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Thermal Decomposition of Ammonium per chlorate: Part-I: Effect of Sample Heating Rate

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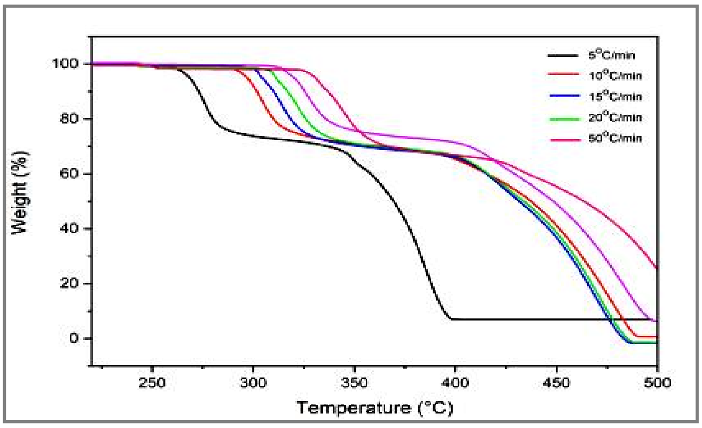
ABSTRACT

Thermal decomposition (TD) of ammonium per chlorate (AP) is the subject matter of this presentation. Various physical parameters influence the thermal decomposition of ammonium per chlorate. The focus in the present work is on the influence of sample heating rate (5℃ min^{-1} to 50℃ min^{-1}) on TD of AP. Thermo-analytical techniques employed in this study include-Thermo gravimetric (TG), Derivative thermo gravimetric (DTG), and Differential Scanning Calorimetry (DSC), in an inert atmosphere of pure nitrogen, at a gas flow rate of 50 mL min^{-1}. As expected, the reaction front moves forward towards higher temperature region with the increase in sample heating rate. At the sample heating rate of 10℃ min^{-1}, the system shows maximum heat release of 623 J g^{-1} attributed to the attainment of system's equilibrium. The observed heat releases at each sample heating rates (5, 10, 15, 20, and 50℃ min^{-1}) are in tune with the reported literature values.

Graphical Abstract



TG-Curves of pure ammonium per chlorate at different heating rates.

Keywords: Ammonium perchlorate, Thermal decomposition, Enthalpy, Heating rate.

INTRODUCTION

Ammonium per chlorate is a inorganic crystalline oxidizer extensively used in composite solid rocket propellants for space applications all over the world. It is a well established fact that, its thermal decomposition characteristics play a vital role on the combustion rates of composite solid rocket propellants based on this oxidizer [1, 2]. In spite of great amount of research on various aspects of thermal decomposition of AP, key aspects of the mechanism of the process remain controversial [3]. Many of the experimental and theoretical studies reviewed by Boldyrev [4] favour the proton – transfer hypothesis. Recent *ab initio* MD simulation indicated no proto-transfer in the ideal crystal structure [5, 6]. Since the first review on ammonium per chlorate by Hall and Pearson in 1967 [7], extensive studies both experimental and computational have been made. Yet, the exact decomposition mechanism and distinction between primary and higher order products have remained elusive [8].Therefore, the present study is an effort to understand in this direction.

MATERIALS AND METHODS

Ammonium per chlorate (AP) employed in this study was procured from Vikram Sarabhai Space Centre, Indian Space Research Organization, Department of Space, and Government of India. Thermo gravimetric (TG) and derivative thermo gravimetric (DTG) experiments on pure AP were conducted employing DuPont -990 TA System, at sample heating rate of 10°C min^{-1}, in an inert atmosphere of pure nitrogen, at a gas flow rate of 50 mL min^{-1}.

Detailed studies were carried out employing TA Instruments SDT Q600 Model (TGA); and DSC experiments were carried out on TA instruments - SDT DSC 250 Model. The sample heating rates maintained in this study are: 5, 10, 15, 20 and 50°C min^{-1}, respectively.

RESULTS AND DISCUSSION

Thermo gravimetric (TG) and derivative thermo gravimetric (DTG) curve for pure AP at a sample heating rate of 10°C min^{-1}, in an inert atmosphere of pure nitrogen are presented in figure 1. From figure 1 it is clear that, AP undergoes low-temperature decomposition (LTD) with maximum decomposition rate peak appearing at 288°C; and high-temperature decomposition (HTD) with its maximum rate of decomposition occurring at 430°C.

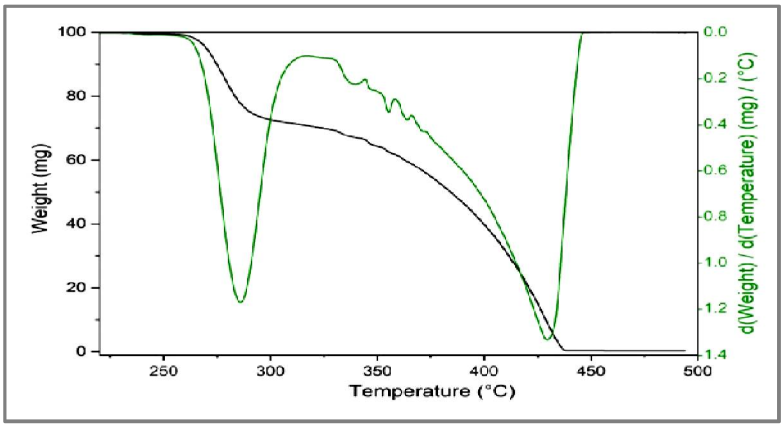
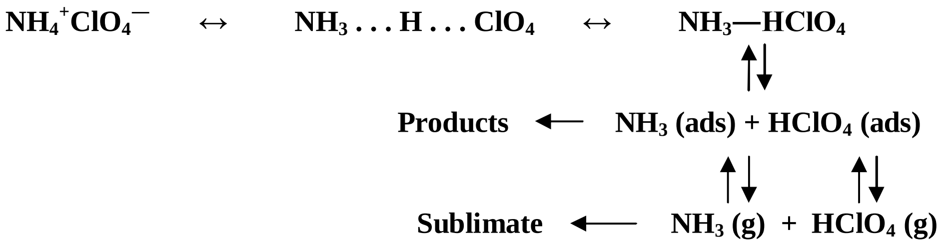


Figure 1. TG – DTG Curves of pure NH_4ClO_4 in pure N_2 atmosphere.

During the LTD temperature regime only 28.2 percent of the material decomposes and the decomposition ceases for a while. In the HTD temperature regime, the remaining AP decomposes. The cessation of decomposition after an initial mass loss of 28.2 percent is in agreement with the literature [2, 9 - 11]. This is because, in the low-temperature regime, the decomposition nuclei begin at isolated sites on the surface of the crystal and growth of three-dimensional nuclei leading to the reaction interface. When the reaction interface proceeds into the interior of the crystal lattice, the cessation of decomposition occurs. Jacobs et al [12] assumed that in the thermal decomposition of AP all the three processes take place by proton-transfer mechanism, according to the following reaction scheme:



$$\begin{tikzcd}
NH_4^+ClO_4^- \arrow[r, leftrightarrow] & NH_3 \ldots H \ldots ClO_4 \arrow[r, leftrightarrow] & NH_3\text{—}HClO_4 \arrow[d, shift left] \\
 & \text{Products} & NH_3\ (ads) + HClO_4\ (ads) \arrow[l] \arrow[u, shift left] \arrow[d, shift left] \\
 & \text{Sublimate} & NH_3\ (g) + HClO_4\ (g) \arrow[l] \arrow[u, shift left]
\end{tikzcd}$$

It is assumed that the adsorbed $HClO_4$ is more rapidly desorbed than the NH_3. In other words, the oxidation of adsorbed ammonia is incomplete, and therefore as the reaction progresses the surface becomes saturated with ammonia, leading to the suppression of the decomposition. This explains the cessation of AP decomposition after an initial conversion of ~ 30 percent.

Thermo gravimetric (TG) curves of pure AP at heating rates of 5°, 10 °, 15°, 20°, and 50°C min^{-1}, using TA Instruments SDT Q600 Model are presented in figure 2. As expected, the reaction front moves forward towards higher temperature region. This is attributed to the fact that, the individual reactions didn't have sufficient time to progress to completion, before which the rapidly rising temperature has already reached the initiation temperature of the subsequent higher temperature reaction.

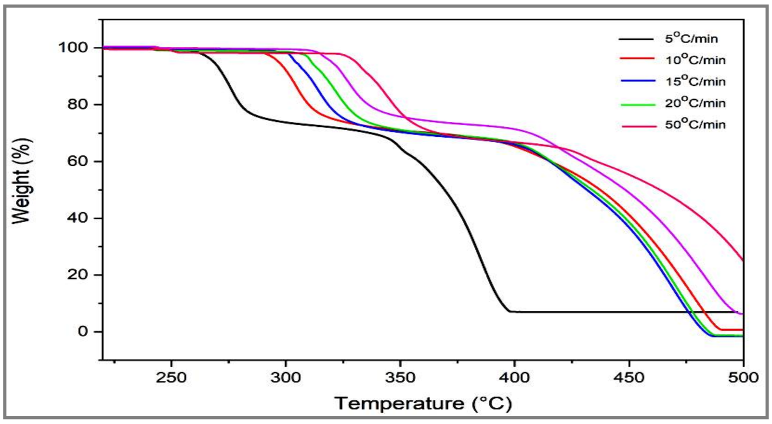


Figure 2. TG – Curves of pure ammonium per chlorate at different heating rates.

From the data in figure 2, it can be observed that, AP decomposes in two distinct stages identified as low-temperature decomposition (LTD) and high-temperature decomposition (HTD). The onset and end set of decomposition temperatures for both LTD and HTD are shown in table 1.

Table 1. Onset and End set Temperatures of LTD and HTD of pure AP

Sample Heading Rate (β)	**Low-temperature Decomposition (LTD) (°C)**		**High –temperature Decomposition (HTD) (°C)**	
	Onset	**End-set**	**Onset**	**End-set**
5	266.7	283.2	349.8	395.5
10	281.4	299.2	367.8	395.5
15	287.4	305.3	372.8	436.0
20	293.7	312.9	370.2	437.5
50	309.0	333.8	385.5	474.0

In the case of HTD, the influence of sample heating rates of 15 and 20°C min^{-1} on both the onset and end set temperatures of decomposition is of the same order of magnitude. At other heating rates, the temperature is shifted towards high-temperature region.

The differential scanning calorimetric (DSC) curves for pure AP at sample heating rates of 5°C min^{-1}, 10°C min^{-1}, 15°C min^{-1}, 20°C min^{-1}, and 50°C min^{-1}, in an inert atmosphere of pure nitrogen, at a gas flow rate of 50 mL min^{-1} are presented in figure 3. The endothermic peak temperature corresponding to crystallographic phase-transition from orthorhombic to cubic, and exothermic decomposition peaks corresponding to LTD and HTD of AP at different sample heating rates are summarized in table 2. From the total heat release data (Table 2) it can be inferred that, at the sample heating rate of 10°C min^{-1} maximum enthalpy output is obtained.

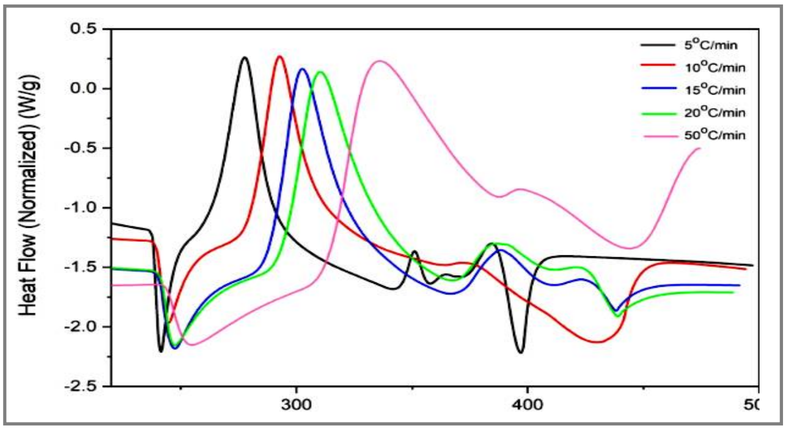


Figure 4. DSC-Curves of pure AP at different heating rates.

Table 2. DSC data for pure AP at different sample heating rates

Heating Rate (β) (°C.min^{-1})	Endothermic Peak		Exothermic Peak-1		Exothermic Peak-2		Total Heat Release (J/g)
	Temp.	Heat Absorbed (J/g)	Temp.	Heat Released (J/g)	Temp.	Heat Released (J/g)	
5	241.4	78.6	277.7	305.5	385.5	250.0	555.5
10	244.7	91.0	292.7	339.0	452.5	284.0	623.0
15	247.2	84.4	302.6	342.2	388.4	115.6	457.8
20	247.9	72.0	310.3	347.2	391.4	127.3	474.5
50	254.0	53.0	334.6	216.6	473.0	93.0	309.6

Thus, from the above data it can be inferred that, the significant role played by the sample heating rate towards realising the maximum enthalpy output, and this is highly dependent on the nature of the material under consideration. In the case of ammonium per chlorate, competitive reactions play very important role, as both sublimation and decomposition processes are parallel. The observed total exothermic heat release values of AP (Table-2) are justified in terms of the reported literature values of Wang *et al* [13] reported a heat release value of 450.3 J g^{-1}; Hu *et al* [14] 378 J g^{-1}; Wang *et al* [15] 576 J g^{-1}; Farhadi *et al* [16] 409 J g^{-1}; Hu *et al* [17] 768 J g^{-1}; Li et al [18] 584 J g^{-1}; Shalini *et al* [19] 834 J g^{-1}.

APPLICATION

The results are important with respect to assessing the performance of composite solid rocket propellants.

CONCLUSION

- Selecting an appropriate sample heating rate for experimentation strongly depends on the nature of the sample under consideration.
- For a given material, there is a specific sample heating rate at which optimum energy release is realized.
- In the case of ammonium per chlorate, the optimum sample heating rate is 10°C min^{-1} is the ideal one.

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REFERENCES

[1]. L. J. Chen, G. S. Li, P. Qi, L. P. Li, Thermal decomposition of Ammonium Per chlorate Activated via Addition of NiO Nano-crystals, *Therm. Anal. Calorim.*, **2008**, 92, 765-769.
[2]. W. M. Abdel-Wareth, X. U. Xu, Ammonium per chlorate decomposition characteristic parameters determination - a simplified approach, *Applied Mechanics and Materials*, **2012**, 110-116, 155-162.
[3]. D. Majda, A. Korobov, U. Filek, B. Sulikowski, P. Midgley, D. Vowles, J. Klinowski, Low-temperature thermal decomposition of large single crystals of ammonium per chlorate, *Chemical Physics Letters*, **2008**, 454**,** 233**-**236.
[4]. V. V. Boldyrev, Thermal decomposition of ammonium per chlorate, *Thermochimica Acta*, **2006**, 443, 1**-**36.
[5]. L. Rosso, M. E. Tuckerman, Direct evidence of an anomalous charge transport mechanism in ammonium per chlorate crystal in an ammonia-rich atmosphere from first-principles molecular dynamics, *Solid State Ionics*, **2003**, 161**,** 219 229.
[6]. L. Rosso, M. E. Tuckerman, Solid-state proton conduction: An ab-initio molecular dynamics investigation of ammonium per chlorate doped with neutral ammonia, *Pure Appl. Chem*., **2004**, 76, 49-61.
[7]. A. R. Hall, G. S. Pearson, Ammonium per chlorate: A review of its role in composite propellant combustion, Technical Report 67/1, UDC No. 546.391.37:662.34:536.46, Rocket Propellant Establishment, Westcott, **1967**.
[8]. S**.** Góbi, L**.** Zhao, B. Xu, U**.** Ablikim, M**.** Ahmed, R. I. Kaiser, A vacuum ultraviolet photo ionization study on **t**he thermal decomposition of ammonium per chlorate, *Chemical Physics Letters*, **2018**, 691, 250**–**257.
[9]. F. Solymosi, Structure and Stability of Salts of Halogen Oxy acids in the Solid Phase. Chapter-4: Structure and Thermal Stability of Ammonium per chlorate; p.250, John Wiley and Sons, New York, **1977**.
[10]. W. A. Rosser, S. H. Inami, H. Wise, Thermal Decomposition of Ammonium per chlorate, *Combust. and Flame*, **1968**, 12, 427-435.
[11]. J. N. Maycock, V. R. Pai Verneker, Role of Point Defects in the Thermal Decomposition of Ammonium Per chlorate, *Proc. Roy. Soc*., **1968**, A307, 303-315
[12]. J. V. Davies, P. W. M. Jacobs, A. Russel-Jones, Thermal Decomposition of Ammonium Per chlorate**,** *Trans. Faraday Soc*., **1967**, 63, 1737**-**1748.
[13]. D. Wang, Y. Jiang, Y. Hu, D. Hao, Y. Yang, R. Fan, D. Xia, K. Lin, Porous Cr_2O_3 bead with a3D continuous pore architecture: Synthesis and its catalytic performance for decomposition of ammonium per chlorate, *New J. Chem.*, **2019**, 43, 10560-10566.

[14]. Y. Hu, Y. Yang, R. Fan, K. Lin, D. Hao, D. Xia, P. Wang, Enhanced thermal decomposition properties and catalytic mechanism of ammonium per chlorate over CuO/MoS_2 composite, *Applied Organometallic Chemistry*, **2019**, 33 (9), e5060

[15]. S. Wang, B. Ye, C. An, J. Wang, Q. Li, Synergistic effects between Cu metal-organic framework (Cu-MOF) and carbon nanomaterials for the catalyzation of the thermal decomposition of ammonium per chlorate (AP), *J. Materials Sci*., **2019**, 54(4), 4928-4941.

[16]. F Farhadi, A. Eslami, M. Kubicki, Direct synthesis of Zn (II) and Cu (II) coordination polymers based on 4, 4' – bipyridine and 1, 10 – phenanthroline and evaluating their effects as catalysts on ammonium per chlorate thermal decomposition, *J. Thermal Anal Calorim.*, **2019**, DOI: 10.1007/s10973-019-08936-9.

[17]. Y. Hu, B. Tao, F. Shang, M. Zhou, D. Hao, R. Fan, D. Xia, Y. Yang, A. Pang, K. Lin, Thermal decomposition of ammonium per chlorate over proviskite catalysts: Catalytic decomposition behaviour , mechanism, and application, *Applied Surface Science*, **2020**, 513, 145849.

[18]. H. Li, K. Zhao, S. Tian, D. Zeng, A. Pang, X. Wang, C. Xie, Origin of the efficient catalytic thermal decomposition of ammonium per chlorate over (2-1-10) facts of ZnO nanosheets: surface lattice oxygen, RSC Adv., **2017**, 7, 40262-40269.

[19]. C. Shalini, N. D. Pragnesh, Nano-metal Oxide: Potential catalyst on thermal decomposition of ammonium per chlorate, J. Experimental Nanoscience, **2012**, 7(2), 205-231.