

## EFFECT OF TETRAMETHYLAMMONIUM PERCHLORATE ON AMMONIUM PERCHLORATE AND PROPELLANT DECOMPOSITION

S. R. JAIN\* AND P. R. NAMBIAR\*\*

*Department of Aeronautical Engineering, Indian Institute of Science,  
Bangalore 560012 (India)*

(Received 12 December 1975)

### ABSTRACT

The thermal decomposition of ammonium perchlorate (AP) is considerably modified when it is cocrystallized or mixed with small amounts of tetramethylammonium perchlorate. The decomposition is sensitized when tetramethylphosphonium perchlorate is added to AP. The effect on the isothermal decomposition of AP when it is mixed with tetramethylammonium perchlorate, appears to be similar to that of AP-based composite propellant having the same mixed AP composition.

### INTRODUCTION

The effect of various additives on the thermal decomposition of ammonium perchlorate (AP) has been studied elaborately<sup>1-6</sup> mainly because of the belief that the key reaction in the ignition process of AP-based composite propellants is the low temperature decomposition of AP<sup>7</sup>. The effect of non-metallic perchlorates on the thermal decomposition of AP and AP-based propellants has, however, not been examined in any details. Our recent study on the thermal decomposition of tetramethylammonium perchlorate<sup>8</sup> (TMAP), revealed that unlike other methylammonium perchlorates it decomposes without melting and does not produce perchloric acid as one of its decomposition products. Further, although fuel rich, TMAP does not ignite at any pressure<sup>9</sup>. In the present study we report the effect on the thermal decomposition of AP when it is cocrystallized or mixed with small amounts of TMAP. In order that these studies be of relevance, we have carried out decomposition studies on AP based propellants using AP mixed with TMAP and compared the thermal decomposition results.

### EXPERIMENTAL

#### *Materials*

AP used in the present study was provided by V.S.S.C., Trivandrum and was used after recrystallizing it once from water. The preparation and characterization of

\*To whom all correspondence should be addressed.

\*\*Present address: Department of Chemistry, University of Houston, Houston, Texas, U.S.A.

TMAP and tetramethylphosphonium perchlorate (TMPP), have been reported earlier<sup>8,10</sup>.

### Methods

The cocrystallized samples were prepared by using standard stock solutions of TMAP. 1 g of AP was weighed out into a beaker and the required volumes of the stock solution were pipetted out into it so that the concentration of TMAP in the AP solution would become 1.0 and 0.1 mol %, respectively. The AP solutions were concentrated on a hot plate at 70–90°C and the crystals formed were filtered using a sintered crucible. The crystals were dried at 90°C for 4 h. An unaged sample of the particle size range 90–125  $\mu\text{m}$  was used in each experiment.

An X-ray diffraction method was employed to see if the impurity has gone into the crystal lattice. The X-ray diffractograms obtained for AP and AP cocrystallized with TMAP, using a Shimadzu recording X-ray diffractometer Type GX-3B, were found to be virtually identical and did not show any change like shifting or broadening of peak or the appearance of any new feature. It, therefore, appears that crystallographic doping has not taken place. It is, however, possible that the diffractometer might not have detected very minor changes in the lattice as reported by Hartman<sup>5</sup> and Pai Verneker and Maycock<sup>7</sup>. In the case of mixing, crystallized AP (90–125  $\mu\text{m}$ ) was carefully mixed with required amounts of the impurity. AP-based propellants were prepared using carboxyl-terminated polybutadiene (CTPB) as binder with 80% AP or AP+1 mol % TMAP, loading. The details of the formulation and curing procedure are given elsewhere<sup>11</sup>.

The differential thermal analysis (DTA) and thermogravimetric analysis (TG) experiments were carried out using the equipments described earlier<sup>12</sup>. 50 mg samples were used in all experiments. The heating rates employed were 12°C min<sup>-1</sup> and 5°C min<sup>-1</sup> in the case of DTA and TG, respectively. All DTA experiments were carried out in air using platinum cups.

### RESULTS AND DISCUSSION

The results of the DTA and TG experiments show that the thermal decomposition of AP is considerably modified when it is mixed or cocrystallized with TMAP. The DTA (Table 1) of AP shows an endotherm at 240°C due to phase transformation which remains unchanged when AP is cocrystallized or mixed with the impurity. The thermal decomposition of AP occurs in two steps as shown in DTA by two exotherms, one at  $\sim 300^\circ\text{C}$  attributed to incomplete (30%) decomposition and another at  $\sim 400^\circ\text{C}$  due to complete decomposition. The DTA of AP cocrystallised or mixed with 1 mol % TMAP on the other hand show only one exotherm corresponding to the complete decomposition. It is interesting to note that whereas in the case of the mixed sample the exotherm occurs at 350°C, the cocrystallized sample with the same impurity concentration, decomposes completely at 285°C. The decomposition results obtained by isothermal TG for the AP samples mixed and cocrystallized with

1 mol % TMAP (Figs. 1 and 2) again, are significantly different. Whereas the mixed sample shows considerable desensitization, the cocrystallized sample shows significant sensitization. This difference in thermal decomposition shows that in the case of the cocrystallized samples crystallographic doping has taken place at least to a certain extent.

TABLE I  
DTA DATA ON AP SAMPLES

Sample	Peak temperatures (°C)		
	Endotherm	1st exotherm	2nd exotherm
Pure AP	240	298	380
AP cocrystallized with 1 mol % TMAP	240	285	—
AP mixed with			
(i) 1 mol % TMAP	240	350	—
(ii) 1 mol % TMPP	240	307	—

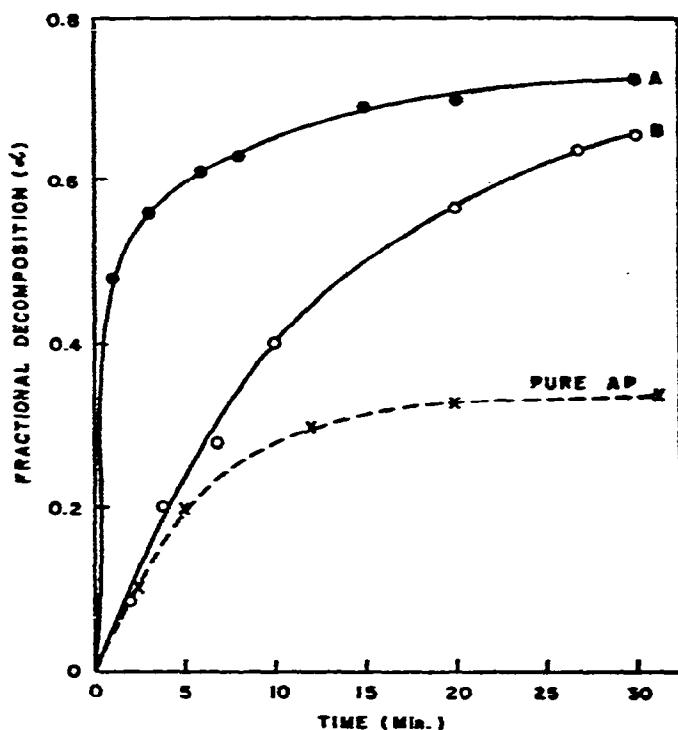


Fig. 1. Isothermal TG curves at 285°C of, AP cocrystallized with 1.0 (A) and 0.1 (B) mol % of TMAP.

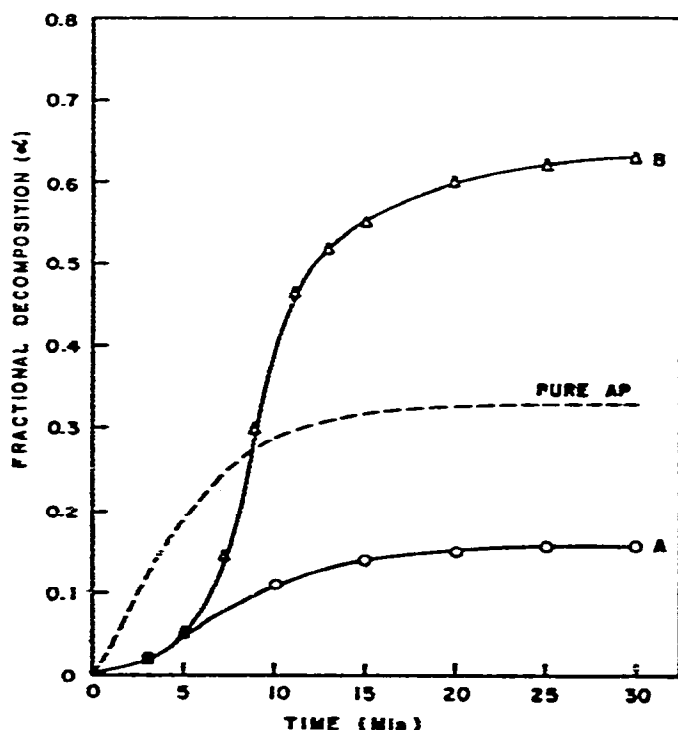


Fig. 2. Isothermal TG curves at 285°C of: (A), AP+TMAP (1 mol %) and (B), AP+TMPP (1 mol %) mixtures.

To account for the observed effect of cocrystallization it may be assumed that when AP is cocrystallized with  $(\text{CH}_3)_4\text{N}^+$  ion, the defect structure of the host lattice does not change. The sensitization effect may, however, be attributed to the bigger size of the impurity ion and the consequent strain created in the crystal. This strain appears to be not significant enough to be shown by X-ray diffraction technique but it is sufficient to induce decomposition.

In order to establish the effect of mixing TMAP we studied the effect of the addition of another analogous compound, TMPP on AP decomposition. As can be seen by the DTA (Table 1) and isothermal TG at 285°C (Fig. 2), the effect of mixing these impurities with AP is quite revealing. While the decomposition of AP is desensitized when mixed with TMAP, significant sensitization is observed when mixed with TMPP. This may be explained by taking into account the thermal decomposition characteristics of TMAP and TMPP. The TMAP decomposes essentially without melting whereas TMPP melts before decomposition<sup>10</sup>. Further, assuming trimethylamine as a product of decomposition<sup>8</sup>, the desensitization effect observed may be due to the inhibiting action of the ammine. On the other hand, the sensitization observed in the case of AP mixed with 1 mol % TMPP may be attributed to the solid-liquid interface provided by the melting of this compound<sup>1,13</sup>.

The results of the thermal decomposition of AP may at this stage be compared with those of the AP-based propellants. The DTA (Fig. 3) of the propellant samples

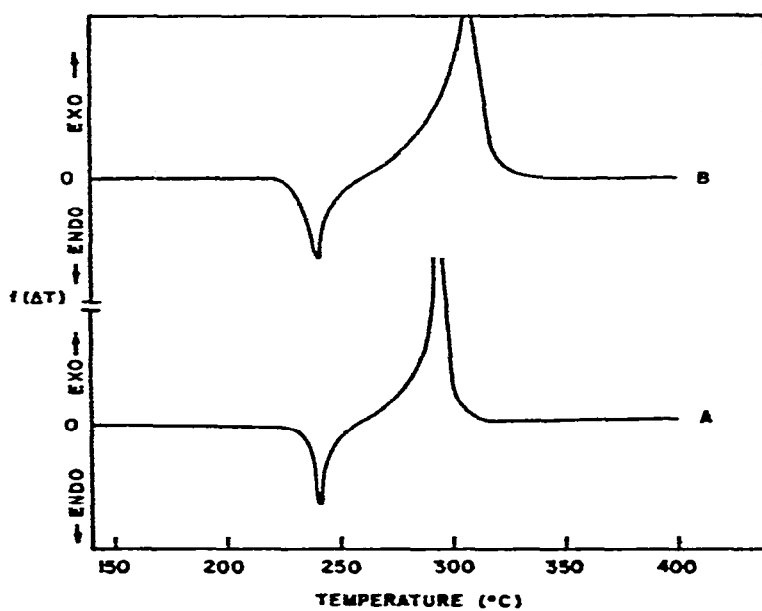


Fig. 3. DTA traces of: (A). AP composite propellant and (B), AP+TMAP (1 mol %) composite propellant.

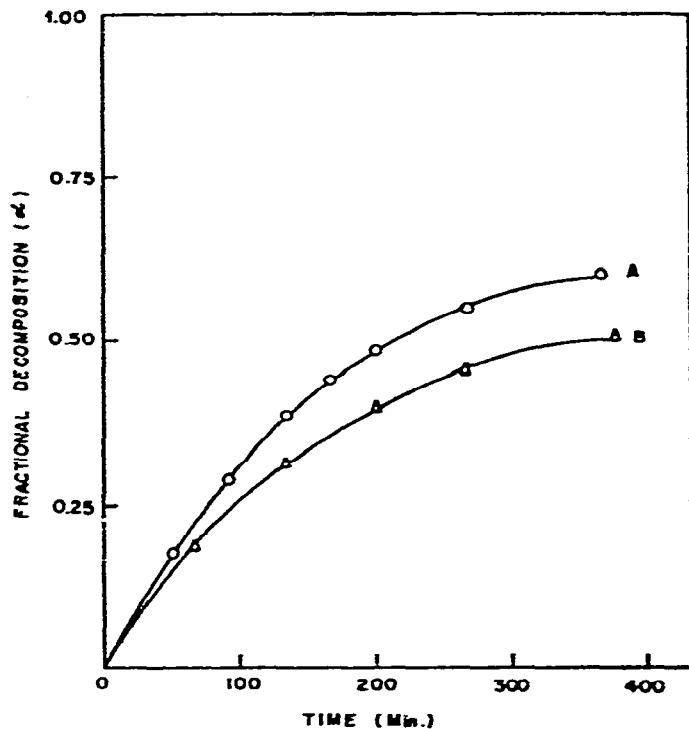


Fig. 4. Isothermal TG curves at 285 °C of: (A), AP composite propellant and (B), AP+TMAP (1 mol %) composite propellant.

reveal that the phase change of AP, occurring at 240°C remain unchanged and the decomposition occurs with ignition in one step only. As discussed earlier, the decomposition of AP is desensitized when it is mixed with 1 mol % TMAP. It is interesting to note that a similar effect is shown by DTA as well as isothermal TG at 285°C (Fig. 4) of the propellants. The decomposition of AP-based propellant shows considerable desensitization when AP+ 1 mol % TMAP is used as oxidizer. The low temperature decomposition of AP therefore appears to be related to the thermal stability of AP-based propellants.

#### REFERENCES

- 1 P. W. M. Jacobs and H. M. Whitehead, *Chem. Rev.*, 69 (1969) 551.
- 2 J. N. Maycock and V. R. Pai Verneker, *Proc. Roy. Soc.*, A307 (1968) 303.
- 3 V. V. Boldyrev, V. V. Alexandrov, A. V. Boldyreva, V. I. Gristan, Yu. Ya. Karpenko, O. P. Korobeinichev, V. N. Penfilov and E. F. Khairtdinov, *Comb. Flame*, 15 (1970) 71.
- 4 T. L. Boggs, E. W. Price and D. E. Zurn, *13th symp. on Combustion*, The Combustion Institute, Pittsburg, Pa., 1971, p. 995.
- 5 K. O. Hartman, *Western States Section Meeting*, The Combustion Institute, WSSI paper no. 69-18, 1969.
- 6 W. G. Schmidt, *NASA Contract Report*, 1969, NASA-CR-66757.
- 7 V. R. Pai Verneker and J. N. Maycock, *J. Inorg. Nucl. Chem.*, 29 (1967) 2723.
- 8 P. R. Nambiar, V. R. Pai Verneker and S. R. Jain, *J. Therm. Anal.*, 8 (1975) 15.
- 9 A. E. Fogelzang, B. S. Svetlov, V. S. Opryshko and V. Ya. Adzhemyan, *Comb. Explosion Shock Waves*, 8 (1972) 206; (Eng. trans.).
- 10 P. R. Nambiar and S. R. Jain, *Thermochim. Acta*, 9 (1974) 295.
- 11 S. R. Jain and H. K. Nagpal, *Indian J. Tech.*, in press.
- 12 S. R. Jain and P. R. Nambiar, *Indian J. Chem.*, 12 (1974) 1087.
- 13 K. C. Patil, V. R. Pai Verneker and S. R. Jain, unpublished results.