

Effect of additional copper(II) oxide on the combustion of 5-amino-1H-tetrazole and lithium perchlorate mixtures (II) — Thermal analyses of 5-amino-1H-tetrazole, lithium perchlorate, and copper(II) oxide —

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Abstract

The authors have previously reported that 5-amino-1H-tetrazole (5-ATZ) / lithium perchlorate LiClO_4 mixture has displayed high linear burning rates and generated large amount of gas per unit mass. It has also been clarified that adding small amount of copper(II) oxide CuO to the mixture has enhanced the linear burning rates even though the adiabatic flame temperatures have decreased. In this study, factors leading to the enhancement of linear burning rates were examined through thermal analyses of the mixtures. According to the thermal analyses, decomposition of 5-ATZ was found to initiate prior to the decomposition of LiClO_4 , and the addition of CuO has caused a drastic decrease in the initiation temperature for exothermic reaction of 5-ATZ / LiClO_4 mixture. Therefore, through addition of a small portion of CuO , exothermic reactions between 5-ATZ and CuO may have initiated at a relatively low temperature, and then from this exothermic reaction, the reactions of 5-ATZ / LiClO_4 mixtures may have initiated at a lower temperature, leading to an increase in the linear burning rate. Furthermore, an increase in the heat of exothermic decomposition through CuO addition may have contributed to an increase in the linear burning rate.

Keywords: 5-Amino-1H-tetrazole, Lithium perchlorate, Copper(II) oxide, TG-DTA analyses, Mass spectrometry.

1. Introduction

Performances of gas generating mixtures are determined generally by the combination of a fuel and an oxidizer. The authors¹⁻⁴⁾ have been studying on 5-amino-1H-tetrazole (5-ATZ), a tetrazole compound which has attracted attention in recent years as a substitute fuel component to conventionally used sodium azide and which has been utilized as part of gas generating mixtures for airbag inflators, and mixing with various oxidizers; the authors have been investigating on combustion characteristics of the mixtures that generates large amount of gas within a relatively short period of time, as compared to those that have already been put into practical use. In the previous study⁵⁾, the authors have selected as an oxidizer, lithium perchlorate LiClO_4 which has high oxygen content per unit mass and which generates more oxygen per unit volume as compared to liquid oxygen, and the authors have reported on the combustion behavior of 5-ATZ / LiClO_4 mixture. It

has been found that the mixture has displayed a higher linear burning rate as compared to 5-ATZ / strontium nitrate mixture, and it has displayed the highest pressure gradient during the closed vessel test, suggesting its superior performance as a gas generating mixture. Furthermore, the authors have reported that addition of CuO to the mixture has enhanced the burning rate and the rate of gas generation. In this paper, the authors have clarified, through thermal analyses, the reason for the increase in linear burning rate with the addition of CuO .

2. Experimental

2.1 Materials

As a fuel component of the non-azide gas generating mixtures, non-toxic 5-ATZ (Fujimoto Chemicals Co., Ltd., free sample) was used. This compound has drawn attention as a substitute to toxic sodium azide, and it has been used as gas generating mixtures for part of the air-

Table 1 Compositions of 5-ATZ / oxidizer mixtures.

Designation	Component	(wt%)
MixA	5-ATZ / LiClO ₄	47.7 / 52.3
MixB	5-ATZ / LiClO ₄ / CuO	46.4 / 49.3 / 4.3
MixD	5-ATZ / CuO	23.4 / 76.6

Table 2 Reaction products of 5-ATZ / LiClO₄ mixture.

Reaction products*	mol % at 298 K	mol % at 3101 K
H	—	1.02
CO ₂	17.01	8.29
H ₂ O	25.37	17.16
N ₂	42.55	38.77
CO	—	7.51
H ₂	—	2.08
OH	—	3.08
NO	—	1.47
O ₂	—	2.96
HCl	—	2.12
LiCl	14.73	10.86
LiOH	—	2.60

*Concentrations of more than 1 mol %.

bags. LiClO₄ (Kanto Chemical Co., Inc., Kanto extra pure reagent >97 %) and CuO (Kanto Chemical Co., Inc., JIS special grade reagent >98 %) were used as oxidizers.

5-ATZ and oxidizers were crushed in separate ball mills for approx. one hour, and the particle diameter was controlled within 75 - 149 μm by using standard sieves. The samples were then dried through a vacuum dryer (Kuramotikagaku Co., Ltd., RG-501) at chamber temperature of 328 K and at pressure of 10 Pa for four hours, and they were mixed at stoichiometric ratio at 80 r.p.m. through a rotary mixer (Tsutsui Scientific Instruments Co., Ltd., S-3). Mixing ratio for each sample mixed at stoichiometric ratio is given in Table 1.

2.2 Measurement of thermal decomposition process

Measurement of thermal decomposition process was conducted by using TG-DTA (Shimadzu Corp., DTG-50 H), at heating rate of 20 K min⁻¹ and helium flow rate of 20 ml min⁻¹. In addition, mass spectrometry (MS) was conducted by using a mass spectrometer (Shimadzu Corp., QP-5000) connected to TG-DTA, in order to qualitatively analyze gas products of thermal decomposition.

3. Results and discussion

3.1 Decomposition products

Table 2 gives the calculated values of concentrations of the main products (concentrations of more than 1 mol%), derived from the chemical equilibrium calculation⁶⁾, for the reaction of MixA. The main products at room temperature were: CO₂ and N₂ in gaseous state, H₂O in liquid state, and LiCl in solid state.

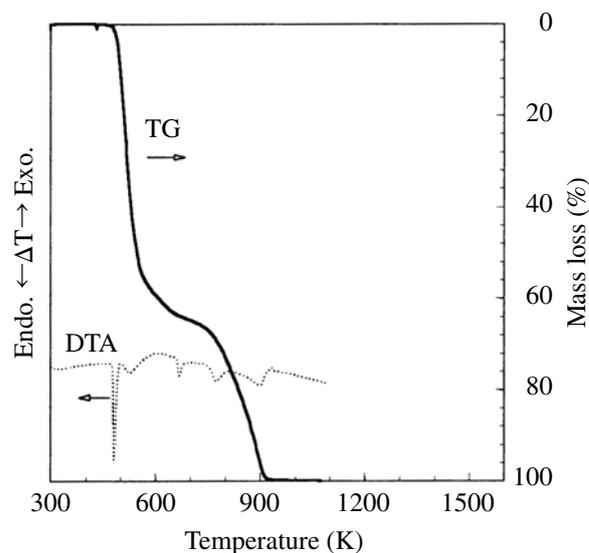


Fig. 1 Thermal decomposition process of 5-ATZ measured by TG and DTA at a heating rate of 20 K min⁻¹ in helium atmosphere.

3.2 Thermal analyses

TG-DTA curves for 5-ATZ are shown in Fig. 1. As reported previously³⁾, the decomposition of 5-ATZ was found to be divided into approx. two stages, with the temperature of decomposition starting at approx. 500 K, and terminating at approx. 900 K. In the past study regarding 5-ATZ decomposition, melting point was reported to be 458 K and the decomposition temperature was reported to be 502 K⁷⁾. These temperatures agree well with the initiation temperatures for the endothermic peak of DTA curve and the mass loss in TG curve as shown in Fig. 1. According to the MS analyses, a value of mass (m) divided by charge (z) (m/z) 28, which was estimated to be N₂, was observed at the first stage of the decomposition process. Wu *et al.*⁸⁾ have reported that the decomposition products of 5-ATZ were: N₂ and NH₃ at 631 K and HN₃, N₂, NH₃, and HCN at 707 K. There have also been reports regarding decomposition initiation accompanying generations of HN₃ and NH₂CN at 478 K⁹⁾.

TG-DTA curves for LiClO₄ are given in Fig. 2. It was found that the decomposition process of LiClO₄ was divided into approx. two stages. Mass loss and endothermic peaks near 400 K probably originated from the dissociation of water of crystallization from LiClO₄ · 3H₂O. Small amount of LiClO₄ · 3H₂O may have been formed during storage due to the hygroscopicity of LiClO₄. An endothermic peak of the DTA curve which has started from approx. 510 K and which has shown maximum value of 524 K was probably related to the melting of LiClO₄ (melting point: 509 K¹⁰⁾). The decomposition of LiClO₄ has started at 779 K and the peak temperature was 796 K, as compared to the past experimental results at 703 K¹⁰⁾. It was also found that the decomposition of LiClO₄ was an exothermic reaction. Decomposition reaction of LiClO₄ being exothermic was probably the main reason for high linear burning rates of the mixture with 5-ATZ. Percentage of mass loss at the first stage of the TG curve was approx. 60 % which agreed

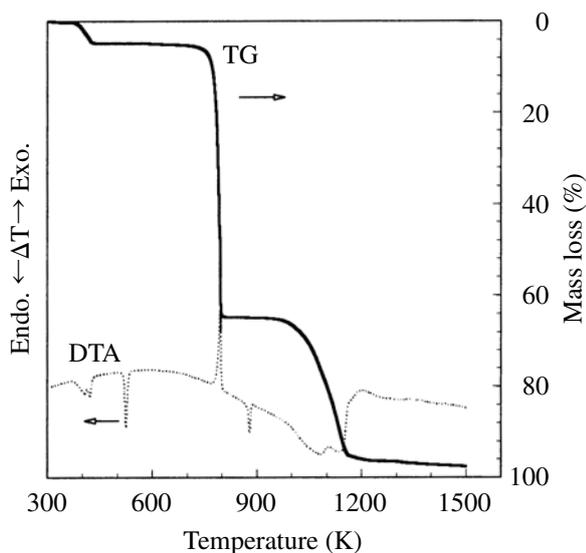


Fig. 2 Thermal decomposition process of LiClO_4 measured by TG and DTA at a heating rate of 20 K min^{-1} in helium atmosphere.

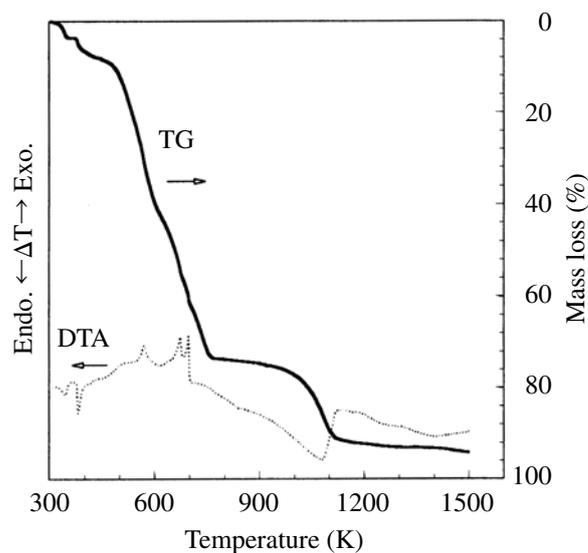


Fig. 3 Thermal decomposition process of 5-ATZ / LiClO_4 mixture measured by TG and DTA at a heating rate of 20 K min^{-1} in helium atmosphere.

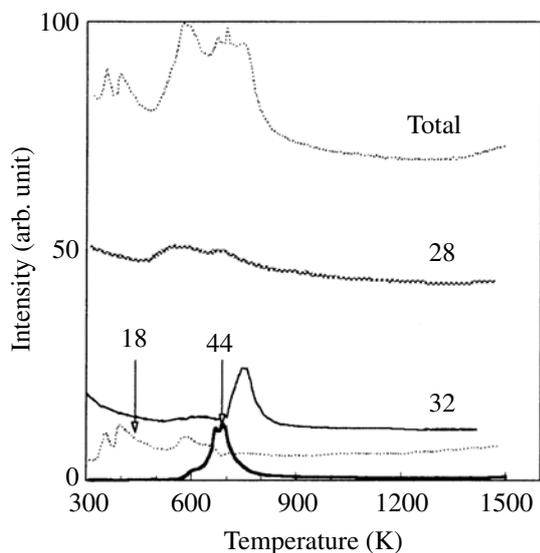


Fig. 4 Mass fragmentograms of 5-ATZ / LiClO_4 mixture at a heating rate of 20 K min^{-1} in helium atmosphere.

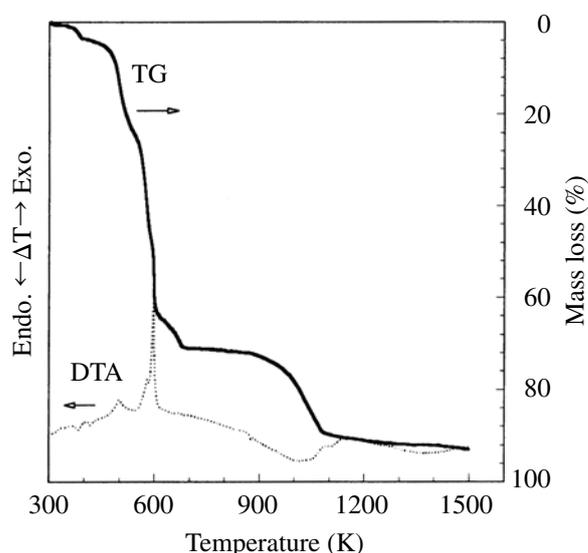
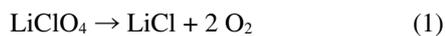


Fig. 5 Thermal decomposition process of 5-ATZ / LiClO_4 / CuO mixture measured by TG and DTA at a heating rate of 20 K min^{-1} in helium atmosphere.

with the theoretical value of 60.2 %. Therefore, the decomposition reaction of LiClO_4 was suggested to be



in which oxygen atoms detached initially. The reaction scheme was verified from the appearance of an endothermic peak at 870 K which is close to the melting point of LiCl (past experimental value: 883 K^{11}). The mass loss at the second stage was probably due to the evaporation of LiCl .

TG-DTA curves of MixA are given in Fig. 3. Mass loss and endothermic peak within the temperature range up to approx. 400 K were the same as observed in Fig. 2; therefore they were probably due to the dissociation of water of crystallization from $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$. Also, since the TG curve shows the decomposition starting at approx. 500 K

which agrees with that of 5-ATZ, the decomposition of the mixture probably started with the decomposition of 5-ATZ. This was then probably followed by the decomposition of LiClO_4 . Also from the DTA curves, three exothermic peaks were observed at 572 K, 667 K, and 701 K.

The mass fragmentograms are presented as intensity versus temperature for the selected mass fragments in Fig. 4. Peaks of the mass fragmentogram of m/z 44 were observed at 572 K, 667 K, and 701 K and the mass fragmentogram had the same profile as the DTA curve at 667 K and 701 K as shown in Fig. 3. The m/z 44 was estimated to be CO_2 or N_2O , suggesting the combustion of part of the sample. Therefore, exothermic peaks that appeared at Fig. 3 were estimated to originate from a partial reaction between the fuel component 5-ATZ and the oxidizer LiClO_4 . Since N_2O was not estimated to be the

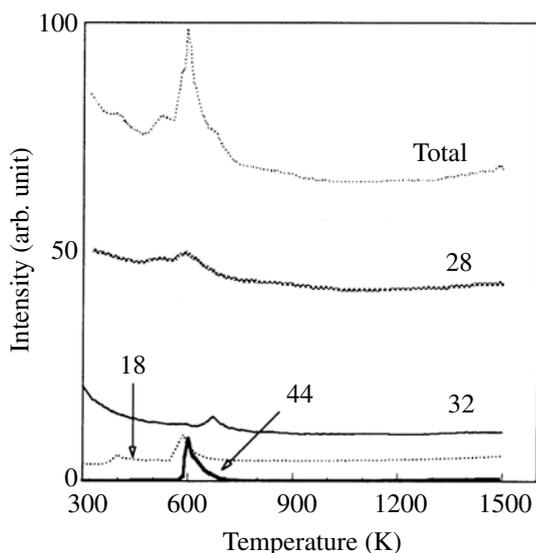


Fig. 6 Mass fragmentograms of 5-ATZ / LiClO₄ / CuO mixture at a heating rate of 20 K min⁻¹ in helium atmosphere.

evolved gas according to the chemical equilibrium calculation as shown in Table 2, CO₂ was concluded to be the evolved gas in this study. As for m/z 32, O₂ or N₂H₄ was estimated to be the evolved gas. However, since N₂H₄ was not estimated to be the evolved gas according to the chemical equilibrium calculation as shown in Table 2, O₂ was concluded to be the evolved gas in this study. Since m/z 44 was observed at 701 K, it was found that m/z 32, observed near 760 K, was detected at a temperature higher than the ignition point. Since the decomposition temperature for LiClO₄ was 779 K as previously mentioned, m/z 32, which was detected after the detection of m/z 44, was estimated to be the remaining O₂ which were not consumed during combustion. The sample have probably become oxygen-rich because of partial decomposition of the fuel component 5-ATZ prior to the combustion as a consequence of relatively slow heating rate during the thermal analysis. Candidate species for m/z 18 were estimated to be H₂O or NH₄, but H₂O was concluded to be the evolved gas according to Table 2.

Figure 5 shows TG-DTA curves of MixB. Mass loss and endothermic curve within the temperature range up to approx. 400 K were probably due to the escape of water of crystallization from LiClO₄ · 3H₂O. In addition, decomposition have initiated at approx. 500 K according to the TG curve, hence, as same as in MixA, the decomposition process of MixB may have initiated following the decomposition of 5-ATZ which decomposes at relatively low temperature. However, when comparisons were made for the TG curves within the temperature range between 500

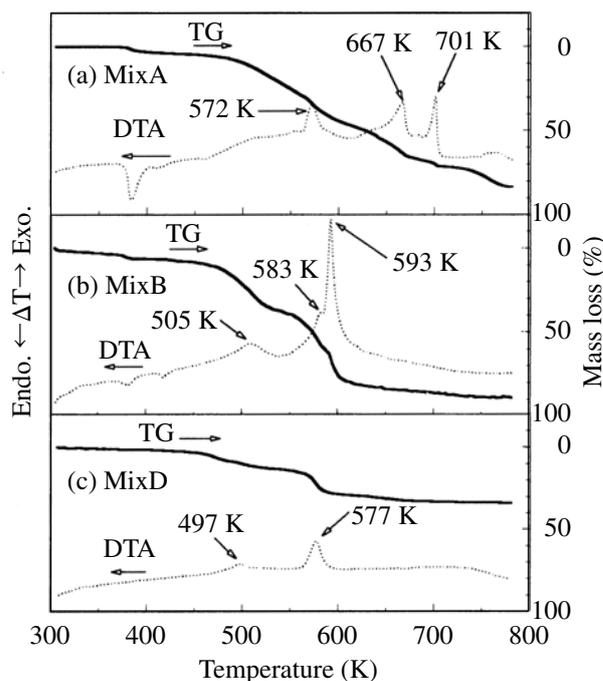


Fig. 7 Thermal decomposition process of 5-ATZ and oxidizer mixtures measured by TG and DTA at a heating rate of 20 K min⁻¹ in helium atmosphere. (a) 5-ATZ / LiClO₄ (mass of sample: 4.53 mg) (b) 5-ATZ / LiClO₄ / CuO (mass of sample: 0.932 mg) (c) 5-ATZ / CuO (mass of sample: 2.63 mg)

- 800 K, the decomposition processes were observed to differ remarkably, and at temperature range beyond 800 K, the decomposition processes were observed to be similar. Therefore, decomposition processes within the temperature range between 500 - 800 K were suggested to be differ considerably depending on whether or not the mixture contained CuO. The shift in reaction mechanism within such temperature range may have been the reason behind the enhancement of r . In addition, according to the DTA curve, three exothermic peaks have appeared within the temperature range between 550 - 700 K.

Figure 6 shows the mass fragmentograms of evolved gases during the appearance of these exothermic peaks. The exothermic peak has appeared at temperatures above 572 K and at this temperature, m/z 44 was found. Since m/z 44 was concluded to be CO₂, part of the sample may have undergone combustion above this temperature.

In order to examine in detail the decomposition process of MixB within the temperature range between 500 - 800 K which was suggested to be the reason behind the enhancement of r , the enlarged TG-DTA curves of the three mixtures, MixA, MixB, and MixD were compared, as given in Fig. 7 (a), (b), and (c), respectively. From the finding that TG curve of Fig. 7(b) was more similar to Fig. 7 (c) rather than Fig. 7 (a), and from the finding that the peak temperatures of the first exothermic peak (505 K) and the second and third exothermic peaks (583 K and 593 K) of the DTA curve of Fig. 7 (b) were close to the peak temperatures of the first exothermic peak (497 K) and the second exothermic peak (577 K) of the DTA curve of Fig. 7

(c), CuO was suggested to be earlier than LiClO₄ in reacting with 5-ATZ during thermal decomposition of MixB as shown in Fig. 7 (b). Therefore, it is suggested that, whereas a relatively long period of time was required for the decomposition of 5-ATZ before the temperature for the initiation of reaction between LiClO₄ and 5-ATZ (572 K in Fig. 7 (a)) in the case of MixA, temperature for the initiation of the reaction between LiClO₄ and 5-ATZ may have been lowered in the case of MixB, leading to an increase in *r*. This is because the reaction between CuO and 5-ATZ initiates at a relatively low temperature (497 K, Fig. 7 (c)).

Measuring the heats of exothermic peaks from DTA curves of Fig. 7 (a) and (b): quantity of heats for Fig. 7 (a) were 87.2 J g⁻¹ at the first peak, 156.3 J g⁻¹ at the second peak, and 72.5 J g⁻¹ at the third peak; and 169.6 J g⁻¹ for the first peak, and a total of 1070 J g⁻¹ for the overlapping second-and-third peaks for Fig. 7 (b). Since the total of the second and the third exothermic peaks for Fig. 7 (b) was greater than the total of the second and the third exothermic peaks for Fig. 7 (a), addition of CuO has been found to increase the quantity of heats. Addition of CuO may have increased the quantity of heats at the burning surface, contributing to an increase in *r*.

4. Conclusions

In order to investigate the reasons behind the enhancement of the burning rate through CuO addition, thermal analyses were conducted regarding 5-ATZ / oxidizers (LiClO₄ and CuO) mixtures. The initial temperature of exothermic reaction for 5-ATZ / CuO mixture was lower than that of 5-ATZ / LiClO₄ mixture. Initial temperature of exothermic reaction for 5-ATZ / LiClO₄ mixture was lowered up to the same temperature as that of exothermic

reaction for 5-ATZ / CuO mixture when CuO was added. Therefore, since exothermic reaction between 5-ATZ and CuO initiates at a relatively low temperature, reaction between 5-ATZ and LiClO₄ may have initiated at a lower temperature when CuO was added, as compared to the reaction without CuO addition, thus leading to an increase in the linear burning rate. In addition, the heat of exothermic reaction has increased with the addition of CuO, probably because exothermic heat at the burning surface has increased, contributing to an increase in the burning rate.

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5-amino-1H-tetrazole と過塩素酸リチウム混合物の 燃焼に対する酸化銅(II)の影響(第2報) —5-amino-1H-tetrazole, 過塩素酸リチウム, 酸化銅(II)の熱分析—

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前報で5-amino-1H-tetrazole (5-ATZ) と過塩素酸リチウム混合物は線燃焼速度が速く, 単位質量当たりのガス発生量が多いことを報告した。この混合物に酸化銅(II)を少量加えると, 断熱火炎温度は, 減少するにもかかわらず線燃焼速度が増加することを報告した。本報では熱分析により, 線燃焼速度が増した原因を検討した。5-ATZは, 過塩素酸リチウムより低温で分解し, 酸化銅(II)を添加すると混合物の発熱反応の開始温度が著しく低下することがわかった。5-ATZと酸化銅(II)の発熱反応が低温で開始するため, 5-ATZと過塩素酸リチウムの反応開始温度は低下し, 線燃焼速度の増加となったものであろう。酸化銅(II)の添加により分解熱量が増加することも線燃焼速度の増加に寄与していると考えられる。

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