

## **THERMAL DECOMPOSITION OF DOPED AMMONIUM PERCHLORATE**

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Isothermal decomposition of orthorhombic ammonium perchlorate (AP) has been studied as a function of concentration of the dopants,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ . In either case, the rate of decomposition passes through a maximum as the dopant concentration increases. Activation energy of the decomposition process remains unaltered by doping. The results are interpreted in terms of electron transfer mechanism.

The mechanism of thermal decomposition of orthorhombic ammonium perchlorate (AP), though studied extensively in the past, still remains controversial. Proton transfer [1–4] has been implicated in the rate-determining step by some authors, whereas others have inferred the occurrence of electron transfer [5–7]. More experimental evidence was, therefore, sought to help clarify the controversy.

The proton transfer mechanism has been supported by Boldyrev et al. [3] based on their observation that AP doped with  $\text{SO}_4^{2-}$  (concentration:  $0.8892 \times 10^{-2}$  mole % in solution) or  $\text{PO}_4^{3-}$  (concentration:  $1.181 \times 10^{-2}$  mole % in solution) exhibited a decrease in the decomposition rate. However, Maycock and Pai Verneker [7] have found that AP doped with  $\text{SO}_4^{2-}$  showed an increase in the rate up to a dopant concentration of  $1.0 \times 10^{-2}$  mole % (in solution), and that the rate decreased on further increase of the dopant concentration. These varying observations necessitate a systematic study of the decomposition of AP as a function of  $\text{SO}_4^{2-}$ . A similar behaviour is to be expected for AP doped with  $\text{PO}_4^{3-}$ . Thermal decomposition of phosphate-doped AP has not been studied so far as a function of dopant concentration. This paper deals with the isothermal decomposition of sulphate-doped and phosphate-doped AP in the temperature range 200–230°, where AP exists in its orthorhombic modification.

## Experimental

Doped samples of AP were prepared by co-crystallizing by slow cooling a saturated aqueous solution containing definite proportions of AP and the dopant, as detailed in our earlier publication [8]. The dopants used were  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_3\text{PO}_4$ . All the reagents used were of AnalaR grade. The particle size of the samples used lies in the range 150–180  $\mu\text{m}$ . All samples were stored over anhydrous calcium chloride in a vacuum desiccator. Like earlier workers [3, 7], the actual concentrations of the dopants present were not determined. The concentrations mentioned in this paper refer to the solutions from which they were crystallized.

IR spectra of pure and doped AP were observed in Nujol mull on a Carl Zeiss UR-10 spectrophotometer.

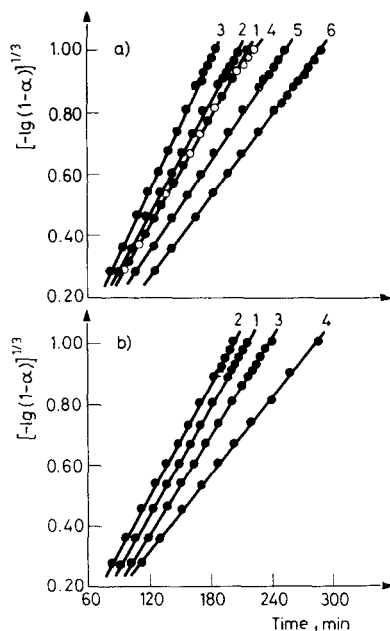
The kinetics of decomposition were followed by measuring the pressure change in a constant volume vacuum system, using a McLeod gauge. The size of sample used was 5 mg and the initial pressure achieved before each run was  $1 \times 10^{-5}$  Torr. Comparative runs were always made with samples of the same age.

## Results and discussion

The thermal decomposition data for both pure and doped samples of AP were fitted to various solid-state kinetic equations such as Prout-Tompkin, Avrami-Erofeyev, contracting cylinder and contracting sphere equation [25]. The Avrami-Erofeyev equation in the form

$$(-\log_{10}(1-\alpha))^{1/n} = kt \quad (1)$$

was found to give the best fits where,  $\alpha$  represents the fraction of the solid decomposed in time  $t$ ,  $k$  the rate constant and  $n$  a number, whose best value in the present investigation was found to be 3 by the method of least squares (only integer values of  $n$ , from 1 to 4, were tested). It may be stated that Eq. (1), with a value of  $n$  ranging from 2 to 4, has been used by earlier workers [1, 9–14] for the kinetic analysis of isothermal decomposition of orthorhombic AP. Typical fits are shown in Fig. 1. The data give very good fit in the range of  $\alpha = 0.06$  to  $\alpha = 0.90$ . The rate constants obtained from these fits at varying dopant concentrations, and at three different temperatures are presented in Table 1. The maximum error in these values was computed to be 2%, from a knowledge of the maximum error in the directly measured quantities, namely, time and pressure. In the case of a few samples, whose decomposition kinetics were repeated, the error in the value of  $k$  was estimated by 'Student  $t$  Test' [15], and was found to be less than 1.5%. It is apparent from Table 1 that at all temperatures studied, the rate of decomposition passes through a



**Fig. 1** Kinetic analysis of thermal decomposition of AP (at 230 °C) containing different concentrations of dopants using Avrami–Erofev equation ( $n=3$ ): a)  $\text{SO}_4^{2-}$  doped AP—dopant concentrations: (1) n.l., (2)  $10^{-4}$  mole %, (3)  $10^{-3}$  mole %, (4)  $8 \times 10^{-3}$  mole %, (5)  $10^{-1}$  mole %, (6)  $5 \times 10^{-1}$  mole %; b)  $\text{PO}_4^{3-}$  doped AP—dopant concentrations: (1) nil, (2)  $10^{-4}$  mole %, (3)  $10^{-3}$  mole %, (4)  $10^{-1}$  mole %

maximum as the concentration of dopant increases. This fact is brought out clearly in Fig. 2, where rate constant at 230° is plotted against dopant concentration.

The results of decomposition of sulphate-doped AP are in general agreement with the work of Maycock and Pai Verneker [7], except that the rate of decomposition reaches the maximum value when the dopant concentration is  $1 \times 10^{-3}$  mole %. At a concentration of  $8 \times 10^{-3}$  mole % the rate is more or less equal to that of the virgin sample. The results indicate that an increase in the rate of decomposition of AP can be expected only below a concentration of  $8 \times 10^{-3}$  mole % of  $\text{SO}_4^{2-}$ . Above this concentration the rate becomes lower than that of pure AP. A similar effect is noticed in the case of phosphate-doped AP, where the rate attains the maximum value in the vicinity of  $10^{-4}$  mole % of  $\text{PO}_4^{3-}$ . When the dopant concentration exceeds  $5 \times 10^{-4}$  mole %, the rate becomes lower than that of the pure sample (see Fig. 2). It is obvious from these results why Boldyrev et al. [3] observed a desensitizing effect on AP doped with  $\text{SO}_4^{2-}$  or  $\text{PO}_4^{3-}$ . The concentrations of these dopants used by them lie in the high concentration range where the dopants show desensitizing effect (see Fig. 2).

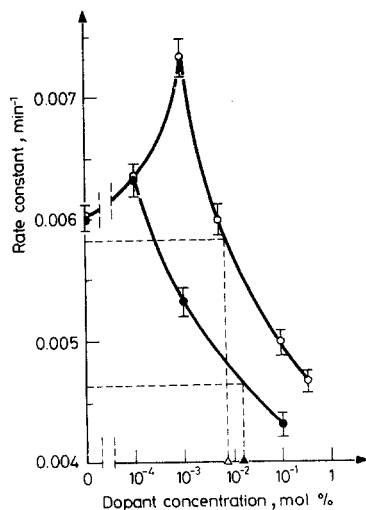
**Table 1** Rate constant of thermal decomposition of pure,  $\text{SO}_4^{2-}$  doped and  $\text{PO}_4^{3-}$  doped AP

Concentration of $\text{SO}_4^{2-}$ in solution (mole %)	$k \times 10^3 \text{ (min}^{-1}\text{)}^*$		
	212 °C	220 °C	230 °C
0.0	2.20	3.47	6.00
$1 \times 10^{-4}$	2.40	3.72	6.33
$1 \times 10^{-3}$	2.60	4.17	7.33
$8 \times 10^{-3}$	2.10	3.50	6.00
$1 \times 10^{-1}$	1.90	2.90	5.00
$5 \times 10^{-1}$	1.74	2.70	4.67

Concentration of $\text{PO}_4^{3-}$ in solution (mole %)	$k \times 10^3 \text{ (min}^{-1}\text{)}^*$		
	210 °C	223 °C	230 °C
0.0	1.87	3.72	6.00
$1 \times 10^{-4}$	2.09	4.37	6.33
$1 \times 10^{-3}$	1.51	3.28	5.33
$1 \times 10^{-1}$	1.38	2.92	4.33

\* The maximum error in  $k$  is  $\pm 2\%$  of the value indicated.



**Fig. 2** Dependence of rate of thermal decomposition of AP (at 230 °C) on dopant concentration: ○,  $\text{SO}_4^{2-}$  doped AP; ●,  $\text{PO}_4^{3-}$  doped AP (●, common points); △ and ▲, concentrations of  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  respectively used by Boldyrev et al. [3]. The vertical lines indicate the maximum error (2%) in the values of  $k$

Boldyrev et al. [3] account for their observations by arguing that the rate-determining step in the decomposition of AP is the transfer of a proton from  $\text{NH}_4^+$  to  $\text{ClO}_4^-$ , and that cation vacancies act as proton traps. Doping of AP with  $\text{SO}_4^{2-}$  or  $\text{PO}_4^{3-}$  causes an increase in the number of anion vacancies and thereby a decrease in the number of cation vacancies according to the equation

$$(+)(-) = \text{constant} \quad (2)$$

where (+) and (-) represent the concentrations of the cation and anion vacancies respectively. This decrease in the number of proton traps, according to the authors [3], leads to a decrease in the rate of decomposition. However, the results of this investigation show that the dopants cause an increase in the rate of decomposition when their concentration is low. The proton transfer model totally fails to explain this effect. Further, throughout the concentration range studied activation energy of the decomposition remains unaltered by doping at  $115.5 \text{ kJ mol}^{-1}$  (Fig. 3). The

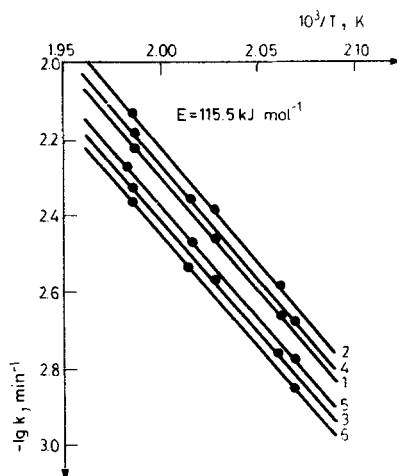
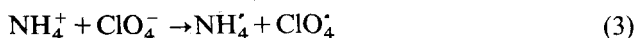


Fig. 3 Arrhenius plots for thermal decomposition of pure and doped AP: (1) pure; (2)  $\text{SO}_4^{2-}$  doped,  $10^{-3}$  mole %; (3)  $\text{SO}_4^{2-}$  doped,  $5 \times 10^{-1}$  mole %; (4)  $\text{PO}_4^{3-}$  doped,  $10^{-4}$  mole %; (5)  $\text{PO}_4^{3-}$  doped,  $10^{-3}$  mole %; (6)  $\text{PO}_4^{3-}$  doped,  $10^{-1}$  mole %

activation energy could be determined only in a restricted temperature range due to two constraints: (i) below  $210^\circ$  the rate of decomposition of AP is too low to follow; (ii) AP undergoes crystallographic transition from its orthorhombic modification to cubic at  $240^\circ$  and the kinetic parameters of the decomposition at and around the transition temperature exhibit larger changes than would follow merely from the temperature change. However, the value obtained agrees well with the values reported for orthorhombic AP [6, 9–13]. Further, it was ensured by repeat

experiments with a few samples (where the error in  $k$ -values was less than 1.5%) that the activation energy in this temperature range did not alter significantly from  $115.5 \text{ kJ mol}^{-1}$ . This means that doping does not affect the basic mechanism of the decomposition. Thus, it is not possible to visualize the decomposition to take place via one mechanism at low dopant-concentration (when the rate is elevated) and via another mechanism at high dopant-concentration (when the rate is depressed). It may, therefore, be inferred that the rate-determining step in the thermal decomposition of orthorhombic AP does not involve proton transfer. This conclusion is in agreement with the results on the sublimation of pre-treated AP. It has been observed that pre-treatments such as sulphate-doping, phosphate-doping and pre-heating brought about desensitization in the sublimation of AP [16, 17]. On the other hand, the thermal decomposition of AP is sensitized by pre-heating [18]. It is also sensitized by the dopants,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  (in the low concentration range) as found in this investigation. A proton transfer process has generally been accepted as the rate-controlling step in the sublimation of AP. The divergence in the behaviour of sublimation and decomposition of AP subjected to the same pre-treatments, therefore, indicates that the decomposition does not involve proton transfer process as the rate-determining step.

The present results can be explained in terms of electron transfer mechanism according to which the rate-controlling step is the transfer of an electron from  $\text{ClO}_4^-$  to  $\text{NH}_4^+$  [6]:



Doping of AP with anion like  $\text{SO}_4^{2-}$  or  $\text{PO}_4^{3-}$  results in an increase of anion vacancies which can capture electrons because of the localization of the positive charge in the neighbouring sites of the lattice. These electron traps promote the electron transfer process (3) as shown below, leading to an increase in the rate of decomposition:



where T stands for the electron trap and Te for the trap-electron combination. In addition, these dopants cause an increase in the concentration of interstitial ammonium ions and thus in the number of sites available for electron transfer process leading to enhanced decomposition. However, when the concentration of the dopants in solution exceeds a certain value, a counter process becomes operative. The uptake of dopant by the lattice of AP possibly reaches a saturation limit and during the process of co-crystallization the excess dopant precipitates on gross imperfections like grain boundaries, where there is an agglomeration of vacancies

and other defects such as dislocations. The aggregation of impurities at dislocations in all kinds of solids is well known. It is also well known [19–22] that, thermal decomposition of a solid occurs preferentially at selective sites such as points of emergence of dislocations, meeting points of grain boundaries, kinks, jogs etc. These special sites ( $S$ ) can trap electrons from the adjacent less well co-ordinated perchlorate ions and thus facilitate the decomposition process [23]. The reaction steps may be represented as



( $S$  does not appear on the r.h.s. of (7) since it is destroyed by the reaction). Evidently, a change in the concentration of the special sites, which function as potential decomposition centers, should alter the rate of decomposition. Excess dopants, by precipitating at the selective sites, cause a decrease in the number of these active sites. This 'poisoning' at high concentration of dopants slows down the electron transfer process and thus leads to a decrease in the rate of decomposition.

Studies on the effect of doping on the IR spectrum of AP provide experimental support for the possibility of precipitation of dopants beyond a concentration limit. It is observed that doping results in the broadening of IR peaks, and that the broadening reaches a constant maximum value as the concentration of the dopants is increased. Figure 4 shows the variation of half-width of the  $\nu_3$  band at ca.  $1119 \text{ cm}^{-1}$  (asymmetric stretching of perchlorate ion) with the dopant concentration. Clearly, the broadening of the band reaches a constant value exactly at the same concentrations of the dopants at which the rate of decomposition commences to decrease. According to Baker [24] the broadening of IR bands reflects the disorder introduced in the crystal lattice. On this basis, IR bands attain maximum

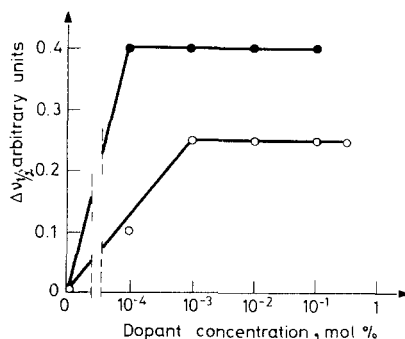


Fig. 4 Dependence of the change in half width of  $\nu_3$  absorption band of AP on dopant concentration: ○,  $\text{SO}_4^{2-}$  doped AP; ●,  $\text{PO}_4^{3-}$  doped AP

breadth when the uptake of dopants by the crystal lattice reaches a saturation limit. The dopants, however, continue to influence the rate of decomposition even beyond the saturation limit. This is possible only by their precipitation in the region of gross imperfections during co-crystallization. Being larger in size, the solubility of  $\text{PO}_4^{3-}$  in the lattice of AP should be less than that of  $\text{SO}_4^{2-}$  and consequently the precipitation process should begin at a lower concentration in the case of phosphate-doped AP. This expectation is borne out experimentally (see Fig. 2 or 4). The low solubility of  $\text{PO}_4^{3-}$  also explains why the observed sensitisation of the decomposition of AP caused by  $\text{PO}_4^{3-}$  is not more than that caused by  $\text{SO}_4^{2-}$  for a given dopant concentration.

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**Zusammenfassung** — Die isotherme Zersetzung von orthorhombischen Ammoniumperchlorat (AP) wurde in Abhängigkeit von der Konzentration der Dopanten  $\text{SO}_4^{2-}$  und  $\text{PO}_4^{3-}$  untersucht. In jedem Falle geht die Geschwindigkeit der Zersetzung mit steigender Dopantenkonzentration durch ein Maximum. Die Aktivierungsenergie des Zersetzungsprozesses wird durch dopen nicht verändert. Die Ergebnisse werden auf einem Elektronentransfer-Mechanismus basierend interpretiert.

**Резюме** — Изучено изотермическое разложение орторомбического перхлората аммония в зависимости от концентрации легирующих добавок сульфат- и фосфат-ионов. В каждом случае скорость разложения с увеличением концентрации легирующей добавки проходит через максимум. Энергия активации процесса разложения остается неизменной при легировании. Результаты объяснены на основе механизма электронного переноса.