研究論文

The thermal behavior of the carbohydrazide complexes of certain metals (4)

—Combustion reaction of Mg complex with oxidizing agent—

by Miyako AKIYOSHI*, Gen KINOSHITA*, Norimasa HIRATA**
Hidetsugu NAKAMURA* and Yasutake HARA*

Carbohydrazide (hereafter, CDH) metal complexes are expected to be a new gas generant for automobile air bags. In this report, the combustion reaction of the Mg complex with oxidizing agent was investigated by thermal analysis and the measurement of the heat of combustion, the burning temperature and the burning rate. (The oxidizing agent; potassium perchlolate ($KClO_4$), potassium bromate ($KBrO_3$), potassium nitrate (KNO_3) and strontium nitrate ($Sr(NO_3)_2$).

For the Mg complex / $KBrO_3$ mixture system, the initial temperature of the exothermic peak in the thermal analysis was the lowest with the most vigorous reaction of any system and the burning rate had a maximum value. When using $KClO_4$ or $KBrO_3$ as the oxidizing agent, the heat of combustion, the burning temperature and the burning rate had a maximum at a stoichiometric composition in eqs. (1) or (2), respectively. On the other hand, for the mixing system with $Sr(NO_3)_2$, a different tendency was found except for the burning temperature. Furthermore, when using KNO_3, it was not possible to burn by the combustion method used in this study.

1. Introduction

Recently, automobiles sold in Japan have been equipped with an airbag system for safer driving. NaN_3 presently used as the main component of the gas generator, which offers high thermal stability and which evolves a large amount of harmless gas upon decomposition, but has a treatment problem. It has a high toxicity[1] and products high-sensitivity and explosive[2] when in contact with a heavy metal. A new gas generant has been desired as a substitute for NaN_3. As for the non-azide gas generant, tetrazole derivatives[3], urazole[4] and azodicarboamide[5] were the objects of the study. The authors evaluated carbohydrazide (hereafter, CDH), which is composed of four nitrogen atoms, a carbon atom and an oxygen atom, and is expected to be one of the new gas generators.

In previous reports[5~8], in order to investigate the possibility of the practical application of CDH, various CDH metal complexes were synthesized and their thermal decomposition behavior investigated.

In this report, the combustion reaction for the Mg complex nitrate ($Mg(CDH)_3(NO_3)_2$) with oxidizing agent, potassium perchlolate ($KClO_4$), potassium bromate ($KBrO_3$), potassium nitrate (KNO_3) and strontium nitrate ($Sr(NO_3)_2$), was investigated by thermal analysis and the measurement of the heat of the combustion, the burning temperature and the burning rate.

2. Experiment

2.1 Reagents

The Mg complex was synthesized by a previously reported method[5]. The oxidizing agent was Wako pure chemical reagent grade. Reagents screened to under 75 μm were mixed using the Irie V-I mixer. Five kinds of samples were prepared by mixing: a stoichiometric composition and two compositions each of positive and negative oxygen

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*Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology
Sensui-machi, Tobata-ku, Kitakyusyu-shi 804, JAPAN
TEL 093-884-3308
FAX 093-884-3308

**Harima Plant, Daicel Chemical Industries, Ltd.,
805 Umaba, Ibogawa-cho, Ibo-gun, Hyogo Prefecture 671-16, JAPAN
TEL 0791-72-5422
FAX 0791-72-5450

Table 1 Compositions of mixtures

oxidizing agent	mol/mol	wt/wt	oxygen balance (g/100g)
$KClO_4$	4 / 5	70.7 / 29.3	-5.38
	4 / 6	66.8 / 33.2	-2.53
	4 / 7	63.3 / 36.7	0
	4 / 8	60.2 / 39.8	2.28
	4 / 9	57.3 / 42.7	4.39
$KBrO_3$	3 / 5	60.0 / 40.0	-4.55
	3 / 6	55.6 / 44.4	-2.11
	3 / 7	51.8 / 48.2	0
	3 / 8	48.5 / 51.6	1.88
	3 / 9	45.5 / 54.5	3.49
KNO_3	5 / 14	59.7 / 40.3	0
$Sr(NO_3)_2$	5 / 5	66.4 / 33.6	-5.07
	5 / 6	62.2 / 37.8	-2.38
	5 / 7	58.6 / 41.4	0
	5 / 8	55.3 / 44.7	2.11
	5 / 9	52.3 / 47.7	4.01

balance based on eqs. (1)～(4). Table 1 shows these compositions. As for the mixing system with KNO_3, the rest is omitted due to no combustion.

$$4Mg(CDH)_3(NO_3)_2+7KClO_4 \rightarrow 4MgO+28N_2+12CO_2+7KCl+36H_2O \quad (1)$$

$$4Mg(CDH)_3(NO_3)_2+7KBrO_3 \rightarrow 3MgO+21N_2+9CO_2+7KBr+27H_2O \quad (2)$$

$$4Mg(CDH)_3(NO_3)_2+14KNO_3 \rightarrow 5MgO+7N_2+15CO_2+7K_2O+45H_2O \quad (3)$$

$$4Mg(CDH)_3(NO_3)_2+7Sr(NO_3)_2 \rightarrow 5MgO+42N_2+15CO_2+7SrO+45H_2O \quad (4)$$

2.2 Apparatus and method

Thermal analysis was carried out using a Rigaku TAS-200 Thermal Analyzer. The sample container was an open alumina cell and the sample amount was three mg. 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 Argon. The results of the investigation at the ambient pressure showed the variation of measurement values of 3% to 4% in the pressure range of 1. 1 MPa to 3. 1 MPa. Also, there was no combustion at 0. 1 MPa. Therefore, the measurement was carried out at the 1. 1 MPa.

The measurement of the burning rate was carried out under the following conditions. A preliminary investigation showed that the linear burning rate in the packing fraction range of 0. 65 to 0. 70 became small as the packing fraction was large, while the weight burning rate was independent of it. Also, the burning rate had a maximum value, when the diameter of the burning tube was 6 mm. Consequently the sample was loaded at 0. 6 of the packing fraction in a 6 mm I.D.aluminum tube. The pressure dependence was measured in the pressure range of 0. 1 to 4. 1 MPa and the influence of the composition on the burning rate was investigated at 1. 1 MPa. 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 of the burning rate. A W/Re thermocouple of 0. 25 mm diameter was vertically inserted into the burning tube against the combustion direction and was connected to a Yokogwahokusinn Analyzing Recorder.

The combustion residue 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 for the Mg complex and the stochiometric mixtures based on eqs. (1)～(4) in the Mg complex / oxidizing agent mixture system. The Mg complex gradually decomposed soon after melting at 220℃ and the final decomposition residue was MgO. As for the Mg complex, the thermal decomposition behavior including the gas evolution rate was reported previously by the authors[6~8].

In the Mg complex / $KBrO_3$ mixture system, the decomposition vigorously progressed at 150℃ after a small endothermic peak. The initial temperature of the decomposition was the lowest of all the systems. The endothermic peak was considered to appear at the lower temperature than that of the complex because of the eutectic. (The melting point of $KBrO_3$ is 350℃[9]) The decomposition residue was MgO and KBr. The final weight loss was 95%, which was inconsistent with the theoretical value, 60%. This might be attributed to scattering of the sample due to the vigorous decomposition. In the mixture system with the other oxidizing agents, there was little distinction compared with the complex only. Consequently, the reaction was assumed to quietly progress, even if it occurred. The weight loss was 70% for these systems. These are nearly consistent with the theoretical value calculated by eqs. (1), (3) and (4) (75%). In the case of $Sr(NO_3)_2$ as the oxidiz-

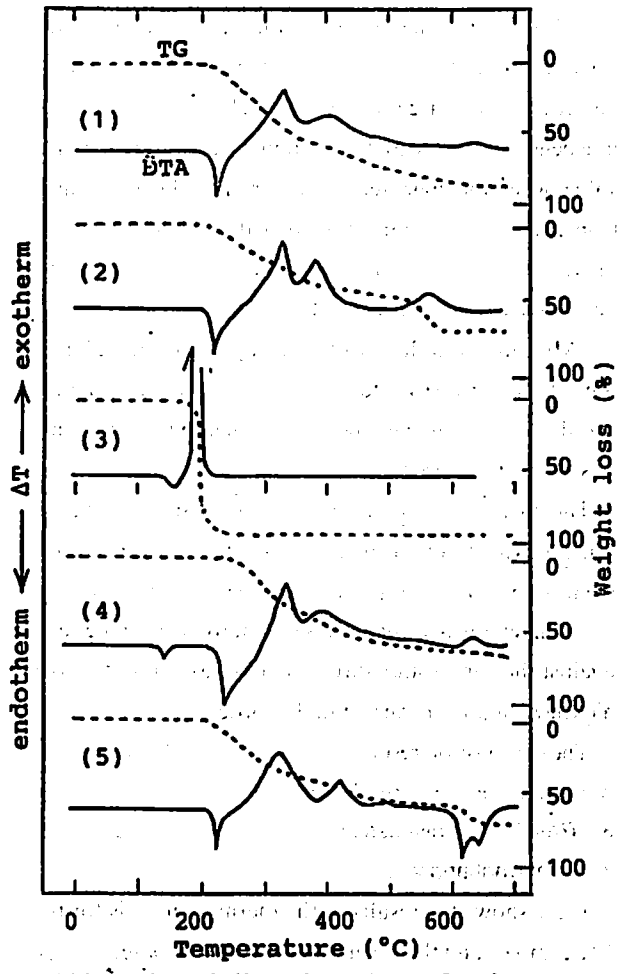


Fig. 1 DTA and TG curves of Mg-complex and mixtures

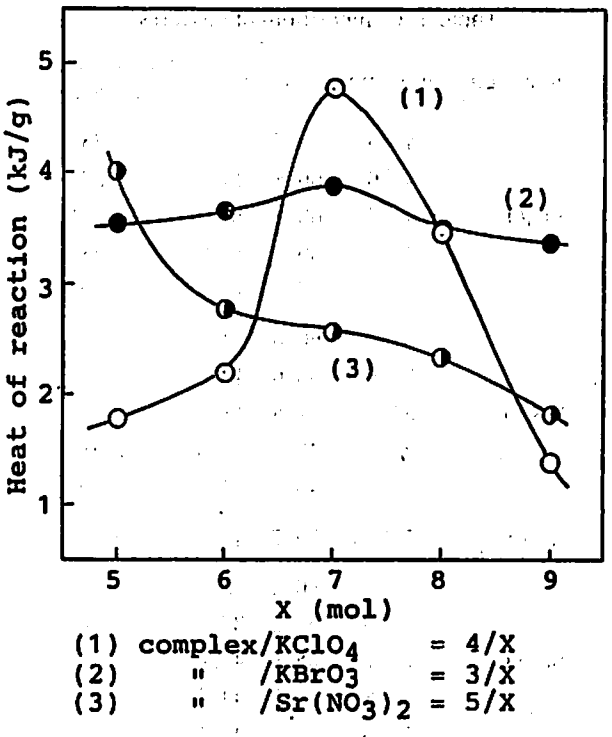


Fig. 2 Heat of reaction of mixtures

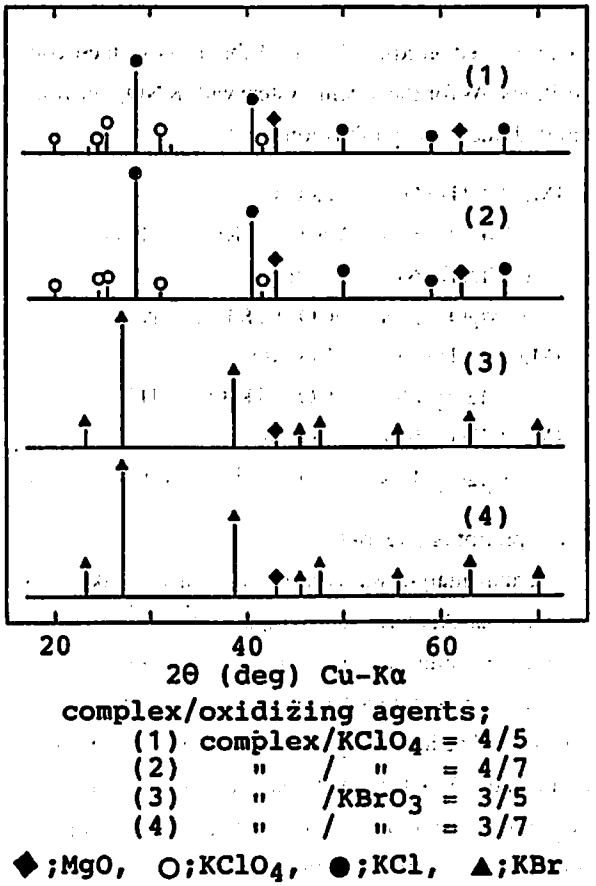


Fig. 3 XRD patterns of reaction residue of Mg-complex / $KClO_4$ or $KBrO_3$ mixtures

ing agent, the endothermic peak appeared at about 600℃, which was postulated to originate in the decomposition of unreactive $Sr(NO_3)_2$. $Sr(NO_3)_2$ decomposes at 570℃ with an endothermic reaction[10].

3. 2 Heat of reaction

Fig.2 shows the results of the heat of reaction measured under Ar. With $KClO_4$ and $KBrO_3$ as the oxidizing agent, it had a maximum value at the stoichiometric composition. For the former, the fractional reaction may vary widely, depending on the composition, based on the large composition dependence as seen in Fig.2. Moreover, the reactivity with $KClO_4$ is thought to be less, because the X-ray diffraction pattern of $KClO_4$ was confirmed in the decomposition residue (Fig.3). For the latter,the heat of reaction was independent of the composition.

Eqs. (5) ~ (8) shows the calorific amount calculated based on eqs. (1) ~ (4) as a function of A[11], in which A is the heat of formation of the Mg complex. In the range of 0 to -1000 kJ/mol of A, the constant in eqs. (5) ~ (8) de-

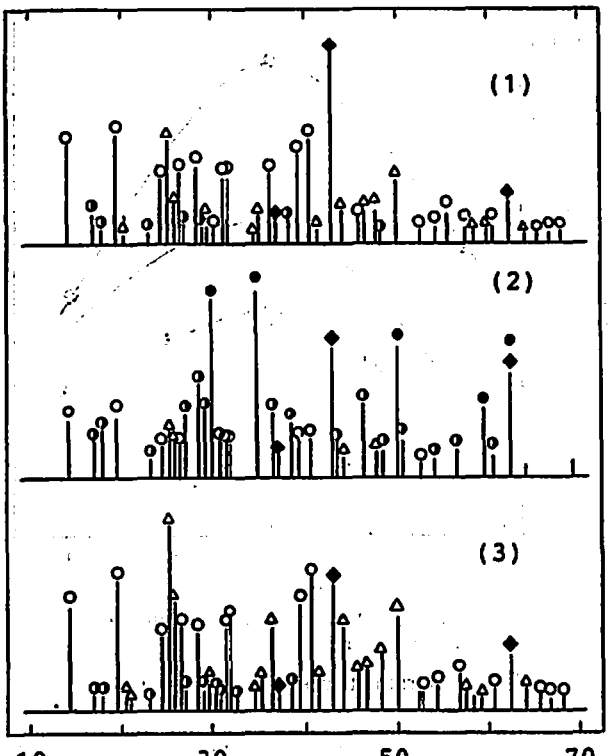


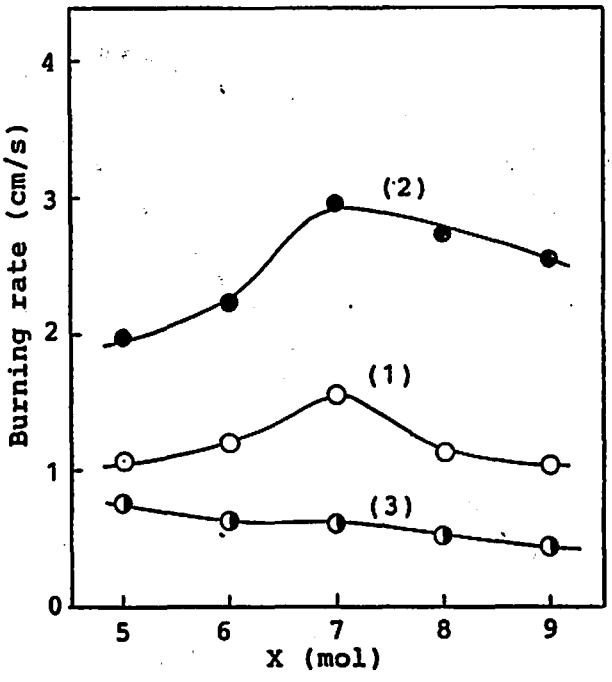
Fig. 4 XRD pattern of residue of Mg-complex / $Sr(NO_3)_2$ mixtures

creased in order of the KNO_3, $Sr(NO_3)_2$, $KBrO_3$ and

$KClO_4$	system ; -6.594 - A / 661.1 kJ/g	(5)
$KBrO_3$	system ; -5.561 - A / 808.3 kJ/g	(6)
KNO_3	system ; -4.961 - A / 714.9 kJ/g	(7)
$Sr(NO_3)_2$	system ; -5.336 - A / 714.9 kJ/g	(8)

$KClO_4$ and this tendency was consistent with that of the calorific amount at a stoichiometric composition. In the mixture system with KNO_3, no combustion but only melting might occur in the vincity of the fuse due to the lack of a calorific amount.

In the mixture system with $Sr(NO_3)_2$, the calorific amount had a maximum value at a negative oxygen balance and that value decreased as the ratio of the oxidizing agent increased. Though the decomposition of only the complex is an exothermic reaction as shown in Fig.1, the calorific amount of the reaction in the mixture system is thought to be influenced by the decomposition of the oxidizing agent. $Sr(NO_3)_2$ decomposes to nitrogen and oxygen with the endothermic reaction of 305.6 kJ/mol (1822 J/g).



X and (1)-(3) are the same as those in Fig.2

Fig. 5 Burning rate of mixture at 1.1 MPa (Ar)

Fig.4 shows the X-ray diffraction of the residue in the Mg complex/$Sr(NO_3)_2$ mixture system. At a stoichiometric composition, the main residue was SrO, $Sr(OH)_2$ fomed by the reaction of SrO with H_2O, and the hydrate of $Sr(OH)_2$. On the other hand, for the positive or negative oxygen balance, the ratio of these products became small and the formation of $SrCO_3$ was confirmed. This was attributed to the rise in the temperature at a stoichiometric composition. $SrCO_3$ starts to decompose to CO_2 and SrO at 900℃ and the dissociation pressure become equal to the atmospheric pressure at 1250.5℃[12].

3.3 Burning rate

Fig.5 shows the results of the burning rate for various compositions. The burning rate of the Mg complex / $Sr(NO_3)_2$ system was independent of the composition, while that in the other systems had a maximum value at a stoichiometric composition. The burning rate increased in the order of $Sr(NO_3)_2$, $KClO_4$ and $KBrO_3$ and that was different from the tendency for the heat of reaction that is quantity of state, as shown in Fig.2. In some factors[13] which exerted a influence on the burning rate in the tube, the burning rate in Mg complex / $KBrO_3$ system is thought to be especially governed by the rate of reaction based on the results of the DTA curves. Namely, the burning rate was postulated to become also fast because of the rapid evolution rate of heat, though the heat of reaction was small.

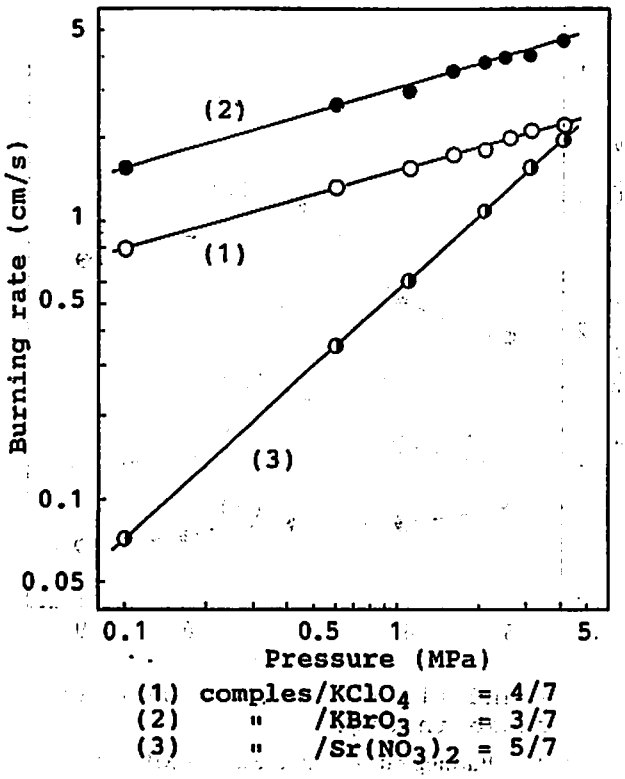


Fig. 6 Burning rate characteristics of stoichiometric mixtures

Table 2 Constants of burning rate

Composition	a	P
Mg-complex/$KClO_4$ = 4/7	1.514	0.279
Mg-complex/$KBrO_3$ = 3/7	3.001	0.292
Mg-complex/$Sr(NO_3)_2$ = 5/7	0.562	0.896

Fig.6 shows the pressure dependence of the burning rate for a stoichiometric composition. Table 2 shows the constant and the pressure power estimated using Vieille's equation ($V=aP^n$). The pressure power in the Mg complex / $Sr(NO_3)_2$ system became unusually large. For the experimental pressure, the burning rate was consistent with the tendency seen in Fig.5.

3.4 Burning temperature

Fig.7 shows the results of the burning temperature. In all cases, the burning temperature had the same tendency as that of the burning rate. Consequently, the rise in temperature of the system was thought to be one of the factors that influenced the burning rate.

4. Conclusion

The combustion reaction of the CDH complex of Mg with various oxidizing agents was investigated by thermal analysis and the measurement of the heat of combustion, the burning temperature and the burning rate. In the case

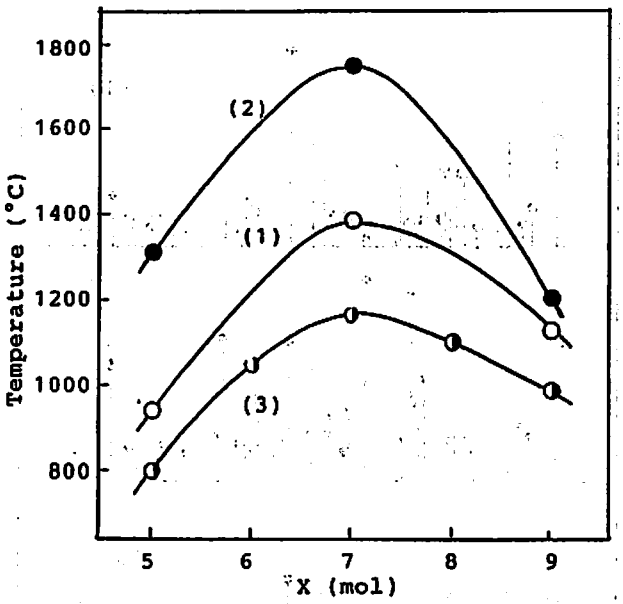


Fig. 7 Burning temperature of mixtures

of the decomposition at a slow heating rate, such as thermal analysis, the initial temperature of the exothermic peak for the Mg complex / $KBrO_3$ mixture system was the lowest with the most vigorous reactive system.

The heat of reaction increased in the order of $Sr(NO_3)_2$, $KBrO_3$ and $KClO_4$ with the same tendency of the calculated value. It had a maximum value at a stoichiometric composition except for the mixture system with $Sr(NO_3)_2$. For the Mg complex / $Sr(NO_3)_2$ system, the heat of reaction became large as the ratio of oxidizing agent decreased.

The burning rate had a maximum value at the stoichimetric composition in all systems except for the mixture system with $Sr(NO_3)_2$. In the Mg complex / $Sr(NO_3)_2$ mixture system, the composition dependence is smaller than that in the other systems and the pressure dependence was larger than that in the other systems.

The burning temperature was consistent with the tendency of the burning rate. It is postulated that the rise in temperature is one of the factors that exerts an influence on the burning rate.

Referrence

1) N. I. Sax, R. J. Lewis, "Dangerous Properties of Industrial Materials, 7th Edition", vol.3, van Nostrand Reinhold (1989), p3046
2) "Chemical Dictionary", vol.1, p63 (1963), ed. by a editorial committee for "Chemical Dictionary"
3) Jian Zhou WU, H. Yuzawa, T. Matsuzawa, M. Arai and M. Tamura, J. Japan Explosives Soc., 55, 66

(1994)
4) K. Ichikawa, M. Arai, M. Tamura and K. Waki, An academic meeting of Japan Explosives Soc., 1997 (autumn), p87
5) T. Kazumi, Y. Suzuki, T. Okada, T. Hasegawa and T. Yoshida, J. Japan Explosives Soc., 56, 248 (1995)
6) M. Akiyoshi, N. Hirata, H. nakamura and Y. Hara, J. Japan Explosives Soc., 57, 238 (1996)
7) M. Akiyoshi, N: Hirata, H. Nakamura, and Y. Hara, ibid., 57, 66 (1996)
8) M. Akiyoshi, N. Hirata, Y. Imanishi, H. Nakamura, Y. Hara, An academic meeting of Japan Explosives Soc., P131, 1997 (Spring)
9) "Chemical Handbook－fumdamental part－", vol.1, pI-140 (1984)
10) ibid., pI-191
11) "Chemical Handbook－fumdamental part－", vol.2, pII-308, 309, 312 (1984)
12) "Chemical Dictionary", vol.5, P727 (1963), ed. by a editorial committee for "Chemical Dictionary"
13) H. Nakamura, J. Japan Explosives Soc., 52, 173 (1991)

カルボノヒドラジド金属錯体の熱的挙動(4)
－Mg錯体と酸化剤との混合物の燃焼反応－

秋吉美也子*，木下　元*，平田哲正**
中村英嗣*，原　泰毅*

自動車用エアバッグのガス発生剤として，カルボノヒドラジドのマグネシウム錯体を取り上げ，その性能を評価する目的で，過塩素酸カリウム，臭素酸カリウム，硝酸カリウム，硝酸ストロンチウムなどの酸化剤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。

マグネシウム錯体は臭素酸カリウムと混合するとき，最も低温で，しかも激しく反応し，燃焼速度も大きくなった。過塩素酸カリウムと臭素酸カリウム都の混合物の場合は，反応熱，燃焼温度，燃焼速度ともに(1)および(2)にともなう量論組成で最大値を示さなかった。また，硝酸カリウムとの混合物では本研究で行った着火法では燃焼させることが出来なかった。

(*九州工業大学応用化学教室　〒804 北九州市戸畑区仙水町１－１
**ダイセル化学工業株式会社技術開発センター　〒671－16 兵庫県揖保郡揖保川馬場805)