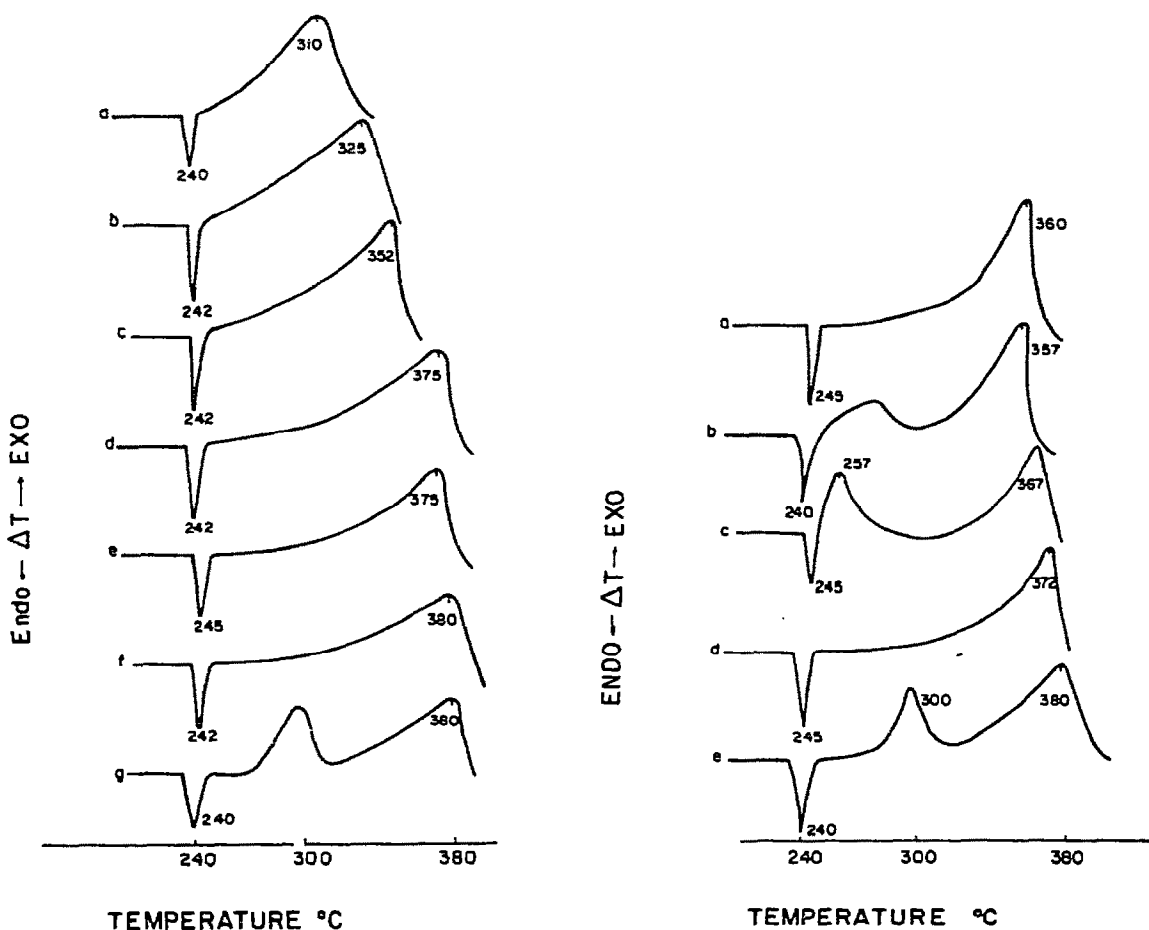


Fig. 3. DTA curves of ammonium perchlorate doped with Co^{2+} (wt.%): a, $4.80 \times 10^{-3}\%$; b, $3.00 \times 10^{-3}\%$; c, $9.8 \times 10^{-3}\%$; d, $1.8 \times 10^{-3}\%$; e, $1.6 \times 10^{-3}\%$; f, $1.4 \times 10^{-3}\%$; g, pure.

Fig. 4. DTA curves of ammonium perchlorate doped with Fe^{3+} (wt.%): a, $6.90 \times 10^{-3}\%$; b, $4.60 \times 10^{-3}\%$; c, $1.60 \times 10^{-3}\%$; d, $1.00 \times 10^{-3}\%$; e, pure.

The data indicate that the differences in behaviour of the doped samples are due to dopant concentration and not to crystallization modes.

In the case of Cu^{2+} it is seen [13] that at low dopant concentrations the temperature of the first exothermic peak ($T_{1\text{max}}$) remains unchanged. Only at relatively high concentrations of 0.05–0.1% Cu^{2+} $T_{1\text{max}}$ is lowered by about 15°C and the peak's amplitude diminishes with rising dopant concentrations till it completely disappears. Mn^{2+} has a different influence [13]. Even at the lowest concentration ($5 \times 10^{-3}\%$) the first exothermic peak disappears. The influence of Fe^{3+} on crystals grown in a solution containing HClO_4 (Fig. 2) is the same as that of Mn^{2+} , i.e. the disappearance of the first exothermic peak (some times a very small and shallow trace of the first peak is seen). In the case of Co^{2+} (Fig. 3), the first exothermic peak disappears at low concentrations. At higher concentrations there is a peak immediately after the endothermic peak. It is not clear, but it seems that this is the second exothermic peak which starts at a much lower temperature. The influence of Fe^{3+} is unclear (Fig. 4), but, as mentioned above, the nature of the dopant is unclear. At lower concentrations the first peak disappears but at higher concentrations it is seen again. In some cases sharp peaks are seen immediately after the endothermic peak and in others they are shallow but always at $T_{1\text{max}}$ lower than $T_{1\text{max}}$ of APC. At higher concentrations the first peak is sometimes seen and sometimes not.

The case of the second exothermic peak seems to be simpler. In the case of copper it is clearly evident from the figures [13] that the first exothermic peak remains and it is the temperature of the second exothermic peak which is lowered with the rising dopant concentration. In the case of Mn^{2+} only the second exothermic peak remains and $T_{2\text{max}}$ is lowered with the rising dopant concentration. But, at high concentrations, there is only one peak at a low temperature and one can argue whether the first one remains (reappearing for some reason) or that the first one disappeared and the second was lowered to the temperature of the first one. The case of Co^{2+} is illustrated in Fig. 3. At low concentrations only the second exothermic peak exists but as Co^{2+} rises $T_{2\text{max}}$ is lowered but the decomposition starts where the first exotherm was, until only one peak remains in the place of the first peak. The influence of Fe^{3+} (HClO_4) is seen in Fig. 2. As in the case of Mn^{2+} even very small amounts of Fe^{3+} cause a complete elimination of the first exothermic peak. But, unlike Mn^{2+} , in the range studied, there is only a small lowering of $T_{2\text{max}}$ (compared with Mn^{2+} , Co^{2+} and Cu^{2+} at the same concentrations). The small decrease in $T_{2\text{max}}$ is not due to H^+ ions in the crystal, as the same behaviour is seen with Fe^{3+} without HClO_4 . It should be noted that the APC reference sample for the Fe^{3+} (+ HClO_4) series had the highest $T_{2\text{max}}$ found in the present study. Fe^{3+} in crystals grown without HClO_4 shows little lowering of $T_{2\text{max}}$ even at high dopant concentrations (Fig. 4).

The lowering of $T_{2\text{max}}$ with rising dopant concentrations is illustrated in Fig. 5 (Cu^{2+} , Mn^{2+} , Co^{2+}) and Figs. 6 and 7 [Fe^{3+} (HClO_4) and Fe^{3+}]. There is a marked difference in the efficiency of the dopant in the two groups. In the concentration levels tested the ions of the first group had a lower $T_{2\text{max}}$ from

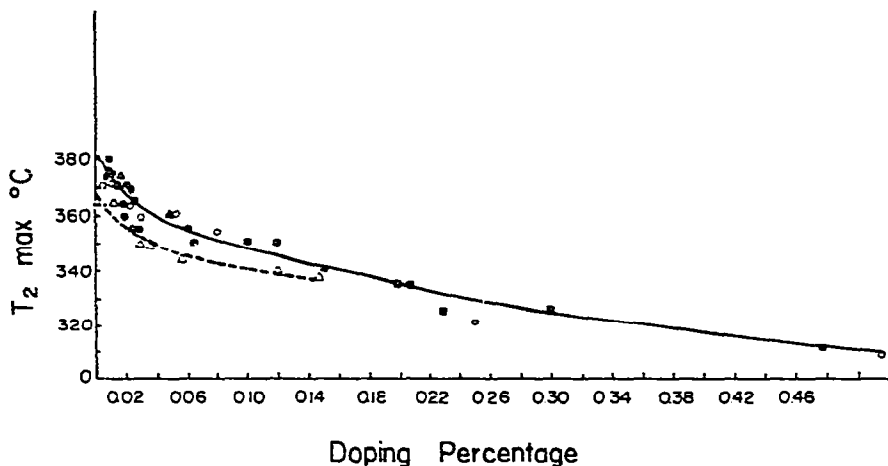


Fig. 5. Lowering of the second exothermic peak as a function of dopant concentration. ●, Co²⁺ slow crystallization; ▲, Co²⁺ medium crystallization; ■, Co²⁺ fast crystallization; ○, Mn²⁺; △, Cu²⁺.

370–380°C to about 300°C while with iron it is lowered to about 360°C, with a much shallower slope. There appears to be no difference between the effect of Fe³⁺ or Fe³⁺ with HClO₄ (when plotted on the same scale). Ions of the first group have about the same effect, though lowering of T_{2max} seems to occur at Cu²⁺ concentrations lower than those of the others causing the same effect.

The problem of sublimation has already been discussed (direct observation, DTA and TG data). From the data in the present study there is no reason to change the conclusion reached formerly [13]. Under the experimental conditions used, sublimation if it exists, is small and cannot explain the observations. This is to be expected in the experiments carried out under atmospheric pressure. In the experiments carried out under continuous pumping, sublimation was dominant. In runs with pure APC the first exothermic peak was seen, but not the second one [13]. In its

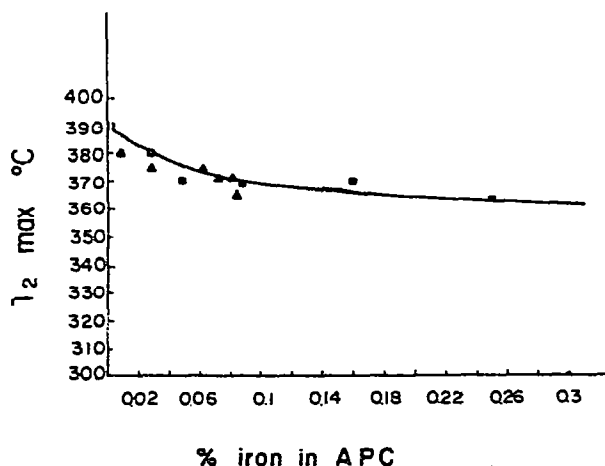


Fig. 6. Lowering of the second exothermic peak as a function of Fe³⁺ concentration (crystals grown from a solution containing HClO₄). ■, Fast crystallization; ▲, medium crystallization.

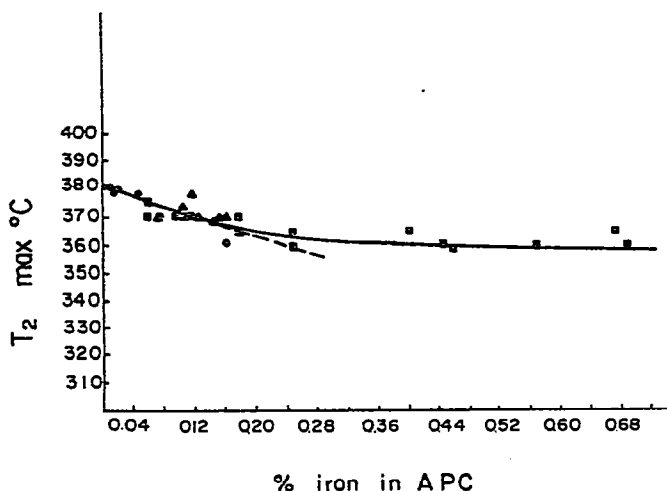


Fig. 7. Lowering of the second exothermic peak as a function of Fe^{3+} concentration. ●, ■, ▲, Slow, fast and medium crystallizations, respectively.

place a large endothermic peak was obtained. With doped samples no exothermic peak was seen and immediately after the phase transformation endothermic peak, only one broad endothermic peak was observed. Its T_{max} was just a little higher than that of the first exotherm ($320\text{--}325^\circ\text{C}$). This indicates an intensive sublimation (probably not leaving APC for the second exotherm) enhanced by the doping.

It seems that the catalytic effect takes place only with relatively high dopant concentrations. At low dopant concentrations the ions studied cause inhibition of the decomposition. This is contrary to the electron transfer mechanism according to which catalysis only should be observed. This inhibition suggests that either the influence of the doping ion on the mechanism of the thermal decomposition is different from that of added oxides or that a modification of the electron transfer mechanism is needed to account for the inhibition at low dopant concentrations.

There is a dispute [14] about the activation energies of the various decomposition stages; whether they indicate an electron or proton transfer mechanism. It should be pertinent to evaluate the activation energies of inhibited decompositions and their meaning. Further research to check the effect of doped APC inhibited decomposition on the reaction of its mixtures with solid organic fuels (polystyrene, etc.) would be interesting. The results of such a study are described in a recent paper [15] but (a) the decompositions were carried out under vacuum where sublimation plays a great part as has been reported already [13]; (b) mixtures of APC and metallic oxides were used; (c) dopant concentrations were high (1%), i.e. in the catalysis range and not in the inhibition range.

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