研究論文

# Reactivity of azodicarbonamide with oxidizing agent mixtures (1)

## Combustion reaction of ADCA-$KBrO_3$ mixtures

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Azodicarbomamide (hereafter, ADCA) is expected to be a new gas generant for automobile airbag systems. In this report, the combustion reaction of ADCA with an oxidizing agent $KBrO_3$ was investigated by thermal analysis and the measurement of the heat of combustion, the burning temperature and the burning rate.

The mixture at a stoichimetric composition of ADCA and $KBrO_3$ vigorously decomposed with an exothermic reaction in the same temperature region as that for only ADCA. The heat of combustion of an unit weight of the mixture had a maximum value at the stoichiometric composition, while that of an unit weight of the ADCA became shifted their maximum value at slightly possitive oxygen balanced composition.

The burning rate had a maximum value at a slightly positive system of the oxygen balance. Under pressurized conditions, the Vieille's equation would be most applicable for the pressure dependence of the burning rate. Under atmospheric pressure, the burning rate became remarkably small and the tendency was contrary to the Vieille's equation.

## 1. Introduction

Recently, many of automobiles sold in Japan have been equipped with an airbag system for safer driving. Sodium azide ($NaN_3$) is presently used as the main component of the gas generator of the system, which offers a high thermal stability and evolves a large amount of harmless gas upon decomposition, but has a treatment problem, such that it has a high toxicity[1] and produces a highly sensitive and explosive substance[2] as a product when in contact with heavy metal. A new gas generant has been desired as a substitute for $NaN_3$. As for non-azide gas generants, tetorazole derivatives[3], an urazole[4], an azodicarboamide[5] (hereafter ADCA) and metal complexes of carbohydrazide[6~9], etc., are the objects of the study.

In this report, in order to investigate the possibility of practical application to the gas generator, the combustion reaction of ADCA with high reactive potassium bromate ($KBrO_3$) as the oxidizing agent was investigated by thermal analysis and the measurement of the heat of combustion, the burning temperature and the burning rate.

## 2. Experiment

### 2.1 Reagent

ADCA from the Otsuka Chemical Co., Ltd. was dried at room temperature under reduced pressure for one week. The $KBrO_3$ of the oxidizing agent was Wako Pure Chemical reagent grade. Reagents screened to under 75 $\mu$m were mixed using the Irie V-I mixer. Six kinds of samples were prepared by mixing which included a stoichiometric composition, three positive and two negative compositions with respect to the oxygen balance based on eq. (1). Table 1 shows these compositions.

$$3C_2H_4N_4O_2 + 4KBrO_3 \cdot \rightarrow 4KBr + 6N_2 + 6CO_2 + 6H_2O \quad (1)$$

Received on September 12, 1997
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Table 1 Composition of mixtures

| Molar ratio | Molecular fraction | Weight fraction | Oxygen balance (g/100g) |
|---|---|---|---|
| 3/2 | 0.600/0.400 | 0.510/0.490 | −14.1 |
| 3/3 | 0.500/0.500 | 0.410/0.590 | −5.7 |
| 3/4 | 0.429/0.571 | 0.343/0.657 | 0.0 |
| 3/5 | 0.375/0.625 | 0.294/0.706 | +4.1 |
| 3/6 | 0.333/0.667 | 0.258/0.742 | +7.1 |
| 3/9 | 0.250/0.750 | 0.188/0.812 | +12.9 |

### 2.2 Apparatus and method

The differential thermal analysis and the thermogravimetry was carried out using a Rigaku TAS-200 Thermal Analyzer. The sample cell was a hermetically sealed aluminum crucible which had pinholes in the center of its cap. The sample amount was 3 mg and the sample was heated to 800℃ at a heating rate of 20℃/min. under Ar.

The heat of the reaction was measured using a Shimadzu CA-4 Type Automatic Bomb calorimeter under Ar. The influence of the ambient pressure on the measurement values was investigated at three different pressures in the range of 0.1 MPa to 2.1 MPa.

The measurement of the burning rate was carried out inside an autoclave in the range of 0.1 to 4.1 MPa under Ar. The sample was loaded at 0.75 of the packing fraction in the aluminum tube (6mm inside diameter, 15mm outside diameter, 30mm length). The burning rate was determined by the time that was needed for the combustion wave to proceed 10 mm.

The burning temperature was also measured using the same packing fraction and tube diameter for the measurement conditions of the burning rate. The Pt-Pt/Rh(13%) thermocouple with a 0.2 mm diameter was directly inserted or by protecting the thermocouple with an insulation tube into the burning tube. The thermocouple was connected to a Yokogawahokusin Analyzing Recorder.

The residue of the combustion was analyzed by X-ray diffraction using a Rigaku rotaflex RU-200.

## 3. Results and discussion

### 3.1 Thermal analysis

Fig. 1 shows the results of the thermal analysis of ADCA, $KBrO_3$ and the mixture at a stoichiometric composition based on eq. (1). The ADCA started to decompose at 200℃ and vigrously decomposed with a exothermic sharp peak at 220 ℃. The endothermic peak accompanied by the weight loss after the exothermic decomposition might

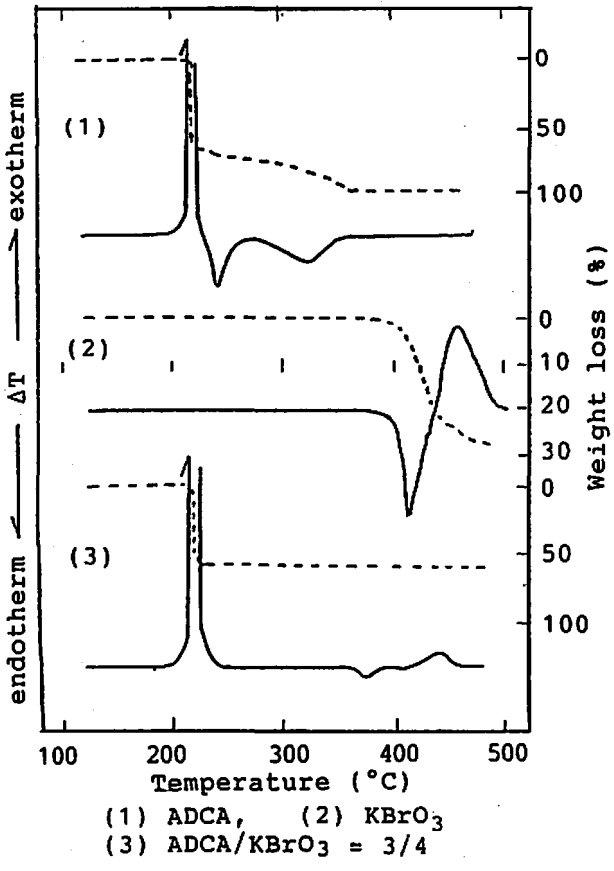



Fig. 1 DTA and TG curves of ADCA, $KBrO_3$ and their mixture

be attributed to the decomposition or the evaporation of the decomposition product at 200℃. On the other hand, $KBrO_3$ decomposed to KBr and oxygen with exothermic reaction of 59.96 kJ/mol[10]. $KBrO_3$ was postulated to start decomposition as soon as it melted at 370℃[11], based on the endothermic peak accompanied by the weight loss. The final weight loss was 28.2%, which was consistent with the calculated value (28.7%). The decomposition temperature of the ADCA/$KBrO_3$ system was consistent with that of the ADCA, while the endothermic peak after the exothermic one disappeared due to the vigorous reaction. The endothermic and exothermic reactions around 400℃ might be the decomposition of any unreacted oxidizing agent. The final weight loss was 59.5%, which was inconsistent with the calculated one based on eq. (1) (53.2%). This was thought to be attributed to the scattering of the sample due to the vigorous reaction at 200℃.

### 3.2 Heat of reaction

Fig. 2 show the results of the heat of reaction per gram of mixture and of ADCA. The heat of reaction per gram of the mixture had a maximum value at a stoichiometric composition at all pressures. On the other hand, the heat

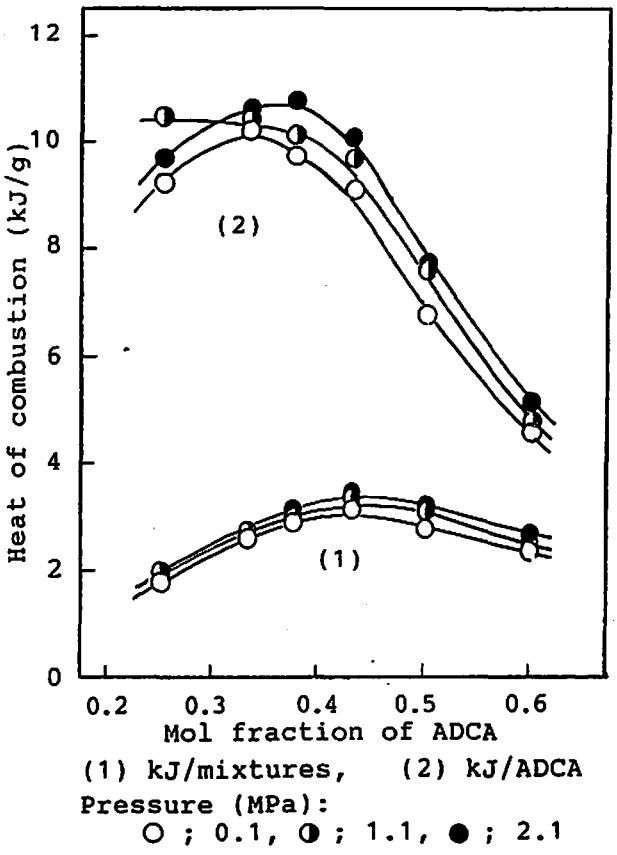



Fig. 2 Heat of combustion of ADCA-$KBrO_3$ mixtures

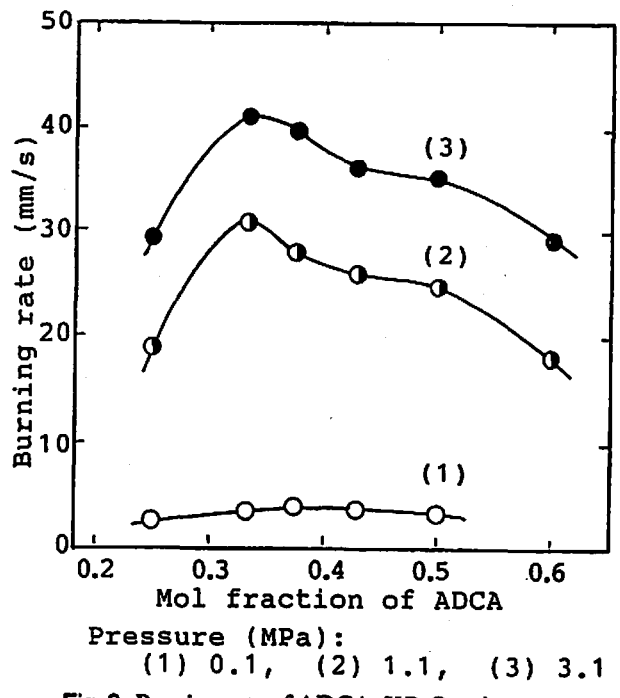



Fig. 3 Burning rate of ADCA-$KBrO_3$ mixtures

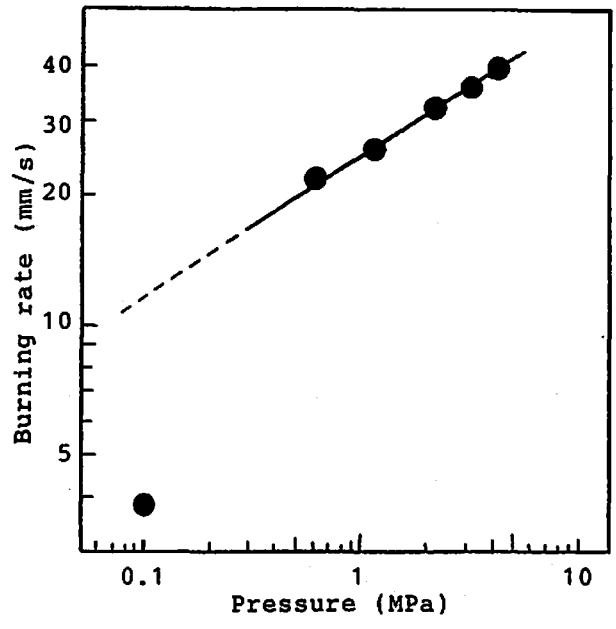



Fig. 4 Burning rate characteristic at a stoichiometric composition

of reaction per gram of ADCA had a maximum value for 0.333 mol of ADCA (+4.1 of the oxygen balance). At 1.1 MPa, there was little composition dependence for less than 0.429 mol ADCA. Consequently, the ADCA was postulated to sufficiently react with $KBrO_3$ at a positive oxygen balance. There was little influence of the ambient pressure on the heat of reaction. But there may be a little tendency that the heat of reaction become slightly larger as the pressure rise.

### 3.3 Burning rate

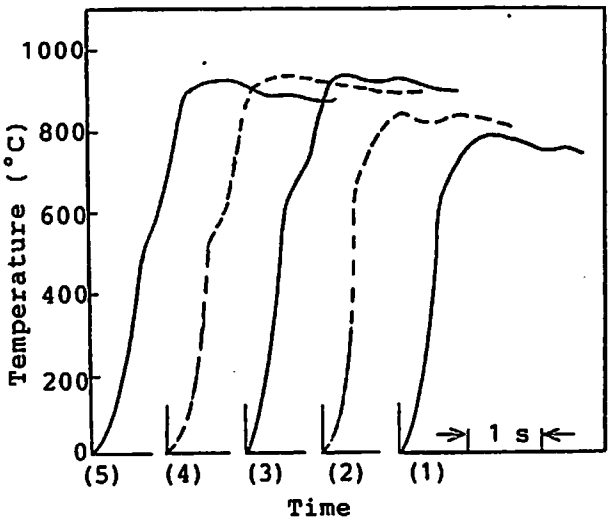
Fig. 3 shows the composition dependence on the burning rate at three different ambient pressures (0.1, 1.1, 3.1). The tendency obtained at atmospheric pressure was remarkably different from the ones under more pressurized conditions. At atmospheric pressure, the combustion was interrupted in the excess ADCA system. This might be in part attributed to the small heat of reaction in this system as seen in Fig. 3. For 1.1 MPa and 3.1 MPa, the burning rate had a maximum value at a slightly positive oxygen balance, which is consistent with the tendency of the heat of reaction per gram of ADCA.

Fig. 4 shows the pressure dependence on the burning rate at the stoichiometric composition. The measurement value at atmospheric pressure was contrary to the tendency estimated using Vieille's equation ($V=aP^n$). Based on the line obtained in Fig. 4, the pressure power was equal to 0.312 and the constant (a) was 25.5 mm/s.

Furthermore, the burning temperature was measured in order to consider these results.

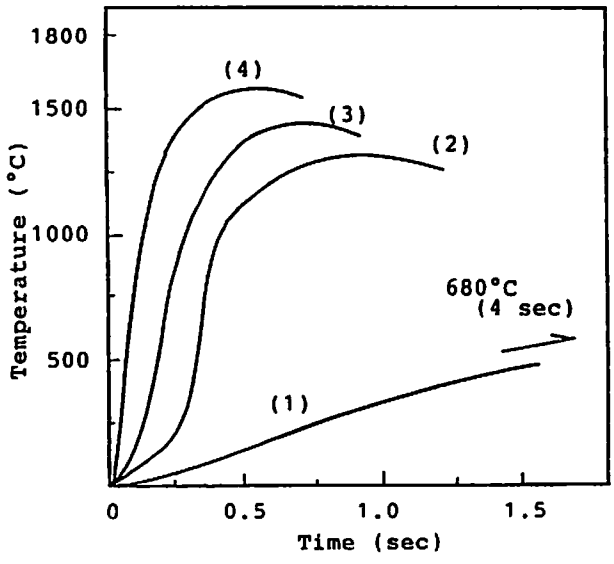
### 3.4 Burning temperature

Fig. 5 shows the temperature profile measured using a thermocouple inserted directly into the burning tube at at-



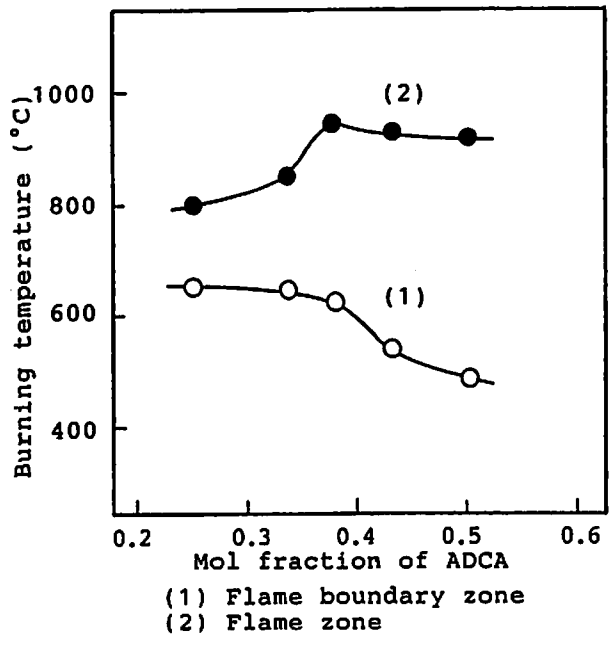

Mol fraction of ADCA:
(1) 0.25, (2) 0.333, (3) 0.375,
(4) 0.429, (5) 0.5

Fig. 5 Combustion temperature of ADCA-$KBrO_3$ mixtures




Pressure (MPa):
(1) 0.1, (2) 0.6, (3) 1.1
(4) 2.1

Fig. 7 Temperature profile for the combustion of ADCA-$KBrO_3$ mixture at various temperature




(1) Flame boundary zone
(2) Flame zone

Fig. 6 Burning temperature of ADCA-$KBrO_3$ mixtures

mospheric pressure.

The burning temperature started to rise with the approach of the combustion wave. The temperature verses time curve has an inflection point, which denoted the boundary temperature between the reaction zone and the preheat zone. The maximum temperature after passing the reaction zone meant the temperature in the flame zone which occurred at the back of the combustion wave front. Fig. 6 shows the composition dependence of the boundary temperature and the flame temperature. The boundary temperature differed before and after a stoichiometric composition and the temperature in excess system of oxidizing agent was 150℃ higher than in the deficient system. On the other hand, the flame temperature increased as the ratio of ADCA increased. In the system with excess ADCA, the combustible gases generated by the insufficient reaction with $KBrO_3$ was considered to burn in the gas phase. The tendency of the composition dependence of the burning rate, as shown in Fig. 2, was consistent with that not for the boundary temperature but for the flame one. However the flame temperature had a maximum value at a slight excess of oxidizing agent (ADCA/$KBrO_3$ =3/5(mol/mol)) and this composition differed from that at the maximum burning rate.

Secondly, the pressure dependence of the burning temperature was investigated with in the measurable pressure range. Namely, a thermocouple broke in two at high temperature in the high pressure region. Also, at more than 3.1 MPa, the burning temperature was postulated to increase over 2200℃, which is the melting point of alumina insulator of the thermocouple. Fig. 7 shows the temperature profile for the combustion of the ADCA-$KBrO_3$ mixture with a stoichiometric composition at various pressures. Incidentally, as for the influence of the insulation tube on the result, the maximum temperature was 250℃ lower and the time to the maximum temperature was 2 to 3 seconds longer than in the case of no protection at the atmospheric pressure.

The burning temperature at atmospheric pressure was remarkably low and this corresponded to the burning rate tendency in Fig. 4. In the X-ray diffraction of the combustion residue, the diffraction pattern of KBr was confirmed at all pressures. Consequently, there is little possibility of the difference in the product or a change in the fractional reaction. As for this, the heat of reaction of an unit time is small under low pressure conditions, though the ambient pressure exerts hardly an influence on the heat of reaction (Fig. 2). Furthermore, the rate of diffusion of the combustible gas generated in the condensation phase is faster than under high pressurized conditions, so that the reaction zone of the gas phase becomes long and the feedback of heat from the gas phase to the combustion wave front becomes small[12], under low pressure conditions. Therefore, the burning temperature was estimated to be low at atmospheric pressure.

## 4. Conclusion

The combustion reaction of Azodicarbomamide (ADCA) with $KBrO_3$ was investigated by thermal analysis and the measurement of the heat of combustion, the burning temperature, and the burning rate.

As for the mixture at a stoichiometric composition, the decomposition temperature was consistent with that of only ADCA, while the reaction was more vigorous than it alone.

The heat of combustion per gram of the mixture and of the ADCA, had a maximum value at a stoichiometric composition and at a slightly positive oxygen balance. The tendency of the burning rate is consistent with that for the heat of combustion per gram of ADCA.

Under pressurized conditions, the burning temperature increased with an increase in the pressure and agreed with the Vieille's equation. However, under atmospheric conditions, the burning rate did not follow the Vieille's equation and was remarkably low.

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# アゾジカルボンアミド－酸化剤混合系の反応性(第１報)
## 臭素酸カリウム混合系の燃焼反応

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自動車用エアバッグのガス発生剤として，アゾジカルボンアミドを取り上げ，その性能を評価する目的で，酸化剤である臭素酸カリウムとの混合物の熱分析，燃焼熱，燃焼温度や燃焼速度を測定して考察した。

量論混合物の発熱分解はADCA単体の場合と同じ温度領域で起こるが，その分解は単体の場合より激しくなる。

混合物の単位重量当たりの燃焼熱は量論組成で最大値を示すがADCA当たりでは酸化剤過剰系で大きくなる。

燃焼速度は少し酸化剤過剰系で最大値を示す。加圧下での燃焼速度は圧力と共に増加して，Vielle式に良く適合するが，常圧下では燃焼温度が低く，燃焼速度は著しく小さくなって，Vielle の式のプロットからはずれる。

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