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# Thermal Decomposition of Ammonium per chlorate-Tetra-n-butyl Ammonium per chlorate Mixtures

**M. R. R. Prasad* and K. Sudhakarbabu**

Department of Chemistry, Sri Krishnadevaraya University, Anantapuram–515003, Andhra Pradesh, **INDIA**
Email: mandapaka.p@gmail.com

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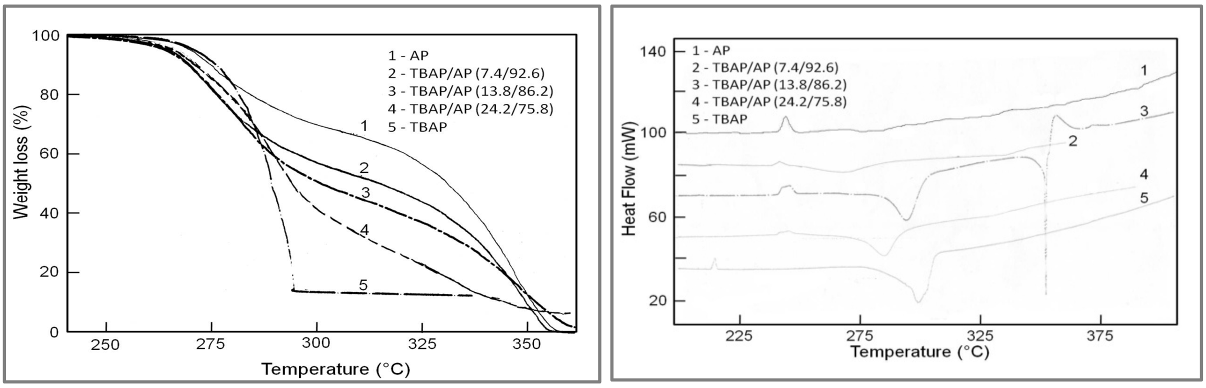
## ABSTRACT

*The role of tetra butyl ammonium per chlorate (TBAP) towards modification of thermal decomposition of ammonium per chlorate (AP) is presented considering their mixtures from oxidizer-rich composition, stoichiometric composition, and fuel-rich composition. Thermo-analytical investigations have been carried out in an inert atmosphere of pure nitrogen, at a sample heating rate of 5℃ min*$^{-1}$*, and in Perkin-Elmer-7 series systems. Since the decomposition temperature regime of TBAP falls in the range of the first-stage decomposition of AP, it is expected to influence the first-stage decomposition of AP in the formulations studied. Experimental observations confirm this hypothesis. Kinetic parameters, evaluated employing Coats-Redfern equation corroborate well with the above observations. These studies indicate that the stoichiometric composition may be considered for rocket propulsion applications in the arena of air-breathing propulsion.*

### Graphical Abstract



Thermal Decomposition of Ammonium per chlorate-Tetra-n-butyl Ammonium per chlorate Mixtures were studied in an inert atmosphere of pure nitrogen, at a sample heating rate of 5°C min$^{-1}$.

**Keywords:** Ammonium per chlorate, Tetra butyl ammonium per chlorate, Mixtures, Air-breathing propulsion, Fuel-rich propellants.

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## INTRODUCTION

Keeping in view of various applications such as propulsion for large space vehicles and tactical missiles, gas generators for airbags; composite solid propellants are being intensively pursued [1-3]. Ammonium per chlorate (AP), a white crystalline inorganic oxidizer; extensively used in composite solid rocket propellant technology even today across the globe. The abundant presence of per chlorate on Mars is 10,000 times more than in soils and sands of Earth. In 2009, NASA's *Phoenix* lander identified per chlorate in the Martian dirt pretty much everywhere it looked [4].

It is a well established fact that, the thermal decomposition characteristics of AP play a very significant role in the combustion process of composite solid rocket propellants, may be due to its presence in larger quantity in the propellant formulation, and thus controlling the combustion characteristics of the propellant [5, 6]. An interesting and individual property of AP is that its slow and fast decompositions can be studied over a wide temperature interval of 200°C-530°C. Further it is understood that, there is no other inorganic salt that decomposes with measurable rate over such a wide temperature interval 200°C-530°C. Further, its stability is very sensitive to the presence of various additives, and particularly nanoadditives, thereby permitting investigation of catalytic processes in the solid–phase [3, 4-15].

Preparation and characterization of tetra butyl ammonium graphite intercalation compound was reported by Weekit *et al* [16]. A non-membrane electrolysis cell for the reduction of $CO_2$ to CO employing $Bu_4NClO_4$ (TBAP) /propylene carbonate (PC) solution as the catholyte, and $H_2SO_4$ solution as anolyte was reported by Jin *et al* [17]. Due to the hydrophobic nature of TBAP/PC system, a liquid-liquid interface exists between the catholyte and the anolyte [17]. In a comprehensive study of the electrochemical reduction of β-nitro styrene and the corresponding heterocyclic analogue carried out in aprotic media using wax-impregnated carbon paste electrodes, the nitro-radical anion couple detected in the presence of tetra butyl ammonium per chlorate was found to be stable only in aprotic media [18].

Thermal decomposition of tetra butyl ammonium compounds of–tetrafluoroborate, hexafluoro phosphate, and per chlorate was reported by Prasad *et al* [19]. The mixture of acetonitrile and 2-propanol containing 1M acetic acid, 20mM sodium acetate, and 2.5 mM tetra butyl ammonium per chlorate (TBAP) was used as electrophoretic buffer, in the demonstration for the analysis of atropine, anisodamine, and scopolamine by nonaqueous capillary electrophoresis (NACE) coupled with electro-chemiluminescence (ECL) and electrochemistry (EC) dual detection [20]. A derivatographic study of the thermal degradation of tetra butyl ammonium per chlorate was made by Jasim *et al* [21]. In the present study, attention is focused towards understanding the role of TBAP, a fuel-rich quaternary ammonium compound, in promoting the thermal decomposition of ammonium per chlorate.

## MATERIALS AND METHODS

Ammonium per chlorate (AP) was procured from the Ammonium Per chlorate Experimental Plant (APEP), Alwaye, Vikram Sarabhai Space Centre (VSSC), Indian Space Research Organization (ISRO), Department of Space (DOS), Government of India. Tetra butyl ammonium per chlorate (TBAP) was procured from Aldrich Chemicals, Hyderabad.

Thermo gravimetric and Differential Scanning Calorimetric (DSC) experiments were carried out in a Perkin-Elmer 7 Series Thermal Analysis System; in an inert atmosphere of pure nitrogen gas, and at a sample heating rate of 5°C $min^{-1}$. The mixture ratios of TBAP: AP considered in these experiments include -TBAP: AP = 7.4/92.6 (Oxidizer-rich); 13.8/86.2 (Stoichiometric); and 24.2/75.8 (fuel-rich), wherein TBAP replaces AP.

## RESULTS AND DISCUSSION

Thermo gravimetric curves of pure ammonium per chlorate; pure tetra butyl ammonium per chlorate (TBAP); and mixtures of TBAP-AP of oxidizer-rich ratio, stoichiometric ratio, and fuel-rich ratio are shown in figure 1.

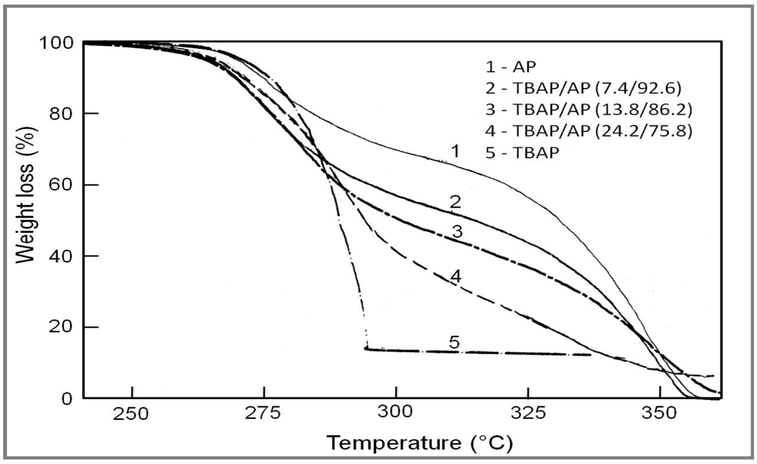

**Figure 1.** Thermo gravimetric curves.

The temperatures of inception of thermal decomposition, decomposition peak, and completion of decomposition of AP and TBAP, and mixtures of TBAP and AP are summarized in table 1.

**Table 1.** Temperatures of Inception, peak decomposition rate, and completion of decomposition of AP and TBAP and their mixtures

| Sample | First Peak Temperatures (° C) | | | Second Peak Temperatures (° C) | | |
|---|---|---|---|---|---|---|
| | Inception Temp. | Peak rate of Decomp. | Completion of Decomp. | Inception Temp. | Peak rate of Decomp. | Completion of Decomp. |
| AP | 269 | 278 | 308 | 308 | 349 | 362 |
| TBAP | 265 | -- | -- | -- | 300 | 300* |
| TBAP:AP:: 7.4:92.6 (Oxidizer Rich) | 260 | 275 | 311 | 311 | 352 | 365 |
| TBAP:AP:: 13.8:86.2 (Stiochio-metric) | 256 | 283 | 313 | 313 | 351 | 367 |
| TBAP:AP:: 24.2:75.8 (Fuel-rich) | 250 | 291 | 319 | 319 | 337 | 370 |

*Auto-ignition Condition

From the data in table 1, it can be expected that, TBAP may influence the second-stage thermal decomposition of AP, when their mixtures are considered. Even though TBAP's decomposition begins in par with that of AP, its peak decomposition rate is achieved around the temperature at which AP's first-stage decomposition ends, justifying our assumption.

As we move down from the oxidizer–rich system to fuel-rich system (Table 1), in the case of first-stage decomposition, we observe that the temperature of inception of decomposition is moving to a lower temperature regime, while the temperature of peak decomposition rate and the temperature of completion of decomposition are moving towards high temperature regime. On the contrary, with respect to the second-stage decomposition, as we move down from the oxidizer-rich system to fuel-rich system; the temperatures of inception and completion of decomposition are shifting to higher temperature regime; and the temperature of peak decomposition rate is shifting towards lower temperature regime. The derivative thermo gravimetric (DTG) curves for pure AP; pure TBAP; and their mixtures are shown in figure 2.

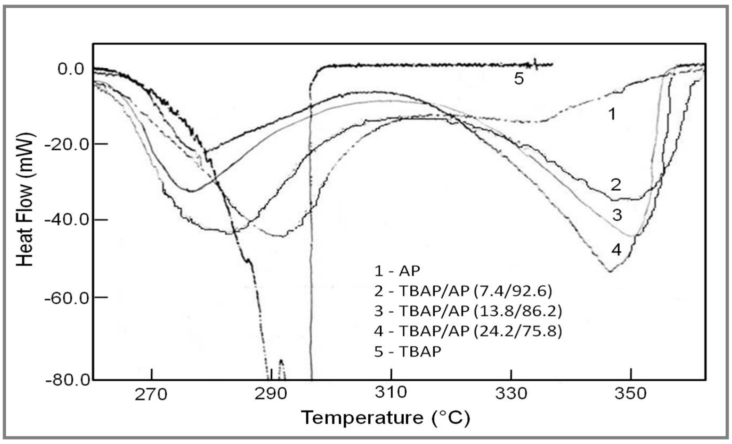

**Figure 2.** DTG - curves of pure AP, pure TBAP and their mixtures.

While pure TBAP decomposes in a single step with its peak decomposition temperature at about 295°C, which corresponds to the first-stage decomposition of AP, it is indicative of influencing the first– stage decomposition of AP. It is clear from figure 2 that, TBAP influences the first–stage decomposition of AP, and as we move from the oxidizer–rich system to stoichiometric system of mixtures, the temperatures of decomposition are shifted towards lower temperature regime. When it comes to the fuel-rich mixture, the tendency is towards shifting the first-stage decomposition peak towards high-temperature regime.

In the case of second-stage decomposition of AP, as we move from the oxidizer–rich system to stoichiometric system of mixtures, the decomposition peaks are shifted to higher-temperature region; while the fuel-rich mixture indicates the peak decomposition temperature moves towards lower temperature region. The differential scanning calorimetric (DSC) curves of pure AP; pure TBAP; and their mixtures are shown in figure 3.

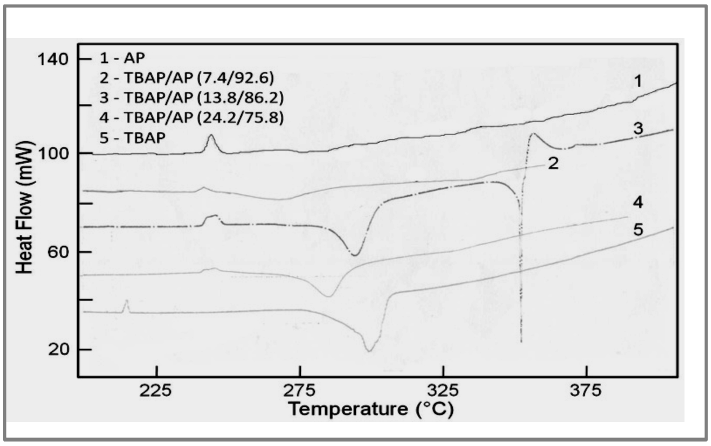

**Figure 3.** DSC-Curves of pure AP, pure TBAP and their mixtures.

From figure 3, the observations from DTG-curves (Figure 2) are corroborating with those observed through DSC experiments. Further, in the case of stoichiometric mixture, the second-stage decomposition reaction becomes auto-catalytic. The kinetic parameters derived using Coats-Redfern equation [22] for the first-stage decomposition of TBAP and mixtures of TBAP-AP are presented in table 2 and those for the second-stage decomposition are presented in table 3.

**Table 2.** Kinetic Parameters for the 1st–Stage Decomposition of Pure TBAP and TBAP-AP Mixtures

| **Sample System** | **‘n’** | **α-Range** | **Energy of Activation (E) (kJ.mol$^{-1}$)** | **Frequency factor (A)** | **Entropy (ΔS)** | **Correlation Coefficient (R)** |
|---|---|---|---|---|---|---|
| TBAP | 0.7 | 0.0349-0.8570 | 380.1±3.7 | 3.2 X $10^{34}$ | 410.3 | 0.9995 |
| TBAP/AP: 7.4/92.6 | 2.5 | 0.1706-0.9378 | 379.4±9.5 | 1.8 X $10^{35}$ | 424.9 | 0.9969 |
| TBAP/AP:13.8/86.2 (Stoichiometric) | 2.2 | 0.1348-0.9424 | 342.5±4.5 | 3.8 X$10^{31}$ | 354.4 | 0.9991 |
| TBAP/AP: 24.2/75.8 | 1.8 | 0.0307-0.9447 | 283.4±2.0 | 4.0 X $10^{25}$ | 240.0 | 0.9996 |

* Kinetic parameters were evaluated using Coats-Redfern Equation

**Table 3.** Kinetic Parameters for the 2nd–Stage Decomposition of Pure TBAP and TBAP-AP Mixtures

| **Sample System** | **‘n’** | **α-Range** | **Energy of Activation (E) (kJ.mol$^{-1}$)** | **Frequency factor (A)** | **Entropy (ΔS)** | **Correlation Coefficient (R)** |
|---|---|---|---|---|---|---|
| TBAP/AP: 7.4/92.6 | 0.6 | 0.0843-0.9960 | 244.2±3.2 | 5.2 x $10^{19}$ | 126.4 | 0.9990 |
| TBAP/AP:13.8/86.2 (Stoichiometric) | 0.7 | 0.1092-0.9933 | 217.6±2.7 | 2.5 x $10^{17}$ | 81.9 | 0.9990 |
| TBAP/AP: 24.2/75.8 | 1.6 | 0.2674-0.9828 | 319.4±3.5 | 5.0 x $10^{26}$ | 260.2 | 0.9994 |

*Kinetic parameters were evaluated using Coats-Redfern equation.

## APPLICATION

The ammonium per chlorate – tetra butyl ammonium per chlorate mixtures could be considered as new possibilities for fuel-rich propellants needed for air-breathing propulsion applications.

## CONCLUSION

- Thermal decomposition of TBAP takes place in single stage corresponding to the first-stage decomposition of AP; and it was found to be true when we considered the mixtures of TBAP/AP.
- Stoichiometric mixture appears to be performing optimally as evident from the experimental curves and the kinetic parameters.
- In the case of first-stage decomposition, as we move down from the oxidizer-rich composition to fuel-rich composition, the ‘n’–values tend towards first-order reaction.
- In the case of second-stage decomposition, as we move down from the oxidizer-rich composition to fuel-rich composition, the ‘n’–values indicate that, the reaction order is changing from the first order towards second order.

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