

Thermal analysis of hydroxylammonium nitrate based monopropellant: effect of heating rate and reaction temperature

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Abstract

For the first time, hydroxylammonium nitrate (HAN)-based monopropellant has been thermally and catalytically decomposed at high heating rate of about $128\text{ }^{\circ}\text{C min}^{-1}$. The obtained results have been compared with lower heating of $8\text{ }^{\circ}\text{C min}^{-1}$. DIP-MS technique showed that the intensity of ejected gas are higher in the case of high heating rate and the catalyst enhances them at low heating rate. Otherwise, it can be seen that pyrolyzer showed two decomposition steps for SHP163 decomposition at low temperature of $280\text{ }^{\circ}\text{C}$ and only one step at high temperature of about $1040\text{ }^{\circ}\text{C}$. The major gas detected are relatively similar using both techniques.

Keywords: high heating rate, pyrolyzer, monopropellant, electronic ionization

1. Introduction

Solid and liquid green propellants have been deeply investigated in the recent years^{1)–9)}. A recent study by JAXA has identified two essential design elements to achieving low cost space access; (i) reduced production, operational, and transport costs due to lower propellant toxicity and explosion hazards, and (ii) reduced costs due to an overall reduction in subsystems complexity and overall systems interface complexity¹⁰⁾. Hydroxylammonium nitrate (HAN) has been selected as alternative for 1 N thruster demonstration under “*Innovative Satellite Technology*” project launched by JAXA. The HAN-based liquid monopropellant was prepared by Hosoya Company (Tokyo, Japan) with some additives such as methanol (CH_3OH) which is selected as a fuel because considered as most effective stabilizer among alcoholic fuels to reduce gas phase instability. On the other hand, ammonium nitrate (NH_4NO_3) is added to minimize the water content to avoid high burning rate

characteristics often observed during HAN-based combustion, and to lower the freezing point of the propellant in order to eliminate heaters from the propellant tanks of satellites. The ionic liquid solution selected has been nominated SHP163 and contains HAN 76.3%; H_2O 6.2%; NH_4NO_3 3.9% and CH_3OH 16.3% as molar composition⁷⁾.

In this early letter, thermal decomposition of SHP163 monopropellant solution using electronic ionization and pyrolyzer has been performed for the first time at high heating rate and violent temperature rising; respectively. These initial conditions set-up influenced on the decomposition behavior of SHP163 and the nature of ejected species investigated via MS-real time analysis.

2. Experimental

The direct insertion probe-mass spectrometry (DIP-MS) L-250G-IA (Canon Anelva Co., Ltd) has been applied for the thermal analysis of HAN-based samples. The

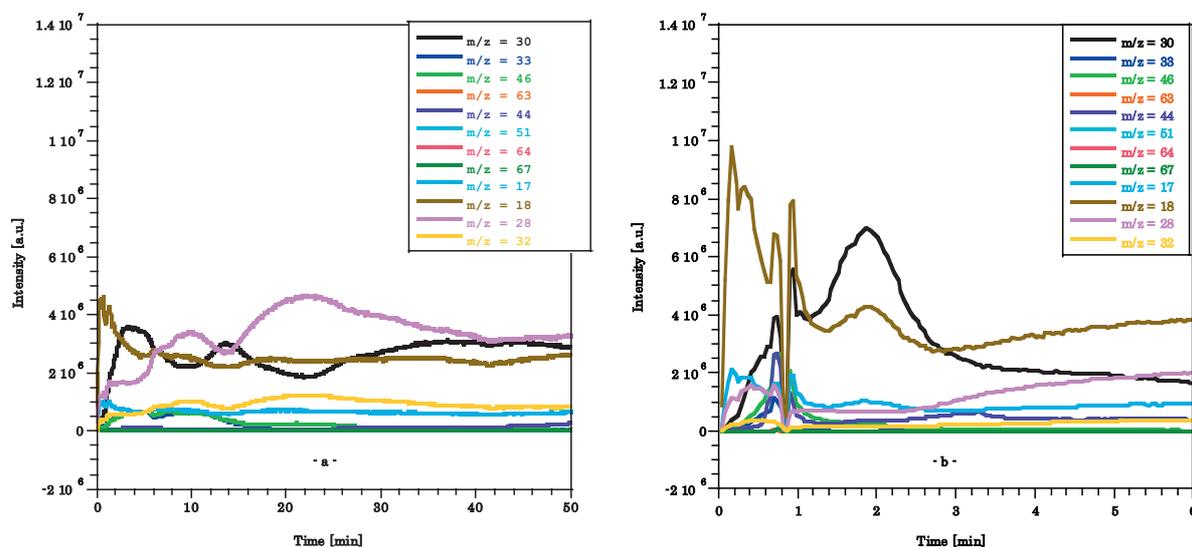


Figure 1 Thermal decomposition of SHP163 monopropellant: (a) low heating rate $8\text{ }^{\circ}\text{C min}^{-1}$ and (b) high heating rate $128\text{ }^{\circ}\text{C min}^{-1}$ using DIP-MS technique.

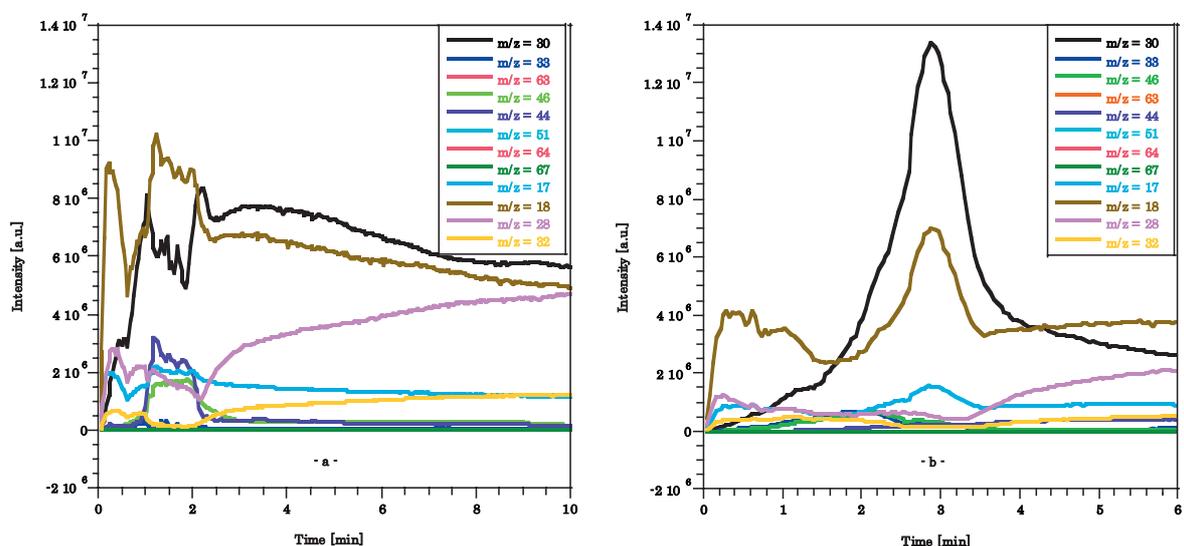


Figure 2 Catalytic decomposition of SHP163 monopropellant in the presence of 20% Ir/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ powder catalyst: (a) low heating rate $8\text{ }^{\circ}\text{C min}^{-1}$ and (b) high heating rate $128\text{ }^{\circ}\text{C min}^{-1}$ using DIP-MS technique.

technique is based on the introduction of the samples into the ionization chamber, followed by their vaporization and eventual ionization by electronic impact. Because it is often mentioned as a fast alternative for polar or thermally labile samples that do not require gas chromatographic separation. Therefore, DIP-MS is considered as a fast tool to identify the real time-gas products of SHP163 thermal decomposition. Two extreme heating rates; that can be reached by heating up of samples by IR lamp; are discussed in this work: 128 and $8\text{ }^{\circ}\text{C min}^{-1}$ in order to check the effect of heating rates on the thermal decomposition. The real-time analysis was performed in the range $40\text{--}450\text{ }^{\circ}\text{C}$ with 3 min hold.

Other experiments have been carried out using pyrolyzer JCI-22 developed by Japan Analytical Industry Co. Ltd. (JAI) using pyro foils of two extreme temperatures: 280 and $1040\text{ }^{\circ}\text{C}$ respectively. The pyro foils are used to quickly achieve the designed temperatures in about 0.2 s . Each temperature was kept for 5 s .

3. Results and discussion

The DIP-MS analysis of thermal decomposition of SHP 163 solution has been performed and the corresponding data have been illustrated in Figure 1.

The Figure 1a showed the real time decomposition species of SHP163 decomposition in the absence of catalyst. For both heating rates, the species detected are mostly H_2O steam, NO , N_2 , NH_3 , O_2 , N_2O and NO_2 fragments as previously reported and corresponded to mass fragments of $m/z = 18$; 30 ; 28 ; 17 ; 32 ; 44 and 46 ; respectively^(10,11). The intensities of ejected gas are higher in the case of high heating rates but the nature of ejected gas is similar.

The decomposition of SHP163 over $20\%\text{Ir}/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst has been reported in Figure 2.

The catalytic decomposition of SHP163 at low heating rate (Figure 2a) initiated by evaporation of solvents (H_2O and CH_3OH). Several fluctuations have been observed; indicating that the evaporation and decomposition of the monopropellant solution has been heterogeneously

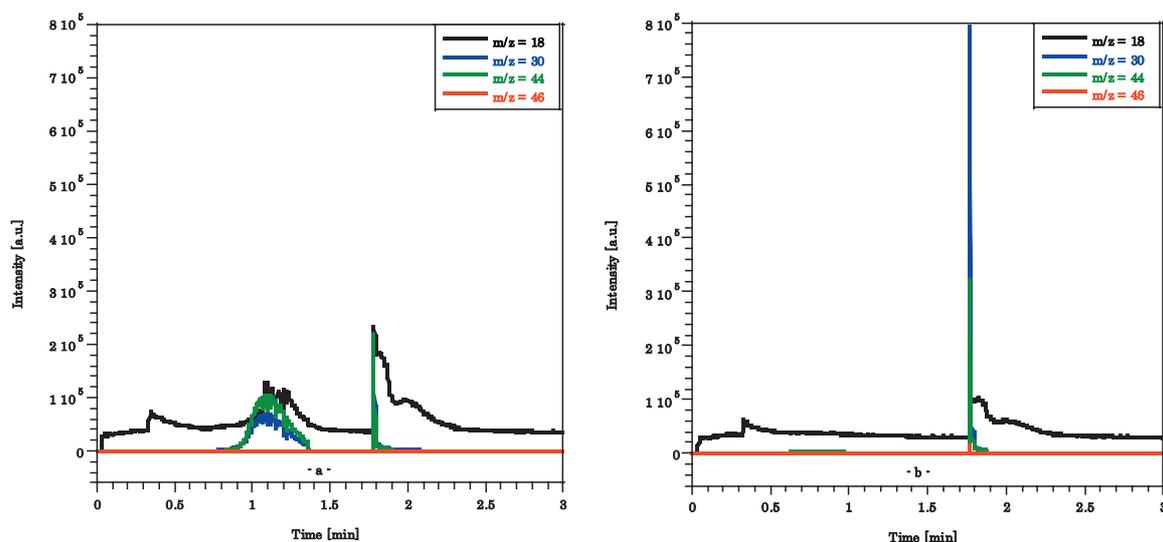


Figure 3 Thermal decomposition of SHP163 monopropellant: (a) at low temperature 280 °C and (b) at high temperature 1040 °C using pyrolyzer.

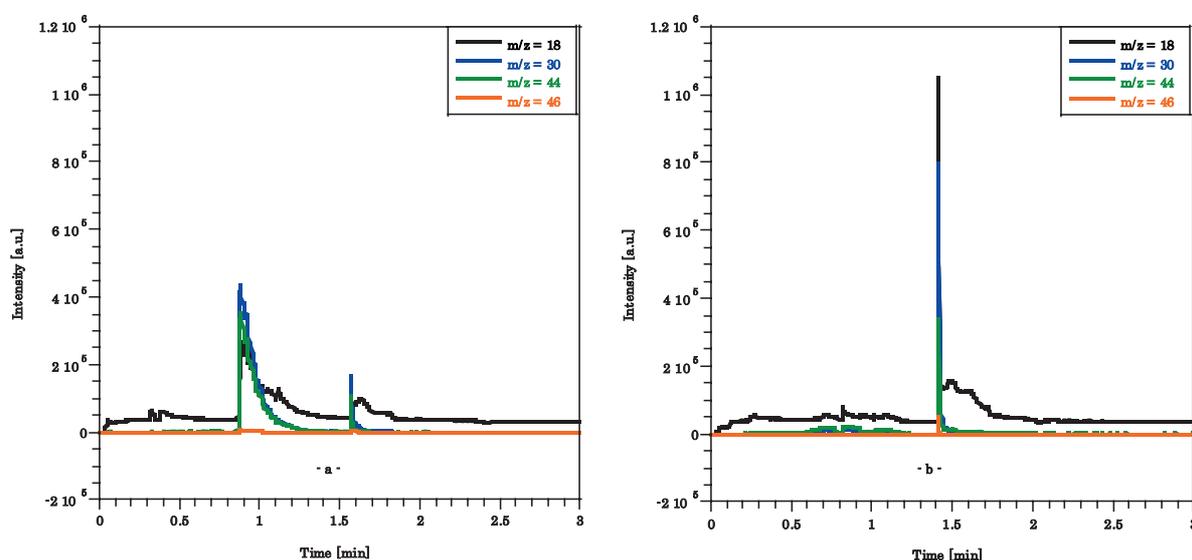


Figure 4 Catalytic decomposition of SHP163 monopropellant in the presence of 20% Ir/SiO₂-Al₂O₃ powder catalyst: (a) at low temperature 280 °C and (b) at high temperature 1040 °C using pyrolyzer.

performed from the catalytic pores. In fact, before manipulation, the solution was injected into the Al-cell contains catalyst and was totally absorbed by the catalytic powder.

It should be noted that the oxygen detected at low heating rates with and without catalyst which may due to the slow burning of methanol and/or thermodynamic decomposition of HAN-based as shown by the following equation⁴⁾:



Other experiments have been carried out using pyrolyzer equipped by pyro foils. The SHP163 decomposition are reported in Figures 3 and 4.

The major gas detected are H₂O steam, NO, N₂O and NO₂ and then the decomposition in four cases began by evaporation of solvents and the pure HAN/AN solutions have been decomposed.

The Figures 3a and 4a demonstrate the obtained data at low temperature of about 280 °C. The thermal tests were

performed without and with catalyst; respectively showed that the decomposition were happen in two steps; in accordance with previously published work at low heating rates of about 1–5 °C min⁻¹ ^{10,11)}. Furthermore, the decomposition of SHP163 at high temperature of about 1040 °C has been performed in one step with high gas intensities. The catalyst plays an import role in order to accelerate the reaction at both temperatures.

4. Conclusion

The thermal and catalytic decomposition of SHP163 monopropellant solution have been performed for the first time at high heating rate and high temperature of reaction according to qualitative control using DIP-MS and pyrolyzer methods.

In the case of DIP-MS, the low heating rate has favorized the appearance of O₂ fragmentation due to slow evaporation of methanol and/or decomposition of HAN/AN solution. However, the high heating rate enhanced the

gas intensities. Moreover, the SHP163 decomposition using pyrolyzer equipped with pyro foils took place in two steps at low initial temperature of reaction (280 °C). On the other hand, the decomposition has been performed in one step at 1040 °C and the catalyst influenced on the reaction velocity. The major gas detected in both cases are water steam, NH₃, N₂, NO, O₂, N₂O and NO₂.

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References

- 1) R. Amrousse, T. Katsumi, N. Itouyama, N. Azuma, H. Kagawa, K. Hatai, H. Ikeda, and K. Hori, *Combust. Flame*, 162, 2686–2692 (2015).
- 2) R. Amrousse, T. Katsumi, and K. Hori, *React. Kinet. Mech. Catal.*, 111, 71–88 (2014).
- 3) R. Amrousse, K. Fujisato, H. Habu, A. Bachar, C. Follet, and K. Hori, *Catal. Sci. Technol.*, 3, 2614–2619 (2013).
- 4) R. Amrousse, K. Hori, W. Fetimi, K. Farhat, *Appl. Catal. B*, 127, 121–128 (2012).
- 5) R. Amrousse, T. Katsumi, T. Sulaiman, B.K. Das, H. Kumagai, K. Maeda, and K. Hori, *Int. J. Energetic Mater. Chem. Propuls.*, 11, 241–257 (2012).
- 6) R. Amrousse, K. Hori, K. Fujisato, H. Habu, S. Laassiri, and S. Royer, *Int. J. Energetic Mater. Chem. Propuls.*, 10, 249–261 (2011).
- 7) T. Katsumi, H. Kodama, H. Ozawa, N. Tsuboi, and K. Hori, *Sci. Tech. Energetic Materials*, 70, 27–32 (2009).
- 8) H. Matsunaga, S. Yoshino, M. Kumasaki, H. Habu, and A. Miyake, *Sci. Tech. Energetic Materials*, 72, 131–135 (2011).
- 9) D.M. Badgujar, N.R. Bulakh, R.M. Wagh, and M.B. Talawar, *Sci. Tech. Energetic Materials*, 77, 59–64 (2016).
- 10) R. Amrousse, T. Katsumi, N. Azuma, K. Hatai, H. Ikeda, and K. Hori, *Sci. Tech. Energetic Materials*, 77, 105–110 (2016).
- 11) R. Amrousse, T. Katsumi, N. Azuma, and K. Hori, *Combust. Flame*, 176, 334–348 (2017).