Article

Combustion characteristics of the consolidated mixtures of 5-amino-1H-tetrazole and sodium perchlorate

Yasuyoshi Miyata*, Hisaya Kanou*, Shingo Date*, and Kazuo Hasue*[†]

*Department of Applied Chemistry, National Defense Academy, 1-10-20 Hashirimizu, Yokosuka, Kanagawa, 239-8686, JAPAN
[†]corresponding author: hasue@nda.ac.jp

Summary

Recently, 5-amino-1H-tetrazole (5-ATZ) has been developed for practical use as a substitute for sodium azide, which has been conventionally used as a main component of gas generating agent for automobile airbags. This paper describes the study concerning fundamental combustion features of the mixtures of 5-ATZ and sodium perchlorate (SP) which has high oxygen content per unit mass. The 5-ATZ/SP mixture was consolidated to form test strands. An optical strand burner was used to measure the burning rate of the strands. The burning rate for 5-ATZ/SP at 2 MPa was about 18 mm s^{-1} for a stoichiometric mixture which was higher than that of 5-ATZ/strontium nitrate (SrN) mixture. The decomposition of 5-ATZ/SP underwent three-stage process and at the second stage, near720K, the reaction between fuel and oxidizer occurred. According to the closed vessel test, 5-ATZ/SP displayed 3.4times larger pressure gradient than that of 5-ATZ/SrN mixture, suggesting the former's superior performance as a gas generating agent. It was also found from the interpretation of the burning rates according to Granular Diffusion Flame model suggested by Summerfield, that combustion mechanism of the samples used in this study was is diffusion controlled. According to the temperature history of the mixtures, an increase in burning rate with an increase in pressure is an increase in the amount of heat transfer from the gas phase to the solid phase because of the approach of the flame to the burning surface.

1. Introduction

Sodium azide has been used as a main component of gas generating agents for automobile airbag inflators. However, sodium azide is toxic and can produce explosive substances as a result of contact with heavy metals. Consequently, researches have been carried out extensively on nitrogen gas generating agents employing 5-amino-1H-tetrazole (5-ATZ) as one of the substitute materials. We have already reported on the combustion characteristics of 5-ATZ/potassium perchlorate (KP) mixtures[1], 5-ATZ/strontium nitrate (SrN) mixtures[2], 5-ATZ/potassium nitrate (KN) mixtures[3], and 5-ATZ/sodium nitrate (SN) mixtures[3]. In this study, we have examined the combustion mechanism of 5-ATZ/sodium perchlorate (SP) through the examination of the effects of mixing ratios and pressure on the burning rate. SP was selected as an oxidizer in this study because it contains relatively large amount of oxygen per unit mass than other oxidizers and theoretically its decomposed solid product is harmless NaCl.

In this study, a restricted strand was burned within a closed vessel based on a chimney-type strand burner and the performances as a gas generating agents have been examined by observing the gas generation behavior. Since burning rate, amount of generated gas per unit mass, and volume of gas expansion due to an increase in temperature are considered in a closed vessel method, it would be possible to estimate the ability of the sample to inflate the actual airbag.

Temperature change in the vicinity of the burning surface was evaluated, based on thermal analyses of the mixtures and mass analyses of generated gases. The burning of 5-ATZ/oxidizer mixtures would be diffusion controlled because of the particle size dependence on r [1]. In this study, the applicability of Granular Diffusion Flame (GDF) model[4] to explain the combustion characteristics has been examined.

2. Experimental
2.1 Samples

As a fuel component of the non-azide gas generating

agent, non-toxic 5-ATZ (Fujimoto Chemicals Co., Ltd., test sample) was used. This compound has drawn attention as a substitute for toxic sodium azide, and it has been used as gas generating agents for part of the airbags. SP (Kanto Kagaku, guaranteed reagent >96%) was used as the oxidizer because of its high oxygen content. 5-ATZ and SP were crushed in separate ball mills (Irie Shokai Co., Ltd., V-2, 100r.p.m., 900ml pot, 15mm diameter porcelain balls) for approximately one hour, and the particle diameter was controlled within 75 - 149μm by using standard sieves. The samples were then dried through a vacuum dryer (Kuramochi Kagaku Kikai Co., Ltd., RG-501) at 318K and 10Pa for 4 hours and were mixed at a designated mixing ratio for 30 minutes at 80r.p.m. through a rotary mixer (Tsutsui Scientific Instruments Co., Ltd., S-3). The 4 grams of mixture was then compressed at approximately 1 GPa for 5 minutes to produce a rectangular strand ($5 \times 5 \times 70$mm). The mass percentages of 5-ATZ were 40, 44.3 (stoichiometric ratio), 50, and 55wt%.

2.2 Measurement of burning rate

The surfaces of the strand were restricted with epoxy resin (Cemedine Co., Ltd., 1500), and with the use of a chimney-type strand burner with observation windows (Kyowa Giken Co., Ltd., SCTA-50), combustion test was performed under 0.7 - 5 MPa nitrogen atmosphere at about 300 K. The ignition of the strand was carried out through a heated nichrome wire (diameter 0.6mm). Pressure was measured through a strain-gauge pressure transducer (Kyowa Electric Instruments Co., Ltd., PG-100KU) and after amplification (Kyowa Electric Instruments Co., Ltd., CDV-230C), recorded on a pen recorder (Rikadenki Kogyo Co., Ltd., R-64). The testing apparatus is described elsewhere [1]. The burning rate (r) was calculated from the duration of burning time by observing the pressure change inside the vessel. The pressure started rising when the strand started burning and the pressure rise stopped at the end of burning. The average ambient nitrogen pressure (P) was obtained by averaging the pressure when the burning started and the pressure when the burning stopped.

The temperature profiles in the vicinity of the burning surface were obtained with K-type thermocouple (diameter 50 μm) embedded in the strand. The output of the thermocouples was acquired on a transient recorder (Iwatsu Electric Co., Ltd., DM-7100) through a direct-current amplifier (Kyowa Electric Instruments Co., Ltd., CDV-230C). The temperature-time curve was obtained and the temperature-distance curve was derived.

2.3 Measurement of pressure within
the closed vessel

The chimney-type strand burner whose orifice was closed to act as a 4 liter closed vessel and pressure-time change was measured at an initial operational pressure of 2MPa and at about 300K. The ignition of the strand was carried out through a heated nichrome wire (diameter 0.6mm). Pressure within the chamber was measured through a strain-gauge pressure transducer (Kyowa Electric Instruments Co., Ltd., PG-100KU) and after amplification

(Kyowa Electric Instruments Co., Ltd., CDV-230C) , recorded on a recorder (Keyence Corp., GR-3000).

2.4 Thermal analysis

Under the heating rate of 20 K min^{-1} in helium atmosphere (20 ml min^{-1}), thermogravimetry (TG) and differential thermal analysis (DTA) was conducted using DTG-50H (Shimadzu Corp.). In addition, mass spectrometry (MS) was conducted by using QP-5000 (Shimadzu Corp.) connected with DTG-50H, in order to undergo qualitative analysis of gaseous products of the pyrolysis.

3 Results and discussion
3.1 Pressure within the closed vessel

Gas generating agents for automobile airbags are required to generate large amount of gas in order to fill the volume of the airbag (*e.g.* 60 liter) in a short period of time.

Figure 1 shows the experimental result of the pressure-time curve. The larger the pressure gradient, the faster it is filling the airbag. From the diagram, the pressure gradient was found to be 0.33 MPa s^{-1} for 5-ATZ/SP mixture as compared to 0.096 MPa s^{-1} for 5-ATZ/SrN mixture, that is SP was 3.4times larger than SrN.

3.2 Amount of generated gas

Gas generating agents for automobile airbags needs to release large amount of gas with small amount of sample in order to downsize the inflator. For stoichiometric mixtures, all of carbon and hydrogen atoms contained in the fuel are assumed to oxidize completely according to the following equations.

$$CH_3N_5+0.875NaClO_4 \rightarrow CO_2+1.5H_2O+2.5\ N_2+0.875NaCl$$
$$CH_3N_5+0.7Sr(NO_3)_2 \rightarrow CO_2+1.5H_2O+3.2N_2+0.7SrO$$
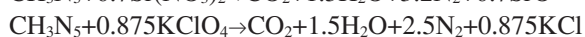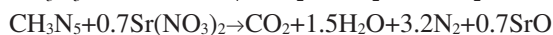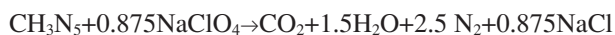$$CH_3N_5+0.875KClO_4 \rightarrow CO_2+1.5H_2O+2.5N_2+0.875KCl$$

Table 1 shows the calculated values of the amount of generated gas per unit mass and the amount of generated gas per unit volume. Here, water is assumed to be in a liquid state and is therefore not included in the calculation. If the amount of generated gas per unit mass is great, it is possi-
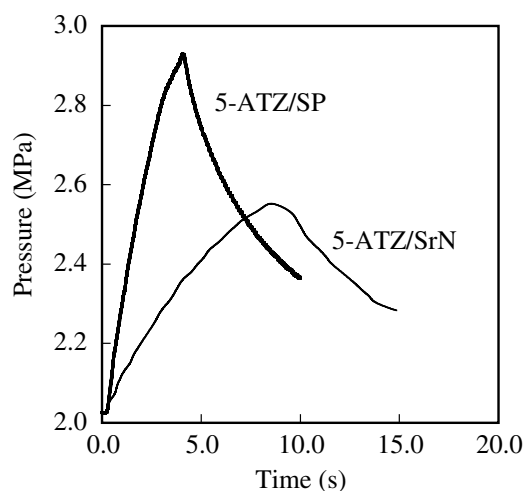

Fig. 1 Pressure-time history of 5-ATZ/oxidizer mixtures from closed vessel test.

Table 1 Theoretical amount of generated gas.

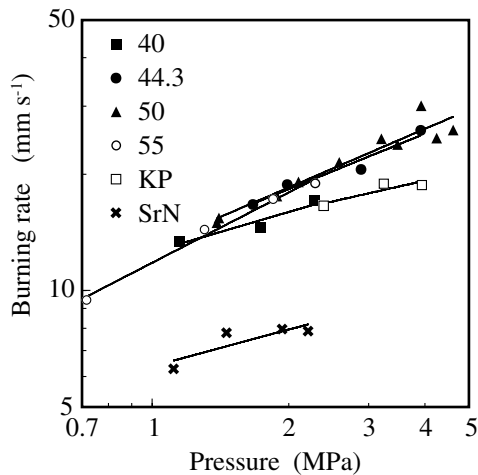| Composition	Generated gas per mass (mol g^{-1})	Generated gas per volume (mol cm^{-3})
5-ATZ/SP=44.3/55.7	0.0182	0.0354
5-ATZ/KP=41.2/58.8	0.0170	0.0335
5-ATZ/SrN=36.5/63.5	0.0180	0.0394

Fig. 2 Burning rate of 5-ATZ/oxidizer mixtures.
■ 5-ATZ/SP=40/60   ● 5-ATZ/SP=44.3/55.7
▲ 5-ATZ/SP=50/50   ○ 5-ATZ/SP=55/45
□ 5-ATZ/KP=41.2/58.8 × 5-ATZ/SrN=36.5/63.5

ble to reduce the mass of an inflator. On the other hand, if the amount of generated gas per unit volume of sample is great, it is possible to reduce the volume of the sample necessary to generate equal volume of gas and downsize the inflator. As for mixtures examined in this experiment, the amount of generated gas per unit mass of 5-ATZ/SP mixture is 1% larger than that of 5-ATZ/SrN mixture, but it is

seen that the amount of generated gas per unit volume for 5-ATZ/SP mixture is 89.8% of 5-ATZ/SrN mixture.

3.3 Burning rate

Generally, it is better for the gas generating agent to have a larger burning rate, since large amount of gas will be released within shorter period of time.

The relationship between r and pressure (p), which is known as Vielle's law, can be expressed as the equation (1).

$$r = a\,p^{n} \tag{1}$$

Where a is a constant and n is the pressure exponent of r. Figure 2 gives the relationship between r and P. There were increases in r with the increase in P, obeying Vielle's law. Comparing 5-ATZ/SP mixture with 5-ATZ/SrN and 5-ATZ/KP mixtures at 2MPa, r of 5-ATZ/SP mixture was approximately 2 and 1.1 times faster, respectively.

3.4 Thermal analyses

TG-DTA curves for 5-ATZ are shown in Fig. 3(a). The lowest endothermic peak of the DTA curve which was caused by melting started at 474K, peaked at 480K, and terminated at 494K. The reported melting point of 5-ATZ was 482 - 483K [5]. The second lowest endothermic peak was due to decomposition and it started at 508K, peaked at 525K, and terminated at 543K.
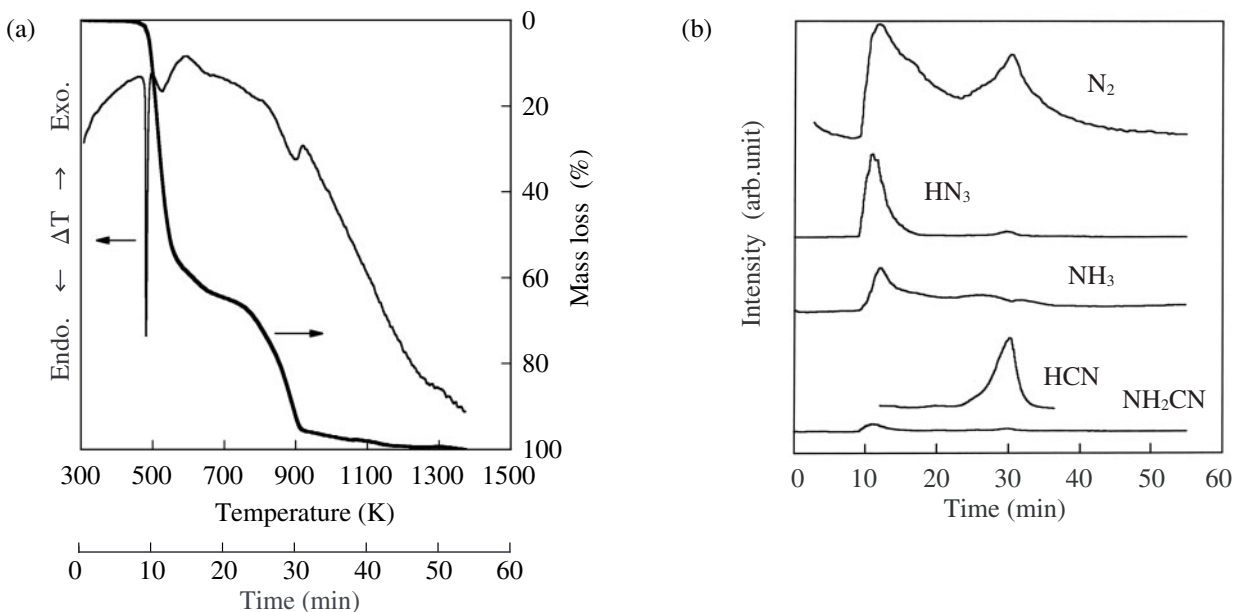
According to the MS analyses as shown in Fig. 3 (b),

Fig. 3 Thermal analysis of 5-ATZ at heating rate of 20K min^{-1} in helium. (a) TG-DTA (b) mass chromatogram

chemical species with a value of mass (m) divided by charge (z) m/z 28, which was estimated to be nitrogen (N_2), was observed at the first and second stages of the decomposition process.

The decomposition products of 5-ATZ by means of a rapid thermolysis were hydrogen azide (HN_3) and trace of ammonia (NH_3) at 473K, cyanamide (NH_2CN) at 533K, ammonium azide (NH_4N_3) and melamine at 623K, and melamine-like products were formed from NH_2CN[6].

In this experiment, m/z 17, 27, 28, 42, and 43 were found and they matched NH_3, hydrogen cyanamide (HCN), N_2, NH_2CN, and HN_3, respectively.

At the first mass loss of TG curve, NH_3, N_2, NH_2CN, and HN_3 were the main products and NH_3, HCN, N_2 and trace of NH_2CN and HN_3 were found at the second mass loss of TG curve. The main difference between first and second mass loss was the formation of HCN which is one of the decomposition products of NH_2CN[7].

TG-DTA curves for SP are shown in Fig. 4(a). An endothermic peak of the DTA curve near 583K would be due to the phase transition from rhombic to cubic form at 586K[8]. The other endothermic peak of the DTA curve that started from approximately 700K and that have shown maximum value of 745K was probably related to the melting of SP (melting point: 746K[8]). The decomposition of SP started at 843 K and the peak temperature was 857K and ended at 876K, as compared to the reported decomposition point of 753K[8]. It was also found that the decomposition of SP was an exothermic reaction in which the heat of decomposition was –72.78 J/g i.e. –8.9 kJ/mol, as compared to DTA peak temperature of KP of 915K and heat of decomposition of –7.6 kJ/mol. Decomposition reaction of SP being exothermic was probably the main reason for high r of the mixtures with 5-ATZ. Percentage of mass loss at the first stage of the TG curve was approximately 53% which agreed with the theoretical value of 52.27%. Therefore, the decomposition reaction of SP was suggested to be

$$NaClO_4 \rightarrow NaCl + 2\,O_2 \qquad (1)$$

in which oxygen atoms detached initially. The reaction scheme was verified from the appearance of endothermic peak at 1076K that is close to the melting point of NaCl (the reported melting point was 1077K[9]) and appearance of m/z 32 that was estimated to be O_2 on mass chromatogram at approximately 30min as shown in Fig. 4 (b). The mass loss at the second stage was probably due to the evaporation of NaCl.

TG-DTA curves for a stoichiometric mixture of 5-ATZ/SP are shown in Fig. 5 (a). The endothermic peak appeared at 458K which may due to the melting of 5-ATZ as observed in Fig. 3 (a). Since the TG curve shows the decomposition starting at approximately 470K, decomposition of the mixture probably started with the decomposition of 5-ATZ whose decomposition started at 508K as previously mentioned.

According to the TG curve of 5-ATZ, the percentage of mass loss at the first stage was approximately 60%. If only 5-ATZ decomposed at the first stage, the value corresponded to 26.5% of mass loss for a stoichiometric mixture. For 5-ATZ/SP, the observed percentage of mass loss at the first stage was approximately 30% and there was no indication of reaction between fuel and oxidizer, it was found that only 5-ATZ decomposed.

The mass chromatograms are presented as intensity versus time for the selected mass fragments in Fig. 5(b). Peaks of the mass chromatogram of m/z 17, 28, 42, and 43 were observed at approximately12min and they matched NH_3, N_2, NH_2CN, and HN_3, respectively. It suggested that only 5-ATZ was decomposed as mentioned above. Candidate species for m/z 28 were estimated to be N_2, CO, or ethylene (C_2H_4). Since there was no oxygen at the first decomposition stage CO was an unlikely candidate and C_2H_4 was not a plausible decomposition product according Wu et al.[10] and also nitrogen is the main atom of 5-ATZ, m/z 28 was estimated to be N_2.

The theoretical mass percentage of NaCl in the stoichiometric mixture is 26.59 wt%. At the end of the second mass loss, at approximately 800K, the percentage of mass loss was approximately 72%, therefore the reaction between fuel and oxidizer completed and only NaCl remained. Peaks of the mass chromatogram of m/z 44 were observed
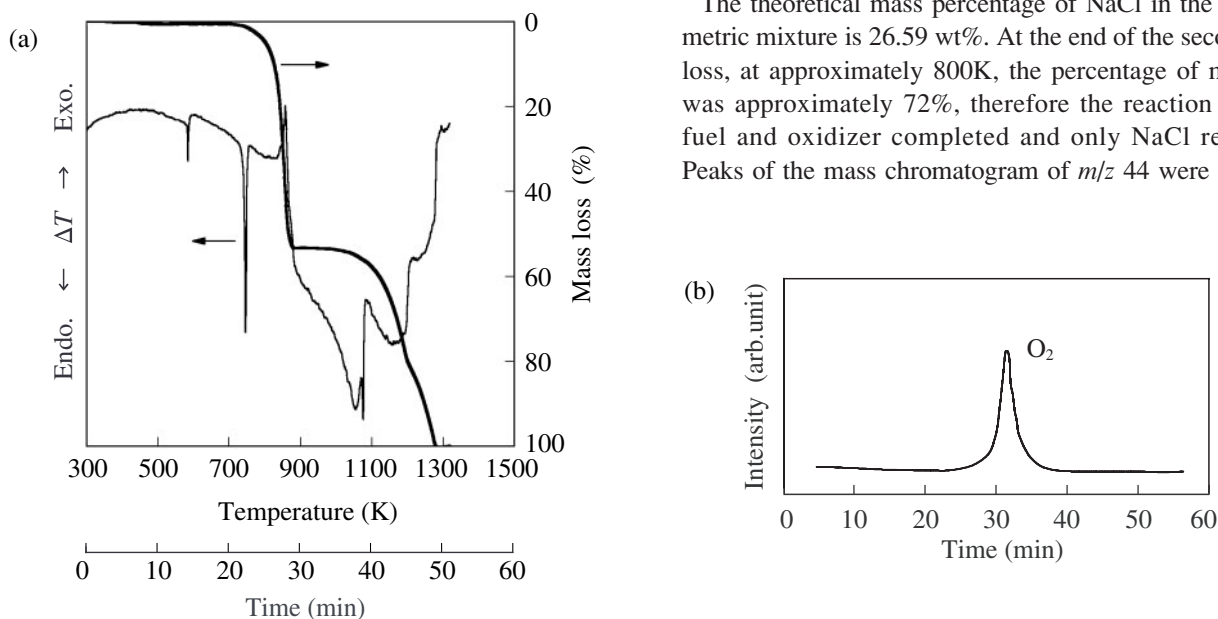

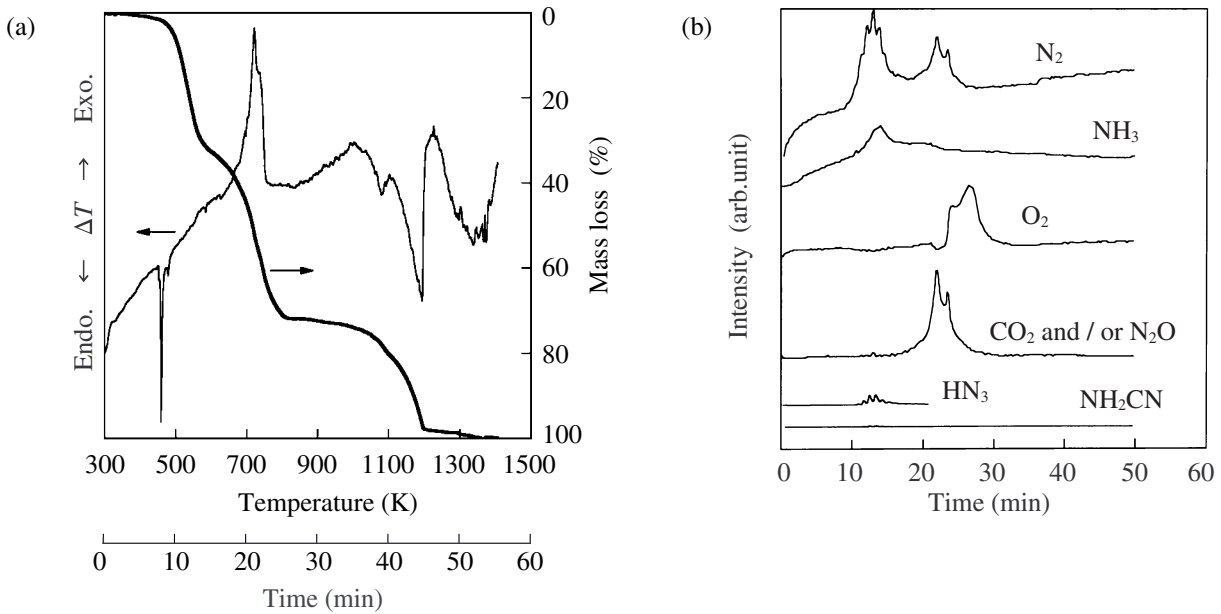Fig. 4 Thermal analysis of $NaClO_4$ at heating rate of 20 K min^{-1} in helium. (a) TG-DTA (b) mass chromatogram

Fig. 5 Thermal analysis of 5-ATZ/NaClO$_4$ at heating rate of 20 K min^{-1} in helium. (a) TG-DTA (b) mass chromatogram

at approximately 22 min or the second stage of mass loss curve, and m/z 44 was estimated to be CO$_2$ or N$_2$O, suggesting the combustion of the sample. Identification of m/z 44 was not conducted in this experiment. An exothermic peak that appeared at Fig. 5 (a) was estimated to originate from a reaction between 5-ATZ and SP. As for m/z 32, O$_2$ or hydrazine (N$_2$H$_4$) was estimated to be the evolved gas. According to the reported decomposition products [6) 10)], N$_2$H$_4$ was an unlikely candidate and m/z 32 was concluded to be O$_2$. Since m/z 44 was observed at approximately 22 min, it was found that m/z 32, observed at approximately 25min, was detected at a temperature higher than the combustion of the mixture. Since the decomposition temperature of SP was 857K as previously mentioned, m/z 32, which was detected after the detection of m/z 44, was estimated to be the remaining O$_2$ which was not consumed during the 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.

The main difference between 5-ATZ and 5-ATZ/SP was that HCN was not found and CO$_2$ and/or N$_2$O were found at the second mass loss of TG curve for 5-ATZ/SP. This could be explained that NH$_2$CN or its derivatives were oxidized instead of their thermal decomposition in the case of 5-ATZ/SP.

3.5 Structure of the combustion wave

Figure 6 shows the temperature-distance curve at different pressure. Burning rate r increased with an increase in P for a stoichiometric mixture: an increase in r from 15.4 mm s^{-1} to 20.4 mm s^{-1} with P increase from 1.25 MPa to 2.52 MPa. Burning rate r increased with increasing P because the rate of heat transfer from the gas phase to the solid phase increased as the flame approached the burning surface.

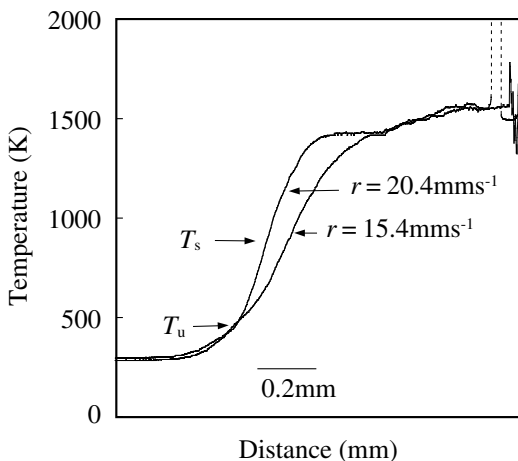The relation between ln (T-T_0) and distance (x) was

Fig. 6 Temperature profile in the vicinity of burning surface of 5-ATZ/NaClO$_4$=44.3/55.7 strand.
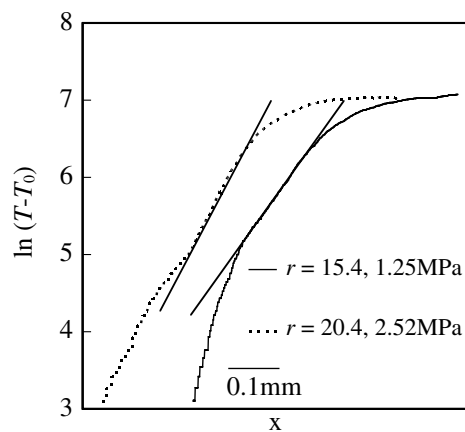

Fig. 7 Relation between ln(T-T_0) and x in the vicinity of burning surface.

shown in Fig. 7. Examining the relation between ln (T-T_0) and x, there were two points at which the data deviate from the straight line. Where T is the temperature, T_0 is the initial temperature. Assuming the point of lower temperature at which the data deviates from the relation between ln (T-T_0) and x to be the temperature at which the decomposition temperature of sample (T_u), T_u were 475K at 1.25MPa and 450K at 2.52MPa, both of which were close to 458K which was attributed to the melting point of 5-ATZ in Fig. 3(a). Assuming T_s to be the point of higher temperature, the temperatures were 950K at 1.25MPa and 835K at 2.52MPa. The thickness of condensed phase reaction zone (δ) was the distance between T_u and T_s on temperature-distance curve [11] as shown in Fig. 6. It was found that δ decreased with an increase in P, that is, δ were approximately 0.1 and 0.2mm for 1.25MPa and 2.52MPa, respectively. δ became thinner probably because the amount of heat transfer to the solid phase per unit time increased, which lead to a decrease in time required between the decomposition of 5-ATZ and the oxidizer.

3.6 Combustion mechanism

Since 5-ATZ and SP particles are packed in a strand, the molten layer may not cover the burning surface if the phase transfer from solid → liquid → gas phase is faster than the liquid diffusion in spaces between the particles.

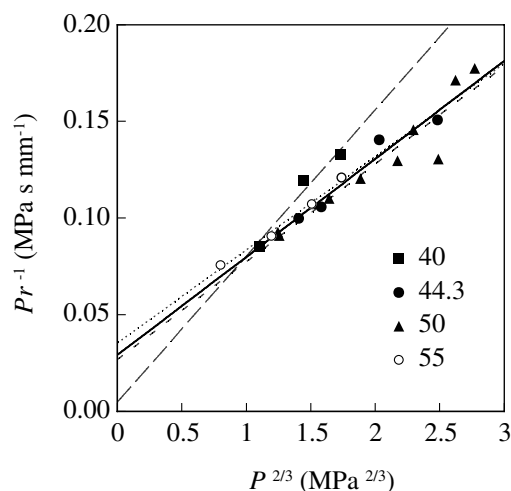Fig. 8 GDF correlation of burning rate of 5-ATZ / NaClO$_4$.
P / r = a + b $P^{2/3}$
Numbers indicate mass percentage of 5-ATZ.

The combustion of 5-ATZ/SP may be affected by the time required for each gaseous product to undergo diffusion and mixing, which means that r is also affected by the diffusion process. In this study, it was examined whether GDF model was acceptable in the combustion of the sample tested by using equation (2) [4].

$$\frac{P}{r} = a + bP^{2/3} \qquad (2)$$

Where a is a chemical reaction time parameter, b is a diffusion time parameter. Relationship between $P^{2/3}$ and P/r are shown in Fig. 8. Good linear relationships were demonstrated with both a and b being positive, regardless of fuel/oxidizer ratio, so it was suggested that GDF model could be applied for 5-ATZ/SP mixtures.

The ratio between the reaction layer and the diffusion layer is given by equation (3).

$$\frac{L_d}{L_c} = \frac{b}{a} \; P^{2/3} \qquad (3)$$

Where L_d is the diffusion distance of the fuel and the oxidizer, and L_c is the distance required for chemical reaction. It is thought that the diffusion layer is thicker than the reaction layer if the value of the right hand side of equation (3) is greater than 1, and vice versa if the value is less than 1. L_d/L_c ratio for each composition is given in Table 2. For those samples considered applicable to GDF model, the values of L_d/L_c = b $P^{2/3}$ / a were all greater than 1 at 1MPa, so it was suggested that the diffusion zone was thicker than the reaction zone. Consequently, for those samples considered applicable for the GDF model, the combustion process was found to be diffusion-controlled, and within the pressure range tested, it was suggested that the diffusion process was the most important factor for r in all cases.

4. Conclusions

Selecting 5-ATZ as the tetrazole fuel component and SP as the oxidizer to produce mixtures, the following conclusions were obtained.
1) Burning rates of 5-ATZ/SP were dependent on pressure and they followed Vielle's law.
2) Burning rates of 5-ATZ/SP were larger than those of 5-ATZ/SrN mixtures.
3) Gas generating ability per gram of 5-ATZ/SP was greater than that of 5-ATZ/SrN.

Table 2 Results of the model L_d/L_c=(b/a)$P^{2/3}$.

Compositon of 5-ATZ/SP (wt%)	a	b	b/a=L_d/L_c at 1MPa
40/60	0.00505	0.0755	15.0
44.3/55.7	0.0292	0.0507	1.74
50/50	0.0270	0.0506	1.87
55/45	0.0355	0.0482	1.36

a: chemical reaction time parameter; b: diffusion time parameter,
L_d: diffusion distance of the fuel and the oxidizer,
L_c: distance required for chemical reaction.

4) GDF model was applicable within the pressure range of approximately 0.7-5MPa and the burning rate was controlled by diffusion process.

5) According to TG-DTA-MS analysis, 5-ATZ decomposed through two-stage process and NH_3, HCN, N_2, NH_2CN, and HN_3 were found at the first stage and HCN and N_2 were found at the second stage. The decomposition of 5-ATZ/SP underwent three-stage process and the decomposition products of 5-ATZ such as NH_3, N_2, and HN_3 were found at the first stage and the reaction products between fuel and oxidizer such as CO_2 and/or N_2O and no HCN were found at the second stage. NH_2CN or its derivatives would be oxidized and CO_2 and/or N_2O were formed instead of forming HCN.

6) According to the temperature history of the mixtures, an increase in burning rate with an increase in pressure was an increase in the amount of heat transfer from the gas phase to the solid phase because of the approach of the flame to the burning surface.

References
1) K. Hasue, T. Akanuma, H. Hodai, and S. Date, J. Japan Explosives Soc., 60, 31 (1999).
2) K. Hasue, P. Boonyarat, Y. Miyata, and J. Takagi, *ibid*, 62, 168 (2001).
3) Y. Miyata, S. Date, and K. Hasue, Propellants, Explosives, Pyrotechnics, 29, 257 (2004).
4) M. Summerfield, G. S. Sutherland, M. J. Webb, H. J. Taback, and K. P. Hall, "Solid Propellant Rocket Research, Progress in Astronautics and Rocketry", Vol. 1, pp.141-182 (1960), Academic Press.
5) F. Volk and H. Bathelt, "User's manual for the ICT-Thermodynamic Code" (1998), Fraunhofer-Institut für Chemische Technologie, Pfinztal.
6) A. Gao, Y. Oyumi, and T. H. Brill, Combustion and Flame, 83, 345 (1991).
7) J. Z. Wu, Doctoral Thesis, The Univ. of Tokyo (1994).
8) S. M. Kaye, "Encyclopedia of Explosives and Related Items", Vol.8, P167 (1978), US Army Armament Research and Development Command, Dover, N. J.
9) M. Windholz (ed.), "The Merck Index", Ninth edition, p.1111 (1976), Merck & Co., Inc.
10) J. Z. Wu, J. M. Chen, M. Itho, M. Arai, M. Tamura, T. Andoh, and S. Morisaki, J. Japan Explosives Soc., 55, 188 (1994).
11) N. Kubota, "Propellants and Explosives", p.46 (2002), Wiley-VCH.

5-アミノ-1H-テトラゾールと過塩素酸ナトリウム混合物の燃焼特性

宮田泰好*，加納久也*，伊達新吾*，蓮江和夫*†

　エアバッグのガス発生剤として用いられているアジ化ナトリウムは毒性があり，重金属との化合物は爆発性があるため，これに代わるガス発生剤の研究が盛んに行われている。本研究ではテトラゾール系化合物のうち一部のエアバッグに使用されている5-アミノ-1H-テトラゾールについて質量当たりの酸素含有量の多い過塩素酸ナトリウムとの混合物を作製し，燃焼特性について調べた。燃焼速度および密閉容器内の圧力発生速度は実用化されている5-アミノ-1H-テトラゾール/硝酸ストロンチウム系以上であることがわかった。粒状拡散炎モデルが適用できることを示し，0.7-5MPaでは拡散過程が律速であることがわかった。TG-DTA-MS装置を用いて分解生成物の解析を行い，5-アミノ-1H-テトラゾール/過塩素酸ナトリウムは3段階で分解し，720K付近で燃料と酸化剤の反応が起きることがわかった。燃焼面近傍の温度変化の測定から，圧力上昇により燃焼速度が増すのは火炎が燃焼表面に近づくためであることがわかった。

*防衛大学校応用化学科　〒239-8686　横須賀市走水1-10-20
†corresponding author: hasue@nda.ac.jp