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Effect of Tetra-n-butyl Ammonium Hexafluorophosphate on Thermal Decomposition of Ammonium Per chlorate

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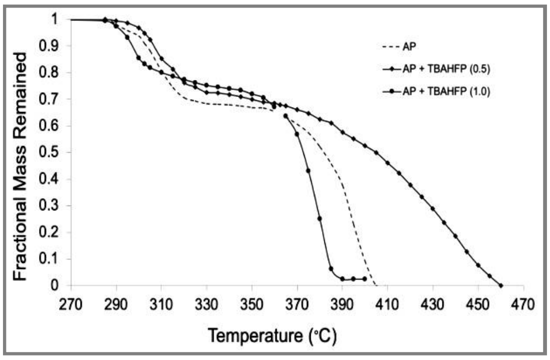
ABSTRACT

Effect of tetra-n-butyl ammonium hexafluorophosphate on the thermal decomposition of ammonium per chlorate was studied employing thermo-analytical techniques of thermogravimetry and derivative thermogravimetry in an inert atmosphere of pure nitrogen (flow rate of 30 mL min^{-1}; sample heating rate of 20^{o}C min^{-1} and a sample mass of ~ 5.5mg. Ammonium per chlorate decomposition takes place in two stages, while that of heaxafluorophosphate takes place in a single stage. Thermal decomposition of heaxafluorophosphate mostly occurs corresponding to the second-stage decomposition of ammonium per chlorate and the same phenomena was observed when their mixtures are considered. Towards suppressing the first-exotherm of ammonium per chlorate, which is responsible for premature re-ignition of stop-restart combustion of reusable solid rocket motors, at 0.5 mass percentage of ammonium per chlorate, the presence of heaxafluorophosphate does meet the requirement. However, at higher concentration of heaxafluorophosphate, catalytic augmentation of decomposition takes place.

Graphical Abstract



TG–Curves of Pure AP, and AP with TBAHFP Mixtures.

Keywords: Ammonium per chlorate, Tetra-n-butyl ammonium hexafluorophosphate, TGA, DTG, Stop- restart rocket motors, Premature re-ignition

INTRODUCTION

Inadvertent premature re-ignition of controllable solid propellant rocket motors was observed leading to the failure of missions. Computations using thermal models [1, 2] of extinguishable motors had shown that, the major factor causing this premature re-ignition is attributed to the first-exotherm of ammonium per chlorate (AP), a widely employed crystalline inorganic oxidizer in composite solid rocket propellant systems [1]. This premature re-ignition can be prevented by limiting the heat radiated to the propellant surface after its extinguishment, or reducing the heat generated in the residual propellant through exothermic decomposition at its elevated temperatures [1]. Following the later approach, Mayer *et al*., [1] observed that, at five percent concentration of the additive, namely, ammonium hexafluorophosphate, the first-exotherm of AP has been shifted completely to the higher temperature regime. In the present context, the focus is to understand the role of fuel-rich compound such as tetra-n-butyl ammonium hexafluorophosphate $[(C_4H_9)_4NPF_6]$ on the thermal decomposition of AP. This may find applications in the arena of stop-restart solid reusable solid rocket propulsion applications.

MATERIALS AND METHODS

Course particles of Ammonium per chlorate as obtained from the Ammonium per chlorate Experimental Plant (APEP), Alwaye, Vikram Sarabhai Space Centre, Indian Space Research Organization, Department of Space and Government of India were used in this study. Tetra-n-butyl ammonium hexafluorophosphate (TBAHFP) was procured from Aldrich Chemicals, Hyderabad, India. The mixtures of AP –TBAHFP were prepared at 0.50 and 1.0 mass percent of AP. The thermo gravimetric), derivative thermo gravimetric (DTG), and differential thermal analysis (DTA) experiments were conducted in an inert atmosphere of pure nitrogen (flow rate of 30 mL min^{-1}. Sample heating rate of 20°C min^{-1}, and a sample mass of ~ 5.5 mg were employed in these experiments.

RESULTS AND DISCUSSION

From figure 1, it can be seen that AP undergoes thermal decomposition in two stages, while TBAHFP undergoes thermal decomposition in a single stage. Secondly, thermal stability of TBAHFP is greater than that of AP. Yet, another interesting observation is that, TBAHFP decomposition temperature interval falls in the temperature regime of second-stage decomposition of AP. From these observations it can be expected that TBAHFP could influence the second-stage thermal decomposition of AP when their mixtures are considered.

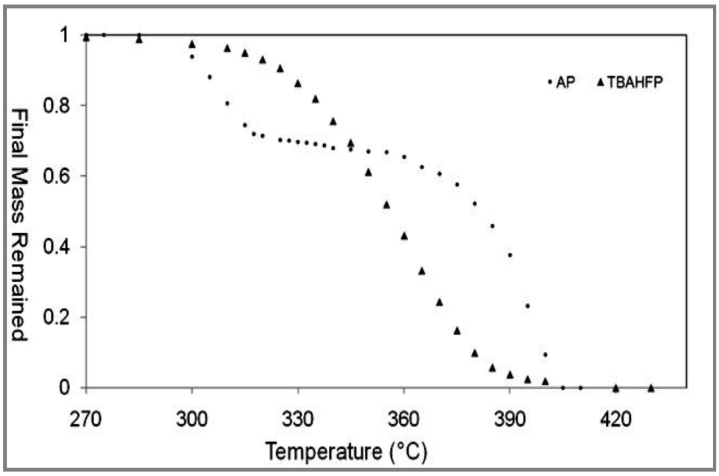
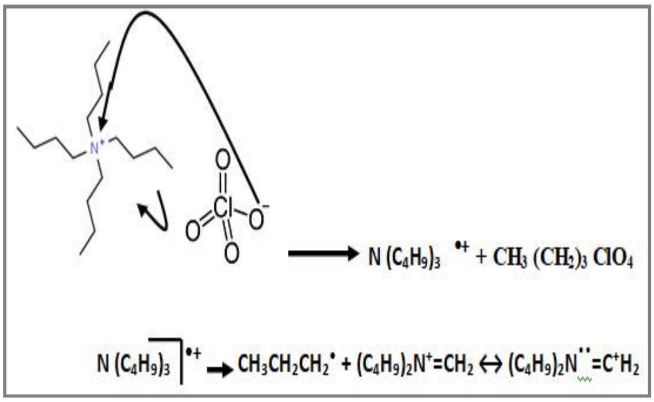


Figure 1. TG Curves of pure AP and TBAHFP.

Thermo gravimetric curves for pure AP and AP-TBAHFP mixtures are shown in figure 2. At 0.5 % by mass of TBAHFP presence has catalyze the second-stage decomposition of AP (Figure 2). At higher concentration of TBAHFP (1% by mass), the tri-n-butyl amine formed can interact with the $HClO_4$ form the decomposition of pure AP, leading to the formation of intermediate per chlorates. These intermediate products formed can act as catalysts for subsequent decompose reactions. Thus, in the case of 1% concentration of the additive (TBAHFP), we have a situation of suppression of the first-stage decomposition of AP and the second-stage decomposition taking place over a long range of temperature interval up to the high-temperature regime. These observations are in tune with the observations made for the case of AP decomposition in the presence of 5% by mass of NH_4PF_6 presence [1].



Scheme I. Thermal Decomposition pattern of TBAHFP.

It is well known fact that, the quaternary ammonium compounds like TBAHFP yield tri-n-butyl amine [N $(Bu)_3$] as one of the intermediate products. Since tri-n-butyl amine is unstable (boils in the temperature range of 216°C-217°C) under the experimental conditions undergoes further dissociation. In this process, the C-C bond (α, β) cleavage next to the heteroatom (namely nitrogen in this case) leaving the charge on the fragment containing the heteroatom whose non-bonding electrons provide resonance stabilization (Scheme-I) [3].

Thus, we have a system that makes it feasible to avoid premature re-ignition in the case of stop-re-start solid rocket motors, as well as, air-breathing propulsion applications.

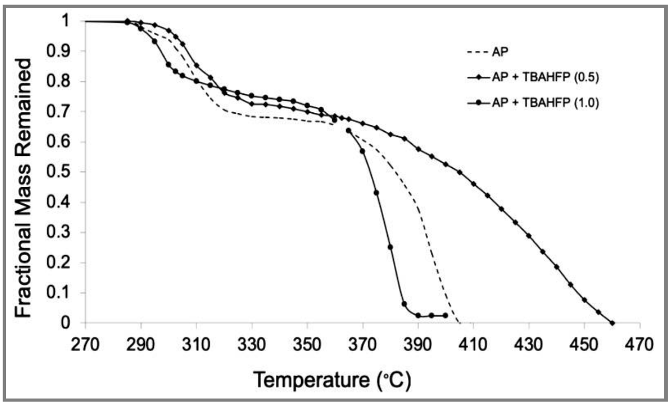


Figure 2. TG–Curves of Pure AP, and AP with TBAHFP Mixtures.

The observations made from the TG–curves (Figure 2) corroborate well with the derivative thermo gravimetric (DTG) curves shown in figure 3 and the mechanistic aspects of decomposition are in tune with the earlier observations [4, 5].

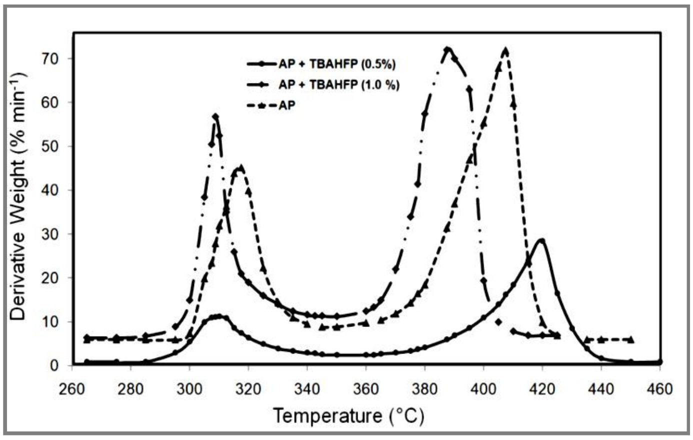


Figure 3. DTG–Curves of AP and AP–TBAHFP Mixtures.

APPLICATION

Since TBAHFP, at lower concentration is able to suppress the first-exothermic peak of AP and delay the second –exothermic peak to a higher temperature regime, at this particular concentration of the additive, it may find use in preventing premature re-ignition of composite solid rocket motors. Since these mixtures are fuel-rich systems, may also find application for air-breathing propulsion application.

CONCLUSION

- Quaternary ammonium compounds such as TBAHFP yield tri-butyl amine as an intermediate product of its thermal decomposition.
- This tri-butyl amine can interact with the $HClO_4$ obtained from the thermal decomposition of AP forming the corresponding intermediate amine per chlorates.
- These intermediate compounds formed undergo further decomposition yielding final products of decomposition.
- There is a clear evidence that, at lower concentration (to a maximum of 0.5% by mass), TBAHFP suppresses the first-exotherm of AP which is responsible for the premature re-ignition of stop – re-start solid rocket motors.
- There are two suggested alternatives for avoiding the premature re-ignition in terms of either suppressing the first-exotherm of AP (or) delaying it to higher temperature regime. From our study, it is suggestive of following the first approach in suppressing the first-exotherm of AP, with limitations on the concentration of the additive employed.

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