研究論文

The thermal behavior of the carbohydrazide complexes of certain metals (5)

—Combustion reaction of the Zn and Mn complexes with oxidizing agents—

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Carbohydrazide (hereafter, CDH) metal complexes are expected to be a new gas generant for automobile air bags. After the previous report[4~7], the combustion reaction of the Zn and Mn complexes with various oxidizing a gents ($KClO_4$, $KBrO_3$, KNO_3 and $Sr(NO_3)_2$) was investigated by thermal analysis and the measurement of the heat of combustion, the burning temperature and the burning rate.

During the decomposition at a slow heating rate, such as in thermal analysis, the initial temperature of the reaction in the binary system with $KBrO_3$ was the lowest with the most vigorous reaction in both complexes. Furthermore, it was clear that the reactivity increased with the addition of CuO to the Zn complex/oxidizing agents system.

In the Zn complex, the heat of combustion at a stoichiometric composition increased in the order of $Sr(NO_3)_2$, KNO_3, $KClO_4$ and $KBrO_3$ of the oxidizing agent. However, this tendency was inconsistent with that of the calculated value. The burning rate in the complex/$KBrO_3$ system was the highest of all systems and increased in the order of the above oxidizing agents with the same tendency as the heat of combustion. The burning rate in the Zn complex/ oxidizing agent/CuO system seems to be governed by the heat of combustion and the reaction rate.

On the other hand, in the Mn complex, both the heat of combustion and the burning rate increased in the order of $Sr(NO_3)_2$, $KBrO_3$ and $KClO_4$, agreeing with the tendency of the calculated value. The burning rate in the Mn complex/oxidizing agent system seemed to be governed by the heat of combustion. However, in the mixture system with $KClO_4$, the pressure exponent was larger, and no combustion occurred at atmospheric pressure.

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1. Introduction

Recently, automobiles sold in Japan have been equipped with an airbag system for safer driving. As candidates for the non azide gas generant in an airbag system, tetrazole derivatives[1], urazole[2] and azodicarboamide[3] were chosen for this 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 generants.

In previous reports[4~7], in order to search after the possibility of the practical application of CDH, various CDH metal complexes were synthesized and their thermal decomposition behaviors were investigated, because the thermal stability and reactivity become larger by coordinating of CDH to a metal compared with the CDH only.

In this report, the combustion reaction for the Zn and Mn complex nitrates of CDH ($M(CDH)_3(NO_3)_2$, M=Zn, Mn) with oxidizing agents, such as potassium perchlorate ($KClO_4$), 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 combustion, the burning temperature and the burning rate. The combustion reaction of the Mg complex nitrate of CDH was investigated in a previous report[7].

2. Experiment

2.1 Reagents

The Zn and Mn complex nitrates of CDH were synthesized by a previously reported method[4]. The oxidizing agents were Wako pure chemical reagent grade: potassium perchlorate ($KClO_4$), potassium bromate ($KBrO_3$), potassium nitrate (KNO_3) and strontium nitrate ($Sr(NO_3)_2$. Reagents screened under 63 μm were mixed using the Irie V-1 mixer. For the Zn complex/oxidizing agents, CuO of 10% by a weight ratio was further added as an oxidizing agent, for no combustion or no ignition occurred in a stoichiometric binary system with any oxidizing agent. Five kinds of samples were prepared by mixing: a stoichiometric composition and two compositions each of positive and negative oxygen balance based on eqs. 1~4. Table 1 shows these compositions.

$$Zn(CDH)_3(NO_3)_2+1.52KClO_4+0.94CuO \rightarrow ZnO+7N_2+3CO_2+1.52KCl+9H_2O+0.94Cu \quad (1)$$

$$Zn(CDH)_3(NO_3)_2+1.97KBrO_3+1.10CuO \rightarrow ZnO+7N_2+3CO_2+1.97KBr+9H_2O+1.10Cu \quad (2)$$

$$Zn(CDH)_3(NO_3)_2+2.41KNO_3+0.98CuO \rightarrow ZnO+8.2N_2+3CO_2+1.2K_2O+9H_2O+0.98Cu \quad (3)$$

Table 1 Compositions of mixtures

oxidizing agent	$Zn(CDH)_3(NO_3)_2$/oxidizing agent/CuO		oxygen balance (g/100g)
	(mol)	(wt.)	
$KClO_4$	42.1/25.9/32.0	75.9/14.1/10	-10.0
	35.0/35.7/29.4	68.9/21.2/10	- 5.0
	29.0/43.9/27.1	61.8/28.2/10	0
	23.8/51.0/25.2	54.7/35.3/10	+ 5.0
	19.3/57.2/23.5	47.6/42.4/10	+10.0
$KBrO_3$	39.5/28.5/32.0	71.3/18.7/10	-10.0
	31.4/39.3/29.3	61.9/28.1/10	- 5.0
	24.6/48.3/27.1	52.5/37.5/10	0
	18.7/56.2/25.1	43.1/46.9/10	+ 5.0
	13.7/62.9/23.4	33.7/56.3/10	+10.0
KNO_3	36.7/34.8/28.5	74.5/15.5/10	-10.0
	28.9/46.0/25.1	66.7/23.3/10	- 5.0
	22.8/54.8/22.4	58.9/31.1/10	0
	17.8/62.0/20.3	51.0/39.0/10	+ 5.0
	13.8/67.8/18.4	43.2/46.8/10	+10.0
$Sr(NO_3)_2$	44.5/20.8/34.7	74.0/16.0/10	-10.0
	37.5/29.6/32.9	66.0/24.0/10	- 5.0
	31.3/37.5/31.2	58.0/32.0/10	0
	25.6/44.7/29.7	49.9/40.1/10	+ 5.0
	20.5/51.2/28.3	41.9/48.1/10	+10.0

$$Zn(CDH)_3(NO_3)_2+1.20Sr(NO_3)_2+1.00CuO \rightarrow ZnO+8.2N_2+3CO_2+1.2SrO+9H_2O+1.00Cu \quad (4)$$

For the Mn complexes, only the results in a stoichiometric system were reported, because the same composition dependence as that in the Mg complex/oxidizing agents without CuO was obtained, as previously reported[7]. In both complexes, the amount of the oxidizing agent per 1 mol of the complex at a stoichimetric composition, respectively, is 7/4 mol of $KClO_4$, 7/3 mol of $KBrO_3$, 14/5 mol of KNO_3 and 7/5 mol of $Sr(NO_3)_2$.

2. 2 Apparatus and method

The differential thermal analysis and the gravimetry were 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 reaction was measured using a Shimadzu CA-4 Type Automatic Bomb calorimeter under Argon. The experimental results at the ambient pressure showed a dispersion of measurement values of 3% to 4% over the pressure range of 1.1 MPa to 3.1 MPa. There was no combustion at 0.1 MPa and, therefore, the measurement was carried out at 1.1 MPa.

The measurement of the burning rate was carried out under the following conditions. A preliminary experiment showed that the linear burning rate in the packing fraction range of 0.65 to 0.70 became smaller as the packing fraction increased, while the mass burning rate was independent of it. When the diameter of the burning tube was 6 mm, the burning rate had a maximum value. 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 over the pressure range of 0.1 to 4.1 MPa and the influence of the composition on the linear burning rate was investigated at 1.1 MPa. The linear burning rate was determined by the time that was needed for the combustion wave to proceed 10 mm.

The burning temperature was also measured by using the same packing fraction and burning

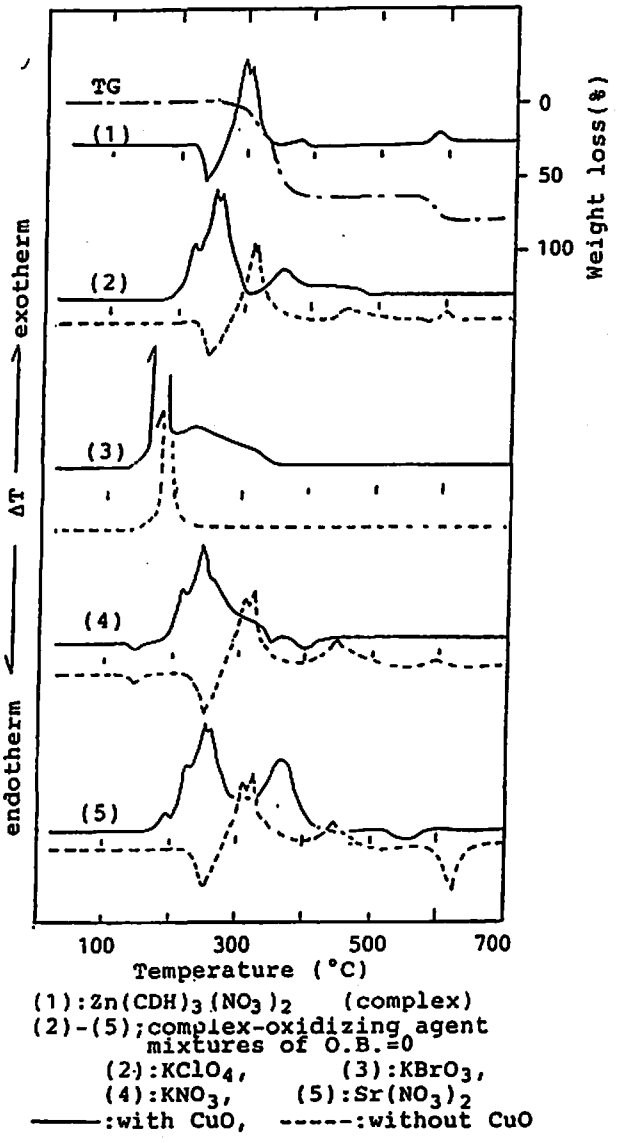

Fig. 1 DTA curves of Zn-complex and mixtures in case (1) TG curve is shown with DTA curves

tube diameter used 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 Yokogawahokusinn 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 Zn complex nitrate of CDH and its stoichiometric mixtures with various oxidizing agents. The Zn complex gradually decomposed after melting at 220 ℃, and the main reaction

was completed at about 350 ℃. The following small exothermic peak was then found; this peak might be due to the decomposition of the residue in the main reaction. The final residue was thought to be ZnO from the final weight loss and the results of the X-ray diffraction.

In the binary systems with various oxidizing agents, there was little distinction from the results in the complex only, except for the complex/$KBrO_3$ system. In the Zn complex/$KBrO_3$ system, the vigorous exothermic decomposition took place at a lower temperature than the melting point of the Zn complex. The final weight loss was 57.3%, which was inconsistent with the theoretical value, 42.3%. This might be attributed to the scattering of the sample due to the vigorous decomposition behavior.

On the other hand, in all tertiary systems with CuO, the initial temperature of the reaction was lower than the melting point of the Zn complex, so that the thermal reactivity was supposed to become higher with the addition of CuO. Particularly, in the system of the Complex/$KBrO_3$/CuO, the initial temperature of the exothermic peak was the lowest with the most vigorous reaction. From these results, the addition of CuO was supposed to raise the combustion reactivity.

Fig. 2 shows the results of the thermal analysis for the Mn complex nitrate of CDH and its stoichiometric mixtures with various oxidizing agents. The Mn complex gradually decomposed after melting at 200 ℃, and the final product was MnO. The final weight loss was 84%, being consistent with the theoretical value for the metallic oxide of the residue (84.2%). As for the binary system, the same results as in the case of the Zn complex were obtained in the thermal reaction with various oxidizing agents. The reaction with the oxidizing agent, except for $KBrO_3$, was supposed to quietly progress. In the system of the Mn complex/$KBrO_3$, the initial temperature of the exothermic reaction was 150 ℃ with vigorous reaction. The final weight loss in this system was 80%, which was inconsistent with the theoretical value for the metallic oxide of

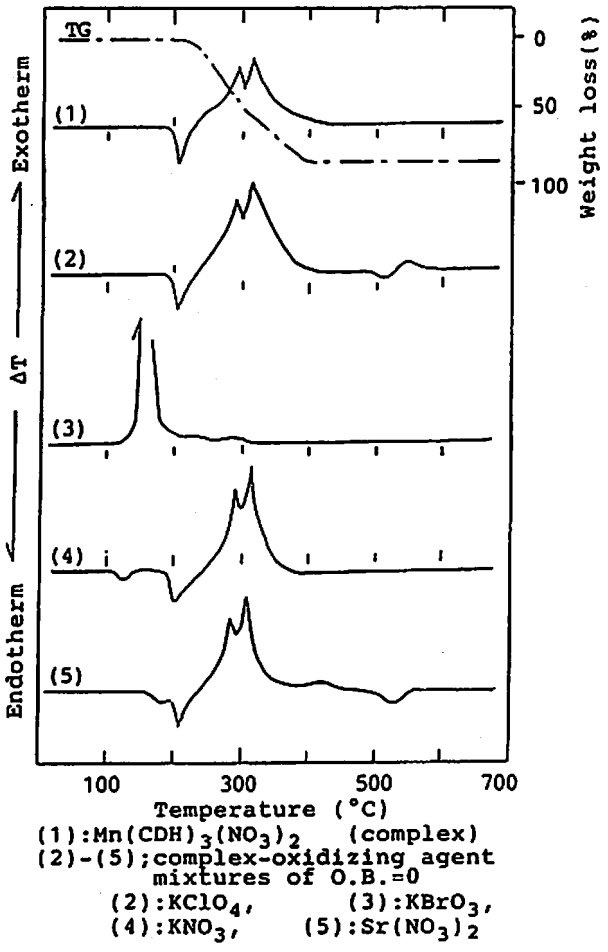

Fig. 2 DTA and TG curves of Mn-complex and mixtures

the residue (58.4%). In the binary system, except for $KBrO_3$, the final weight loss was 65% to 70%, being close to the theoretical value at stoichiometric composition. However, in the case of $Sr(NO_3)_2$ and $KClO_4$, the unreactive oxidizing agent was found to decompose above 500 ℃.

3. 2 Heat of combustion

Fig. 3 gives the heats of reaction for Zn complex nitrate of CDH/oxidizing agent/CuO measured under Ar. As previously mentioned, no ignition occurred without the addition of CuO. In all systems, the heat of combustion had a maximum value at the stoichiometric composition, i.e., oxygen balance = 0. The calorific amount at the stoichiometric composition increased in the order of KNO_3, $Sr(NO_3)_2$, $KClO_4$ and $KBrO_3$ of the oxidizing agent.

Eqs. 5～8 show the calorific amount calculated based on eqs. 1～4 as a function of A, in which A is the heat of formation of the Zn complex.

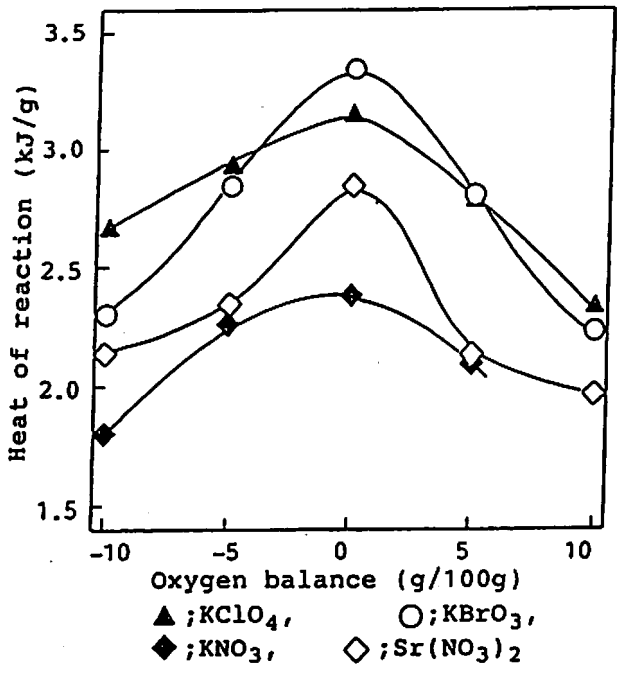

Fig. 3 Heat of reaction for Zn-complex mixtures with CuO at a pressure of 1.1 MPa

$KClO_4$/CuO system ;-5.314-A/745.0kJ/g (5)
$KBrO_3$/CuO system ;-4.621-A/876.2kJ/g (6)
KNO_3/CuO system ;-4.088-A/781.3kJ/g (7)
$Sr(NO_3)_2$/CuO system ;-4.392-A/793.2kJ/g (8)

Over the range of -1000 to 1000 kJ/mol of A, the heat of reaction based on eqs. 5~8 increased in the order of KNO_3, $Sr(NO_3)_2$, $KBrO_3$ and $KClO_4$, which was inconsistent with the tendency of the experimental values. Though the fractional decomposition may be low in the mixture system with $KClO_4$, the diffraction pattern of unreactive $KClO_4$[9] (Fig. 4) could not be identified in the combustion residue. Furthermore, as shown in Fig. 4, CuO may be reduced to Cu_2O in some oxidizing agents. But this was difficult to be identified, because of the small diffraction pattern[9] of copper oxide. In any case, the reverse of the heat of combustion to the calculated value cannot be understood. In the mixture systems with KNO_3 and $Sr(NO_3)_2$, the carbonate[9] was formed by the production of CO_2 and H_2O.

For the heat of combustion of the Mn complex nitrate of CDH, Table 2 lists the measurement and the calculation results[8] as a function of B, where B is the heat of formation for the Mn complex. The tendency of the calculation results was consistent with that of the experimental calorific amount at a stoichiometric composition. In the mixture system with KNO_3, no com-

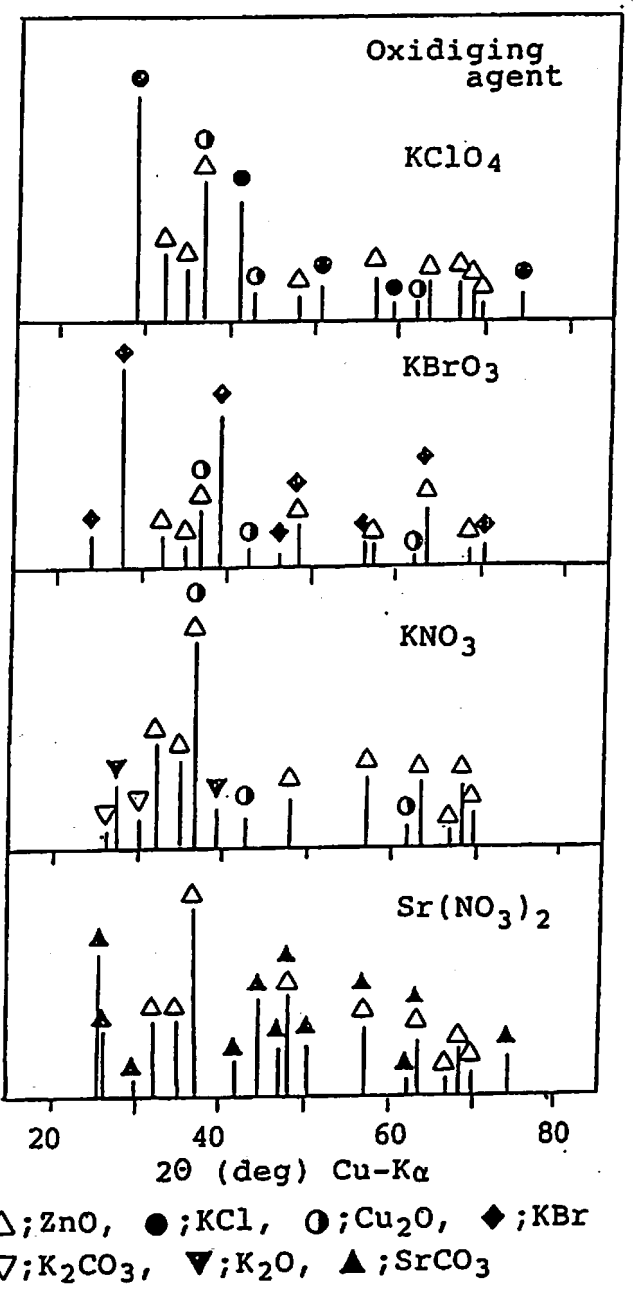

Fig. 4 XRD patterns of reaction residue for Zn-complex mixtures

Table 2 Heat of reaction for Mn complex mixtures

Oxidizing agent	Heat of reaction (kJ/g)	
	experimental	Caluculated
$KClO_4$	-4.61	-5.99-B/691.6
$KBrO_3$	-3.78	-5.03-B/838.6
KNO_3	—	-4.45-B/732.0
$Sr(NO_3)_2$	-3.75	-4.83-B/745.4

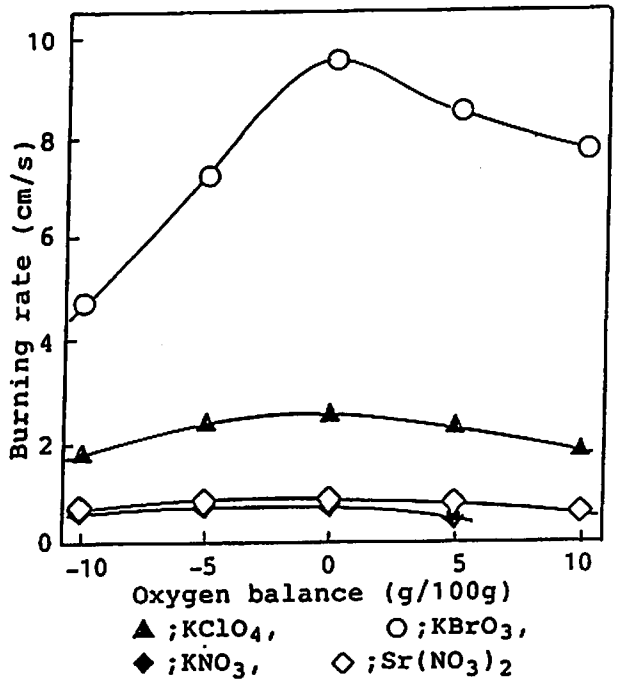

Fig. 5 Burning rate for Zn-complx mixtures at a pressure of 1.1 MPa

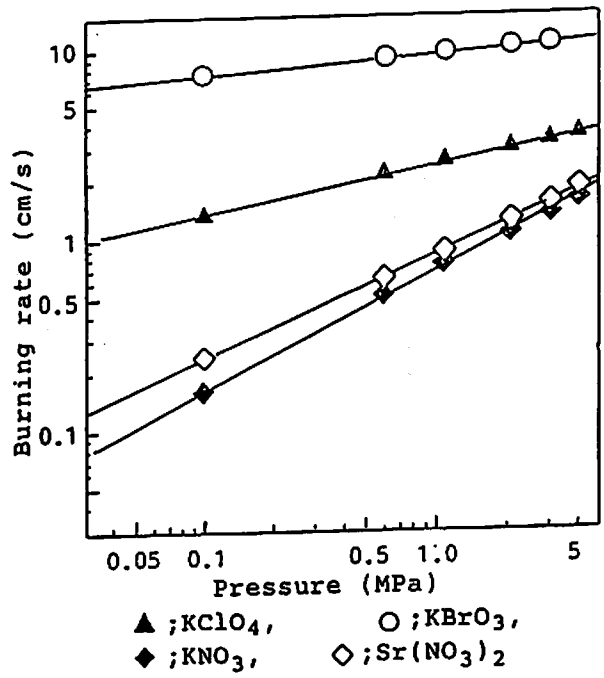

Fig. 6 Burning rate characteristics of stoichiometric mixtures of Zn-complex.

bustion but only melting might occur in the vicinity of the ignition wire due to the lack of a calorific amount.

3. 3 Burning rate

Fig. 5 gives the results of the linear burning rate for various compositions for the Zn complex. The burning rate had a maximum value at a stoichiometric composition in any system. The composition dependence was slight in three systems, except for the complex/$KBrO_3$ system. The maximum burning rate in the Zn complex/$KBrO_3$ system was remarkably higher compared with other ones. The much higher burning rate than one in other systems seemed to be caused by the much higher reactivity based on the results of the DTA curves. This was also consistent with the results of the heat of combustion. The burning temperature decreased in the order of the system with $KBrO_3$, $KClO_4$ and $Sr(NO_3)_2$ or KNO_3. (1600 ℃, 1500 ℃ and 1400 ℃).

Fig. 6 shows the pressure dependence of the burning rates at a stoichiometric composition. Table 3 shows the constant a and the pressure exponent n estimated based on Vieille's equation ($V=aP^n$). Under the experimental pressure of 1.1 MPa, the burning rate was consistent with the tendency seen in Fig. 5. The pressure exponent was larger in two mixture systems with nitrates as an oxidizing agent. Furthermore, for the mixture system with $KBrO_3$, the constant a in the Zn complex was three times as large as that in the Mg complex. Because the constant a in all systems was large compared with the value in the Mg complex, the effect of the addition of CuO was thought to be siginificant in view of the DTA curve (Fig. 1).

Table 3 Constant a and pressure exponent n of burning rate for Zn-complex of stoichiometric composition (O.B.=0)

Oxidizing agent	a	n
$KClO_4$/CuO	2.411	0.250
$KBrO_3$/CuO	9.343	0.104
KNO_3/CuO	0.682	0.622
$Sr(NO_3)_2$/CuO	0.834	0.541

Fig. 7 shows the pressure dependence of the burning rate at a stoichiometric composition for the Mn complex. Table 4 lists the constant a and the pressure exponent n estimated based on Vieille's equation ($V=aP^n$). No combustion occurred in the mixture system of Mn complex with KNO_3. Under high pressurized conditions, the burning rate in the complex/$KClO_4$ system

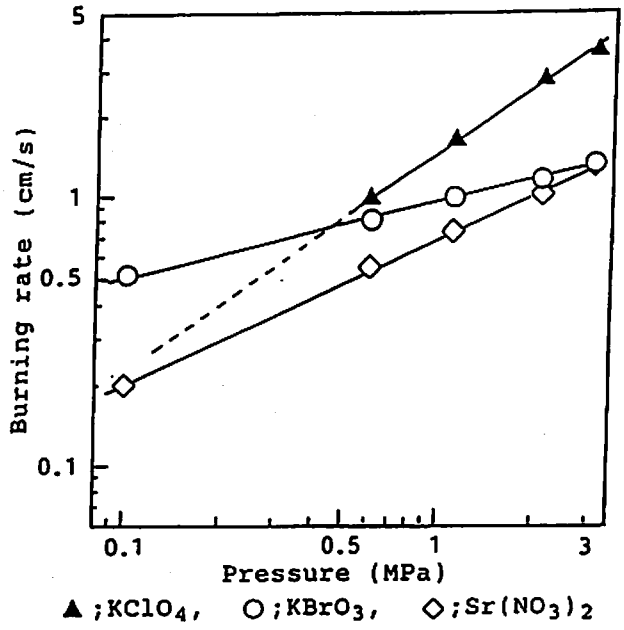

Fig. 7 Burning rate characteristics of stoichiometric mixtures of Mn-complex

Table 4 Constant a and pressure exponent n of burning rate for Mn-complex of stoichiometric composition (O.B.=0)

Oxdizing agent	a	n
$KClO_4$	1.464	0.801
$KBrO_3$	0.936	0.268
$Sr(NO_3)_2$	0.694	0.537

was the highest of all the systems, unlike the case of the Mg and Zn complexes. Because the tendency of obtained results was consistent with that of the heat of combustion, the burning rate in the Mn complex seemed to be governed by the heat of combustion. This tendency also agreed with that of the burning temperature, which was 1800 ℃ in the complex/$KClO_4$ system and 1600 ℃ in the other systems. The pressure exponent was the largest in the Mn complex/$KClO_4$ system, and no ignition and combustion occurred under atmospheric pressure.

4. Conclusions

The combustion reaction of the CDH complex nitrate of Zn and Mn 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 of the decomposition at a slow heating rate, such as thermal analysis, the initial temperature of the reaction in the binary system with $KBrO_3$ was the lowest with the most vigorous reaction in both complexes. Furthermore, it was clear that the reactivity at a slow heating rate rose by the addition of CuO in the Zn complex/oxidizing agents system.

In the Zn complex with CuO, the heat of combustion at a stoichiometric composition increased in the order of $Sr(NO_3)_2$, KNO_3, $KClO_4$ and $KBrO_3$ of the oxidizing agent. However, this tendency was inconsistent with that of the calculated value. Furthermore, the burning rate also increased in the order of the results of the heat of combustion, and that of the complex/$KBrO_3$/CuO was the highest of all the tertiary systems. The burning rate in the Zn complex/oxidizing agent/CuO system seemed to be governed by the heat of combustion and the reaction rate.

On the other hand, in the Mn complex, both the heat of combustion and the burning rate increased in the order of $Sr(NO_3)_2$, $KBrO_3$ and $KClO_4$, agreeing with the tendency of the calculated value. The burning rate in the Mn complex/oxidizing agent system seemed to be governed by the heat of combustion. However, in the mixture system with $KClO_4$, the pressure exponent was large and no combustion occurred at atmospheric pressure.

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カルボノヒドラジド金属錯体硝酸塩の熱挙動(第5報)
—亜鉛錯体及びマンガン錯体と酸化剤混合系の燃焼反応—

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自動車用エアバックのガス発生剤として，前報に引き続きカルボノヒドラジドの亜鉛及びマンガン錯体硝酸塩について，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及び燃焼熱，燃焼温度や燃焼速度の測定を行い，それらの燃焼反応性について考察した。

両錯体とも臭素酸カリウムと混合するとき，最も低温で，しかも激しく反応する。亜鉛錯体の燃焼性を向上させるために添加したCuOの効果は，熱分析のような穏和な加熱条件下で大きい。

亜鉛錯体に関して，CuOを10%添加した種々の酸化剤成分との化学量論比混合物の反応熱は，$KBrO_3 > KClO_4 > KNO_3 > Sr(NO_3)_2$の順になり，計算値は，前2者に関して逆の結果となった。また$KBrO_3$系の燃焼速度が大きく，酸化剤の比較では反応熱の順に大きくなった。燃焼温度も同じ順に高くなり，この系の燃焼速度は，反応熱及び反応速度が支配的となることが分かった。

一方，Mn錯体では反応熱，燃焼速度ともに$KClO_4 > KBrO_3 > KNO_3 > Sr(NO_3)_2$の順番となった。この系の燃焼速度は反応熱が支配的と考えられる。しかし，$KClO_4$系の圧力指数が大きく，常圧下では着火しなかった。また，硝酸カリウムの混合物では，本実験で行った着火法では燃焼させることができなかった。

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