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Thermal Decomposition of Ammonium per chlorate-Tetraethyl Ammonium per chlorate Mixtures

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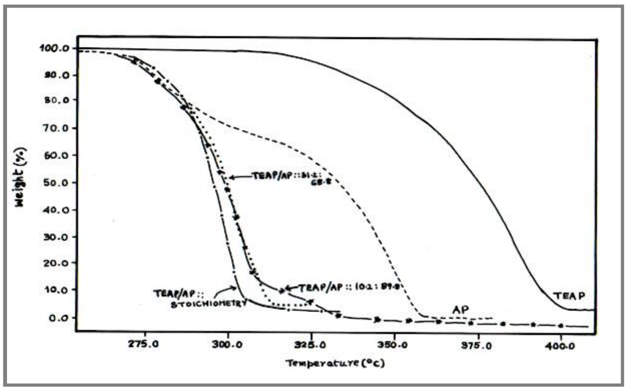
ABSTRACT

The influence of tetra ethyl ammonium per chlorate (TEAP) on the thermal decomposition of ammonium per chlorate (AP) is studied employing thermo-analytical tools of TG, DTG, and DSC in pure nitrogen atmosphere. TEAP catalyzes the HTD of AP by bringing down the reaction temperature more towards LTD region. Stoichiometric composition is more effective than all other ratios studied. Thus, we have a more promising composition for air-breathing propulsion applications.

Graphical Abstract:



TG-Curves of Pure AP, pure TEAP and their Oxidizer-rich,
Stoichiometric and fuel-rich mixtures.

Keywords: Tetra ethyl ammonium per chlorate, Ammonium per chlorate, Thermo gravimetric.

INTRODUCTION

Tetraethyl ammonium per chlorate (TEAP) is formed by mixing the water-soluble tetraethyl ammonium bromide and sodium per chlorate in water, from which the water-insoluble tetraethyl ammonium per chlorate precipitates out [1].

$$Et_4N^+Br^- + Na^+ [ClO_4]^- \rightarrow Na^+ Br^- + Et_4N^+ [ClO_4]^-$$

Tetraethyl ammonium per chlorate salt is useful as a supporting electrolyte for polarographic studies in non-aqueous solvents [1]. The major characteristics of tetraethyl ammonium salts are their use as phase-transfer catalysts [2]. Tetraethyl ammonium salts such as tetraethyl ammonium tetrafluoroborate and tetraethyl ammonium methyl sulfonate are used in super capacitors as organic electrolytes [3]. Kivikoski *et al* [4] studied the behavior of TEAP at 150K. The Et_4N^+ ion undergoes rotational isomerism in aqueous or organic solutions between an all-trans conformation (tt.tt) and a trans-gauche (tg.tg) conformation. The Raman spectra of the two rotamers are distinct and their temperature dependence indicates that, (tt.tt) isomer is more stable than (tg.tg) isomer by about 4.1 kJ.mol^{-1} [5]. TEAP undergoes crystallographic transformation at 98°C and explodes at 298°C. The heat of phase transformation is calculated to be 2.5 kcal.mol^{-1}. The mass spectral data suggest that the salt undergoes thermal decomposition into neutral particles which are then vaporized and ionized as well as oxidized [6]. The modification of thermal decomposition of ammonium per chlorate (AP) by TEAP, a fuel-rich compound, is the subject matter of the present study.

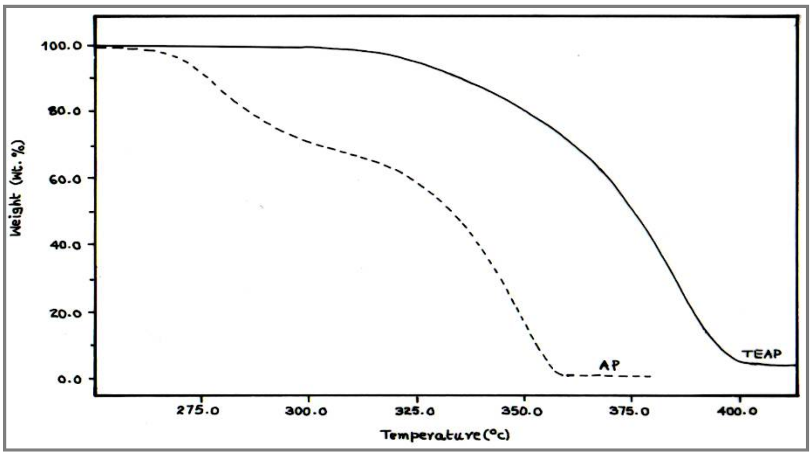
MATERIALS AND METHODS

Ammonium per chlorate (AP) is procured from Vikram Sarabhai Space Centre, Indian Space Research Organization (ISRO), Department of Space, and Government of India. Tetraethyl ammonium per chlorate (TEAP) is procured from Aldrich Chemicals.

The thermal decomposition studies were carried out employing Perkin-Elmer Series-7 instruments of thermo gravimetric (TG), derivative thermo gravimetric (DTG), and differential scanning calorimetry (DSC), in pure nitrogen atmosphere at a sample heating rate of 5°C.min^{-1}. The TEAP/AP mixture ratios considered in this study include-10.2/89.8 (Oxidizer rich), stoichiometric ratio and 31.2/68.8 (fuel-rich), in the increasing order of fuel-rich compound (TEAP).

RESULTS AND DISCUSSION

The thermo gravimetric (TG curves for pure ammonium per chlorate (AP) and pure tetra ethyl ammonium per chlorate (TEAP) are presented in figure 1. From figure 1, it can be seen that the onset and end-set temperatures of decomposition of AP are 258°C and 360°C, respectively. TEAP decomposes in a single step with its onset and end-set temperatures of decomposition occurring at 307.5°C and 405°C, respectively; indicating the thermal stability of TEAP is far higher than that of AP.



Figurer 1. TG curves of AP and TEAP.

The derivative thermo gravimetric (DTG) curves for pure AP and TEAP are presented in figure 2.

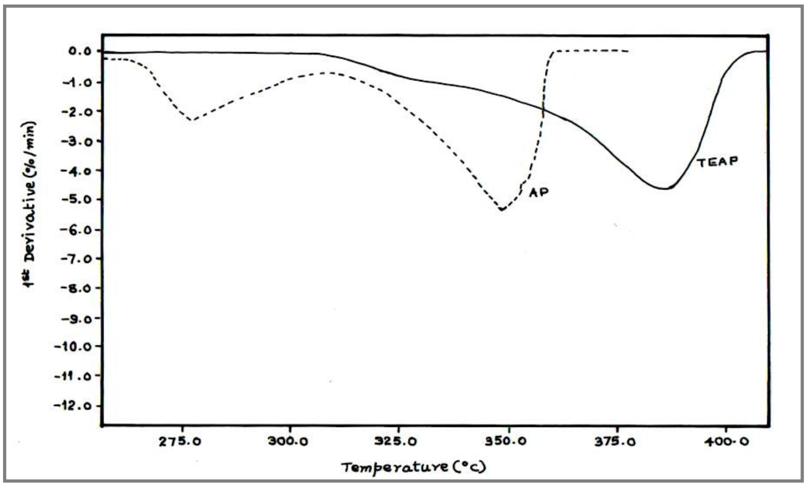


Figure 2. DTG Curves of AP and TEAP.

Thermal decomposition of AP takes place in two distinct stages, the low-temperature decomposition (LTD) peak appearing at 280°C, and the high-temperature decomposition (HTD) peak is appearing at about 348°C. In the case of TEAP, it decomposes in the single step at about 390°C.

The differential scanning calorimetric (DSC) curves for AP and TEAP are shown in figure 3.

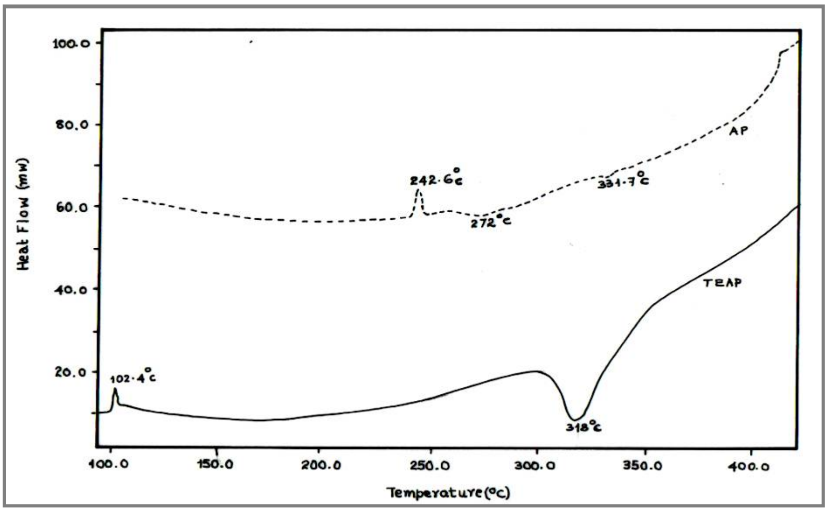


Figure 3. DSC Curves of AP and TEAP.

AP undergoes crystallographic phase-transition from orthorhombic to cubic phase at 242.6°C. It undergoes decomposition in two distinct stages with decomposition peaks appearing at 272°C and 331.7°C, respectively. With respect to TEAP, it undergoes melting at about 102.4°C, with its single stage decomposition peak appearing at 318°C. The TEAP decomposition is closer to HTD of AP, suggesting that, when their mixtures are considered, the TG-curves for pure AP and TEAP; as well as, their mixtures (Oxidizer-rich TEAP/AP:10.2/89.8) ratio, stoichiometric ratio, and fuel-rich ratio TEAP/AP:31.2/68.8) are presented in figure 4.

Their thermal stabilities are in the order of TEAP >> AP>> (TEAP/AP: 10.2/89.8) = Stoichiometric > (TEAP/AP: 31.2:68.8). While pure AP and Oxidizer-rich system (TEAP/AP: 10.2: 89.8) decompose in two stages; both the stoichiometric and fuel-rich (TEAP/AP:31.2:68.8) systems decompose in single step. The percentage decomposition in the HTD region of the oxidizer-rich

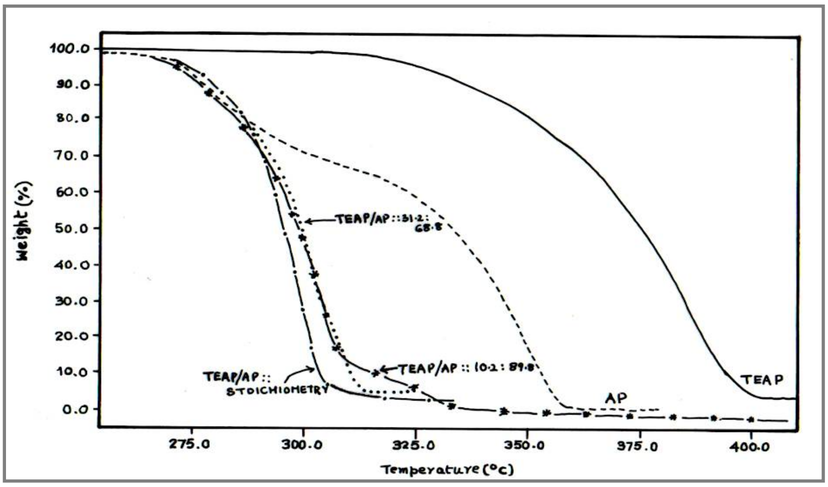


Figure 4. TG-Curves of Pure AP, pure TEAP and their Oxidizer-rich, Stoichiometric and fuel-rich mixtures.

system (TEAP/ AP: 10.2/89.9) is shifted to LTD region indicating catalysis by TEAP. Maximum catalysis is achieved in the case of stoichiometric composition. The temperatures of initiation of decomposition in the case of TEAP/AP mixtures are: 260°C, 268°C, and 264°C, for oxidizer: rich, stoichiometric, and fuel-rich systems, respectively. The end-set temperatures of decomposition are: 280°C, 287°C, and 280°C, in the respective order ad described above. These observations clearly indicate that, the decomposition temperature interval is not affected due to the increased concentration of TEAP. From the maximum rate of decomposition peak temperature point of view, the observations are: 273°C, 280°C, and 274°C for oxidizer – rich, stoichiometric, and fuel-rich systems, respectively. Here again, there is no appreciable change is observed.

The DTG-curves for pure AP and TEAP; as well as, their mixtures (Oxidizer-rich TEAP/AP::10.2/89.8) ratio, stoichiometric ratio, and fuel-rich ratio TEAP/AP::31.2/68.8) are presented in figure 5.

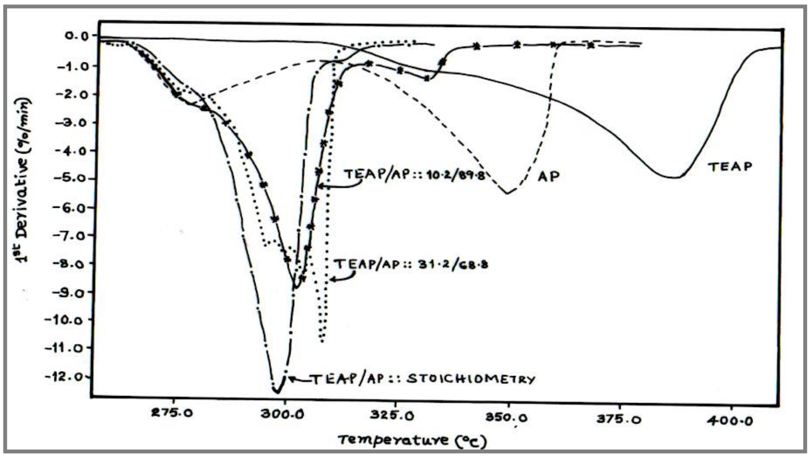


Figure 5. DTG – Curves of pure AP, pure TEAP and their Oxidizer-rich, Stoichiometric and fuel-rich mixtures.

The observations from DTG-curves corroborate well with those observed in the case of TG-curves. The DSC-curves for pure AP and TEAP; as well as, their mixtures (Oxidizer-rich TEAP/AP::10.2/89.8) ratio, stoichiometric ratio, and fuel-rich ratio TEAP/AP::31.2/68.8) are presented in figure 6.

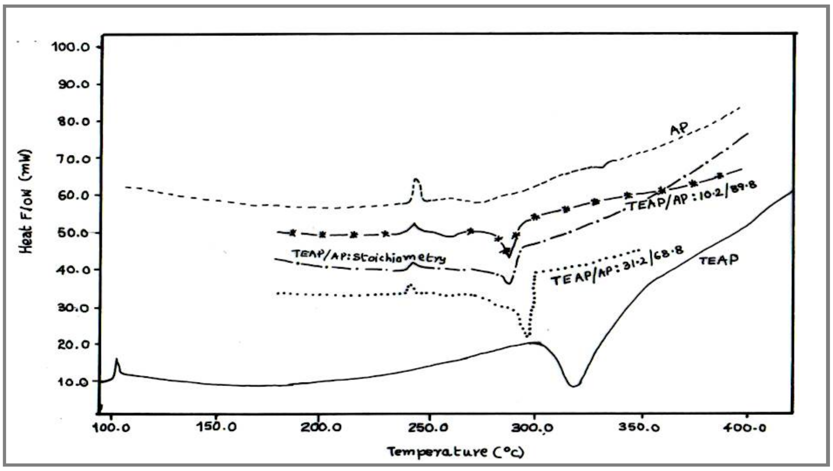


Figure 6. DSC-Curves of pure AP, pure TEAP and their Oxidizer-rich, Stoichiometric and fuel-rich mixtures.

The endothermic, crystallographic phase-transition of AP is not affected by the presence of TEAP. With the addition of more and more TEAP, the HTD of AP is brought down to the LTD region indicating catalysis. As the reaction mixture becomes more and more fuel- rich, the total enthalpy release becomes closer to that of pure TEAP. It is clearly indicative that, the presence of TEAP catalyzes the HTD of AP, as expected of it.

APPLICATION

The stoichiometric composition is more appropriate for fuel-rich propellants in air-breathing propulsion applications

CONCLUSION

- TEAP proves to be an useful additive in the modification of AP thermal decomposition.
- The HTD of AP is catalyzed by the presence of TEAP.

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