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Thermal decomposition of cubic ammonium perchlorate—the effect of barium doping

T. Ganga Devi *, M.P. Kannan, B. Hema

Department of Chemistry, University of Calicut, 673 635, Kerala, India

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Abstract

Isothermal decomposition of cubic ammonium perchlorate (AP) has been studied as a function of concentration of barium dopant by thermogravimetry in the temperature range 530–550 K. The rate of decomposition first passes through a minimum and then a maximum showing opposite effects, as the dopant concentration increases. The decomposition kinetics of both pure and doped AP was found to be best described by first order rate law with an activation energy (E) of ca. 138 kJ mol^{-1}. The results favour an electron-transfer mechanism

Keywords: Ammonium perchlorate; Decomposition; Doping; Electron transfer

1. Introduction

Ammonium perchlorate (AP) undergoes crystallographic transition from the orthorhombic to the cubic structure at 513 K [1]. The mechanism of thermal decomposition of the orthorhombic form has been studied extensively [2–12]. Proton transfer has been implicated in the rate-determining step by some authors [2–7], while others have inferred the occurance of an electron-transfer process [8–11]. However, our recent study [12] has produced compelling evidence in favour of an electron-transfer mechanism for the decomposition of the orthorhombic form of AP.

Similar controversy also exists in the case of the decomposition of the cubic form. Jacobs and Russel-Jones [3] have extended their proton-transfer model to account for the decomposition of cubic AP, while Maycook and Pai Verneker [10] have suggested that the decomposition involves an electron-transfer reaction. More experimental evidence is required to resolve the conflict, and we have, therefore, extended the doping

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* Corresponding author.

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studies, which were quite successful with orthorhombic AP [12], to the decomposition of cubic AP. In this paper we discuss the most probable mechanism of the decomposition of cubic AP on the basis of our results on pure and barium doped AP in the temperature range 530–550 K.

2. Experimental

2.1. Preparation of pure and doped samples

A solution was prepared by dissolving 10 g of AP (BDH, AR) in 100 cm^3 of distilled water at room temperature. This was kept in a water bath at 318 K and was allowed to undergo slow evaporation over a period of about 7 days. The resulting crystals of pure AP were removed, dried, and powdered to fix the particle size in the range 90–75μm. Samples doped with Ba^{2+} were prepared by following the above procedure for an aqueous solution (100 cm^3) containing 10 g of AP and suitable proportion of the dopant. Due to the non-availability of barium perchlorate, $BaCl_2$ (AR, BDH) was used for doping Ba^{2+} at four different concentrations, viz., 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} mol%. As in earlier work [6,10,12], the actual concentrations of the dopant present in the solid samples were not determined; the concentrations mentioned refer to the solutions from which they were crystallized. The samples were stored in a desiccator over anhydrous calcium chloride.

Doping with $BaCl_2$ leads to the inclusion of Cl^- ions also in the AP lattice. However, it has been observed that the presence of Cl^- ions does not significantly affect the rate of decomposition of perchlorates [13], azides [14], etc.

2.2. Thermogravimetric analysis

Samples were decomposed isothermally in static air in a manual thermogravimetric (TG) unit fabricated in this laboratory. The experimental set-up was similar to that adopted by Hooley [15]. The fraction of the solid decomposed (α) was measured as a function of time (t) at four different temperatures (T), viz., 533, 538, 543 and 548 K. The sample size used for each analysis was 50 mg. Comparative runs were made using samples of same age and particle size.

In order to identify the rate law which described the decomposition of cubic AP, a kinetic analysis of the TG data was carried out by fitting the data to the various rate equations of the form

$$g(\alpha) = kt \tag{1}$$

where $g(\alpha)$ is a function of α and k the rate constant, using the method of weighted least squares as described elsewhere [16].

3. Results

The α against t curves of the decomposition of pure and Ba^{2+}-doped samples of AP in its cubic form at four different temperatures in the range 533–548 K are shown in

Fig. 1. The decomposition proceeded only to 30% in this temperature range but 30% conversion was taken to represent $\alpha = 1$ in the analysis. The α–t curves are deceleratory in nature for both pure and doped samples.

Since the decompositions were slow, they could not be followed up to 30% completion (i.e., up to $\alpha = 1$) in all cases, particularly at lower temperatures, and only the initial portion of the α–t curves upto $\alpha = 0.5$ was subjected to kinetic analysis. The first order equation, i.e.

$$-\ln(1-\alpha) = kt \tag{2}$$

was found to best describe the decomposition of both pure and doped samples. The rate constants (k) are listed in Table 1.

It is apparent from the k values that the rate of decomposition was not a simple function of the dopant concentration and the direction of the effect reverses with increasing concentration of the dopant. Fig. 2 illustrates this. The reaction rate first decreases upto a dopant concentration of ca. 1×10^{-4} mol% (region A), then increases sharply until the concentration reaches a value of ca. 5×10^{-3} mol% (region B) beyond which the rate decreases again but more slowly (region C). The decrease in region C becomes more prominent at higher temperatures. It may be seen from the figure that the rate is always lower than that for the pure sample below a dopant concentration of ca. 3×10^{-4} mol%, but always higher above this concentration.

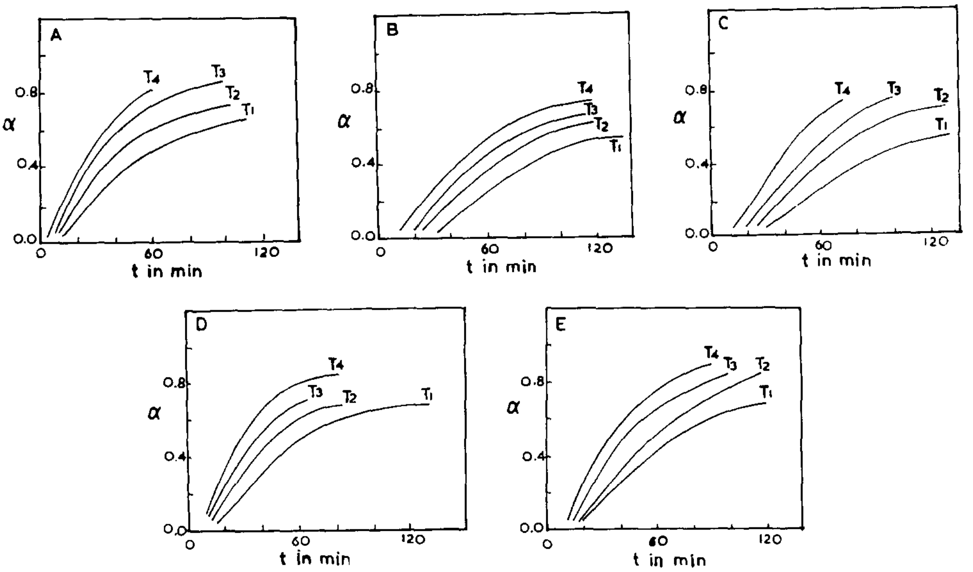

Fig. 1. α–t plots of the decomposition of pure (A) and barium-doped (B = 1×10^{-4}, C = 1×10^{-3}, D = 1×10^{-2}, E = 1×10^{-1} mol%) samples of cubic AP at $T_1 = 533$ K, $T_2 = 538$ K, $T_3 = 543$ K, $T_4 = 548$ K.

Table 1
First-order rate constants (k) and activation energies (E) for the decomposition of pure and barium-doped AP

Dopant concentration/mol%	Rate constant, $k \times 10^4/\mathrm{s}^{-1}$				Activation energy E/ ($\mathrm{kJ\ mol^{-1}}$)
	533 K	538 K	543 K	548 K	
0 (pure)	1.427	2.142	2.680	3.399	141.17
1×10^{-4}	1.340	1.811	2.204	2.565	139.41
1×10^{-3}	2.128	3.064	4.101	5.299	144.18
1×10^{-2}	2.166	3.228	4.050	5.291	134.47
1×10^{-1}	2.122	2.485	3.346	4.298	133.30

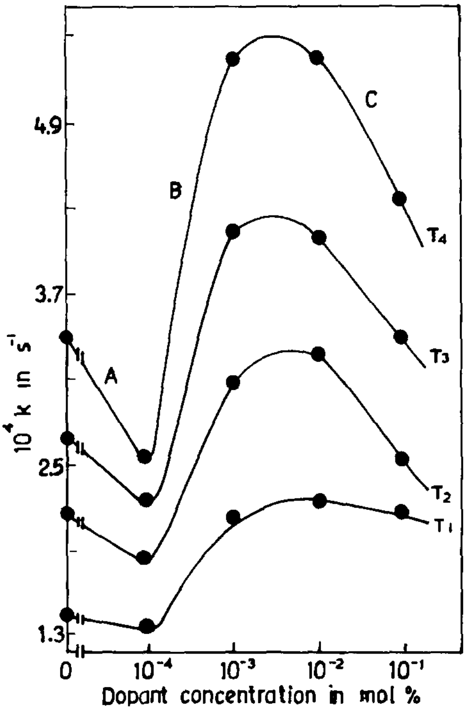

Fig. 2. Dependence of the rate of decomposition of cubic AP on the concentration of Ba^{2+} dopant at the four temperatures mentioned in Fig. 1.

The activation energies (E) of the decomposition of pure and doped samples were not significantly affected by doping (see Table 1). The value obtained for E, $138 \pm 5\ \mathrm{kJ\ mol^{-1}}$, was close to that reported for the decomposition of orthorhombic AP, viz., 115–125 $\mathrm{kJ\,mol^{-1}}$ [4,8–10,12,17–19].

4. Discussion

The low-temperature decomposition of cubic AP (range 513–573 K) has been studied by Bircumshaw and Newman [8,9] who analysed their data using the Prout–Tompkins rate equation and obtained an activation energy of 79 kJ mol^{-1}. Several other workers [4,18,19], however, have used the Avrami–Erofeyev equation to describe this decomposition and obtained an activation energy in the range 104–114 kJ mol^{-1}. Osado and Sakamoto [20] and Maycock and Pai Verneker [10] found that this decomposition was best described by a first order equation with an activation energy of about 84 kJ mol^{-1}. This investigation shows that the decomposition of cubic AP is best described by first order equation with an activation energy of 138 kJ mol^{-1}, thus showing only partial agreement with previous work.

Fig. 1 shows that the α-t curves are deceleratory, and therefore one would expect them to be described by a deceleratory type of equation such as first order equation or contracting square or contracting cube equation. In agreement with this, we find that the decomposition is best described by the first order rate law with an activation energy of 138 kJ mol^{-1}.

4.1. *Effect of doping and the mechanism of the decomposition*

The rate law and the activation energy of the decomposition remain unaltered by doping. This suggests that the basic mechanism of the decomposition is not affected by doping, the only effect of doping being a modification in the concentration of active sites in the solid matrix. We also note that the close correspondence between the E value obtained for cubic AP and that reported for the orthorhombic AP may be indicative of a common mechanism for the decomposition of both these forms.

Three different processes play a decisive role in the decomposition of AP [8,9]:

(1) Transfer of an electron from ClO_4^- to NH_4^+,

$$NH_4^+ + ClO_4^- \longrightarrow NH_4 + ClO_4 \qquad (3)$$

(2) Transfer of a proton from NH_4^+ to ClO_4^-,

$$NH_4^+ + ClO_4^- \longrightarrow NH_3 + HClO_4 \qquad (4)$$

(3) Thermal breakdown of ClO_4^- by rupture of a Cl–O bond,

$$ClO_4^- \longrightarrow ClO_3^- + O \qquad (5)$$

The value of activation energy obtained differs widely from the dissociation energy of the Cl–O bond, viz., 199 kJ mol^{-1} [21]. Thus, the last possibility for the rate-determining step in the low-temperature decomposition of cubic AP must be ruled out, leaving electron transfer or proton transfer as the only possibilities. The present results favour the electron-transfer mechanism as can be seen below.

Impurities usually form defects of the same type as those existing in the pure material since it is energetically more favourable [22]. There is evidence showing that AP has a Frenkel defect structure with NH_4^+ interstitials in its orthorhombic form [23] whereas the Schottky defect structure dominates in its cubic form [10]. The defect equilibria existing in these two types of defect structure may be represented by the following expressions:

$$[\boxplus][\mathrm{I}^+] = \text{constant (Frenkel)} \tag{6}$$

$$[\boxplus][\boxminus] = \text{constant (Schottky)} \tag{7}$$

where $[\boxplus]$, $[\boxminus]$ and $[\mathrm{I}^+]$ are, respectively, the concentrations of the cation vacancies, anion vacancies and cation interstitials.

In cubic AP with the Schottky defect structure [10], therefore, incorporation of Ba^{2+} impurity causes an increase in the number of cation vacancies (in order to preserve the change balance—charge conservation can also be achieved by the destruction of interstitial $NH_4{}^+$ ions, but is neglibible in a Schottky system). This increase in the cation vacancy concentration affects the defect equilibrium represented by Eq. (7) leading to a decrease in the concentration of anion vacancies. An anion vacancy can trap electron by virtue of its net positive change due to the localization of positive charges in the neighbourhood of the vacancy and thus can facilitate the electron-transfer process Eq. (3) in AP as shown below:

$$\mathrm{ClO_4}^- + \boxminus \longrightarrow \mathrm{ClO_4} + \boxminus\mathrm{e} \tag{8}$$

$$\mathrm{NH_4}^+ + \boxminus\mathrm{e} \longrightarrow \mathrm{NH_4} + \boxminus \tag{9}$$

where $\boxminus$e stands for a trapped electron [12]. For similar reasons cation vacancies can act as proton traps and facilitate the proton-transfer process Eq. (4):

$$\mathrm{NH_4}^+ + \boxplus \longrightarrow \mathrm{NH_3} + \boxplus\mathrm{H}^+ \tag{10}$$

$$\mathrm{ClO_4}^- + \boxplus\mathrm{H}^+ \longrightarrow \mathrm{HClO_4} + \boxplus \tag{11}$$

where $\boxplus H^+$ represents a trapped proton. Hence, Ba^{2+}-doped AP, with its increased number of cation vacancies should enhance the process indicated by Eq. (10) and decompose faster than the pure sample if proton transfer determines the rate. But we find a decrease in the rate for low concentrations of dopant, up to ca. 3×10^{-4} mol%; an increase in the rate is observed only above this concentration (Fig. 2). This initial decrease cannot be explained by a proton-transfer model. Point defects such as Ba^{2+} impurity and anion vacancy, which also change on doping, have no direct influence on proton transfer. The invariance of the rate law and activation energy of the decomposition on doping (Table 1) suggests that it is not possible to visualize the decomposition as taking place with two different mechanisms below and above this concentration. A proton-transfer model is thus unsatisfactory to account for the present observation.

Doping AP with Ba^{2+} not only causes an increase in the concentration of cation vacancies but also a reduction in the concentration of anion vacancies (electron traps) in accordance with Eq. (7), as mentioned above. This decrease in the number of electron traps should suppress the electron-transfer reaction, Eq. (8), resulting in a slower decomposition of the doped samples, as we observe at low concentrations of dopant up to ca. 1×10^{-4} mol% (region A, Fig. 2). However, a difficulty arises with this model since the rate does not decrease further when the concentration is increased above 1×10^{-4} mol%; in fact the rate increases (region B in Fig. 2). This could be because of a change in the mechanism of decomposition. But, as already pointed out, it is unlikely that the mechanism changes with increasing dopant concentration, and thus the observed increase in rate must be because of other reasons. We suggest that this effect is due to the direct action of the dopant ions, Ba^{2+}, as electron traps [24] as shown below:

$$ClO_4^- + Ba^{2+} \longrightarrow ClO_4 + Ba^+ \tag{12}$$

$$NH_4^+ + Ba^+ \longrightarrow NH_4 + Ba^{2+} \tag{13}$$

As the concentration of the dopant increases, this sensitizing effect of dopant as electron traps dominates over the desensitizing effect due to the decrease in the number of anion vacancies, leading to a net enhancement of the rate of decomposition as observed in region B in Fig. 2. However, this enhancement of rate reaches a maximum at a dopant concentration of ca. 5×10^{-3} mol% above which the rate decreases gradually without a change in the activation energy (region C in Fig. 2), which, we suggest, could be due to the following reason.

When the concentration of dopant in solution exceeds a certain value a counter process may become operative. The uptake of dopant by the lattice of AP possibly reaches a saturation limit [12] and during the process of co-crystallization the excess dopant precipitates on gross imperfections such as grain boundaries and dislocations, which are special sites where preferential decomposition can occur [25,26]. These special sites can trap electrons from the adjacent less well coordinated perchlorate ions facilitating the decomposition process [27]. However, at high concentrations excess dopant, by precipitating at these potential sites, 'poisons' them and thus causes a reduction in the number of active sites [12] leading to a decrease in the rate of decomposition as seen in region C in Fig. 2. This hypothesis derives strength from the fact that a similar precipitation of the dopant was indicated in our earlier studies with sulphate-doped AP [12].

5. Conclusions

The study reveals that the decomposition reactivity of AP has a very complex dependence on the concentration of the dopant, Ba^{2+}. Invariability of rate law and activation energy of the decomposition on doping, indicates that the complex behaviour is not due to a change of mechanism. The results suggest that cubic AP decomposes via an electron-transfer mechanism similar to that of the orthorhombic form. The study emphasizes that extreme care should be taken in interpreting the effect of a dopant for elucidating the mechanism of decomposition, since the same dopant may show opposite effects depending on its concentration, as found here. Studies using a single concentration of a dopant can easily lead to wrong conclusions on mechanism. For instance, a study of the decomposition of AP with a single concentration of Ba^{2+}, say 10^{-3} mol%, would have prompted the wrong conclusion in favour of a proton-transfer model for the decomposition, on the argument that doping AP with Ba^{2+} increases the number of cation vacancies (proton traps) leading to the observed enhancement in the decomposition. It should also be noted that the low concentration region (A in Fig. 2) plays a vital role in the interpretation. It is, therefore, essential to study the effect of a dopant in a wide concentration range commencing from a very low value, in order to derive conclusions on mechanism.

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