

## The thermal behavior of the carbonylhydrazide complexes of certain metals (VII)

### Gases evolved during the decomposition for the Zn and Mn complexes

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Carbonylhydrazide (hereafter, CDH) metal complexes are expected to be a new gas generant for automobile air bags. In the fifth report, the combustion reaction of the Mn and Zn complexes 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 this report, the evolved gas behavior was investigated for the Zn and Mn complex mixtures with various oxidizing agents. The used oxidizing agents were potassium perchlorate ( $\text{KClO}_4$ ), potassium bromate ( $\text{KBrO}_3$ ), potassium nitrate ( $\text{KNO}_3$ ) and strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ ). In the binary system with  $\text{Sr}(\text{NO}_3)_2$ , 10% CuO was added as another oxidizing agent.

The stability of the Mn complex of CDH was the lowest in the Zn, Mn and Mg complex nitrates of CDH; the result for the Mg complex was reported in the sixth report. In addition, the evolved amount of all gases and nitrogen gas was also the largest for the Mn complex.

The effect of  $\text{KBrO}_3$  as the oxidizing agent was the largest of all the systems. When using  $\text{KBrO}_3$ , the initial temperature of the reaction was the lowest with the most vigorous reaction and the evolved amounts of the nitrogen and carbon dioxide gases were the largest of all the systems. In the mixture system with  $\text{Sr}(\text{NO}_3)_2$ , the evolved amount of the  $\text{N}_2$  gas was the lowest, but that was increased with the addition of CuO.

#### 1. Introduction

As a non-azide gas generant in an airbag sys-

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tem for safer driving, tetrazole derivatives<sup>1)</sup>, urazole<sup>2)</sup> and azodicarboamide<sup>3)</sup> were the subjects of this study. The authors evaluated carbonylhydrazide (hereafter, CDH), which is composed of four nitrogen atoms, a carbon atom and an oxygen atom; various CDH metal complexes were synthesized and their thermal decomposition behaviors were investigated in previous reports<sup>4~9)</sup>.

The combustion reaction for the Mg complex nitrates of CDH ( $\text{Mg}(\text{CDH})_3(\text{NO}_3)_2$ ) with various oxidizing agents was reported in the fourth<sup>7)</sup> of a series of reports on the metallic complex of

Table 1 Compositions of mixtures

No	Mixtures	mol/mol	wt./wt.
1	ZnCDH*/CuO	12.5/87.5	45.2/54.8
2	ZnCDH/KClO <sub>4</sub>	36.4/63.6	65.5/34.5
3	ZnCDH/KBrO <sub>3</sub>	30.0/70.0	54.1/45.9
4	ZnCDH/Sr(NO <sub>3</sub> ) <sub>2</sub>	41.7/58.3	60.8/39.2
5	ZnCDH/Sr(NO <sub>3</sub> ) <sub>2</sub> /CuO	31.7/38.4/29.9	56.0/34.0/10.0
6	MnCDH*/CuO	12.5/87.5	44.7/55.3
7	MnCDH/KClO <sub>4</sub>	36.4/63.6	64.9/35.1
8	MnCDH/KBrO <sub>3</sub>	30.0/70.0	53.5/46.5
9	MnCDH/Sr(NO <sub>3</sub> ) <sub>2</sub>	41.7/58.3	60.3/39.7
10	MnCDH/Sr(NO <sub>3</sub> ) <sub>2</sub> /CuO	31.7/38.4/29.9	57.4/32.6/10.0

\*ZnCDH = Zn(CDH)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>, \*\*MnCDH = Mn(CDH)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>

CDH<sup>4-9</sup>). Similarly, that for the Zn and Mn complexes was reported in the fifth one<sup>5</sup>). On the other hand, for the Mg complex, the evolved gas behavior in the complex only and in the mixtures with various oxidizing agents during the decomposition were investigated in the third<sup>6</sup>) and sixth reports<sup>9</sup>), respectively.

In this report, the evolved gas behavior in the Zn and Mn complex nitrates of CDH only was quantitatively investigated during the isothermal decomposition at 260 °C. Furthermore, that in mixtures with various oxidizing agents was also reported; the oxidizing agents were potassium perchlorate (KClO<sub>4</sub>), potassium bromate (KBrO<sub>3</sub>), potassium nitrate (KNO<sub>3</sub>) and strontium nitrate (Sr(NO<sub>3</sub>)<sub>2</sub>). In the case using Sr(NO<sub>3</sub>)<sub>2</sub>, CuO was added as a part of the oxidizing agent in a ratio of 10% for all components.

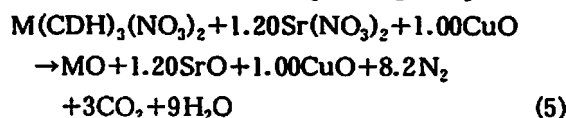
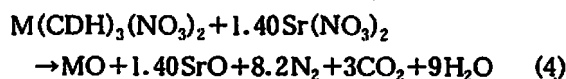
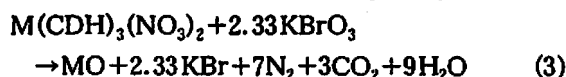
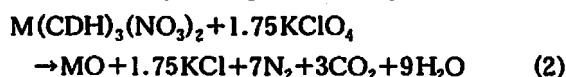
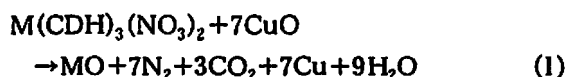
## 2. Experiment

### 2.1 Reagents

The complexes of CDH were synthesized by a previously reported method<sup>4</sup>). The oxidizing agents were Wako Pure Chemical reagent grade. Reagents screened to under 63 μm were mixed for sixty minutes using splittable chopsticks on parchment paper.

The mixture compositions were stoichiometric ones based on eqs.1~4; these are the equations common to the Zn and Mn complexes. Furthermore, for the binary system with Sr(NO<sub>3</sub>)<sub>2</sub> as the oxidizing agent, CuO was added as a part of the oxidizing agent in a weight ratio

of 10% for all components (eq.5). Table 1 shows the mixture compositions.



(M: Zn and Mn)

### 2.2 Apparatus and method

Differential thermal analysis and thermogravimetry were carried out using a Rigaku TAS-200 Thermal Analyzer. The sample container was an open alumina cell and the sample amount was five mg. The sample was heated to 800 °C at a heating rate of 20 °C/min. under air.

The analysis of the evolved gas was carried out by two methods. One was a method in which the sample was decomposed under isothermal conditions. The other one was the method in which the sample was burned in a tube. For the former, a glass tube (A) (16 mm, inside diameter) was fixed in a furnace kept at 400 °C. Fifty mg of the sample was weighed into a boat-shaped container and the container was inserted into the glass tube (A). The decomposition was carried

Table 2 Conditions for gas chromatograph

Gases	N <sub>2</sub> , CO	N <sub>2</sub> O, CO <sub>2</sub>
Column	Molecular sieve 5A	Activated charcoal
Particle size	60~80 mesh	60~80 mesh
Length	2 m	1 m
Temp.	40°C	40°C
Carrier gas	He, 20 ml/min.	He, 60 ml/min.

out under flowing He gas at 20 ml/min. The evolved gases were collected in a collection bag (Tedlar bag, 350ml capacity). The amounts of the N<sub>2</sub>, CO, CO<sub>2</sub> and N<sub>2</sub>O gases evolved were quantified using a Shimadzu GC-4C Gas Chromatograph (hereafter, GC). Table 2 shows the measurement conditions for the GC. The NO and NO<sub>2</sub> gases were quantitatively analyzed by a Gastec gas detector tube. The NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub> gases were quantified by the indophenol method<sup>10)</sup> ( $\lambda = 630 \text{ nm}$ ) and the P-aminobenzaldehyde method<sup>11)</sup> ( $\lambda = 458 \text{ nm}$ ), respectively. For the latter, 1g of the sample was loaded at a 0.6 packing fraction in a 6 mm I.D. aluminum burning tube. The sample was ignited in the burning container (18.3 mm inside diameter; 93.2 mm height). The evolved gas was quantitatively analyzed by the already mentioned method.

The decomposition and combustion residue was analyzed by X-ray diffraction using a Nippon Detam JDX-3500.

### 3. Results and discussion

#### 3.1 Thermal analysis

The results of the thermal analysis for mixture Nos.2~5 and Nos.7~9 in Table 1 were already reported in the fifth<sup>8)</sup> of a series of reports for the metal complexes of CDH<sup>4~9)</sup>. For the mixture with KBrO<sub>3</sub> in all binary systems with various oxidizing agents without CuO, the most vigorous decomposition was observed at the lowest temperature of all the systems, as already reported<sup>8)</sup>. With the addition of CuO to the binary systems, the reactivity increased over a narrower reaction temperature range at a lower temperature compared with the binary systems without CuO<sup>7)</sup>.

Fig.1 shows the results of the thermal analysis for the Mn complex of CDH, the stoichiometric

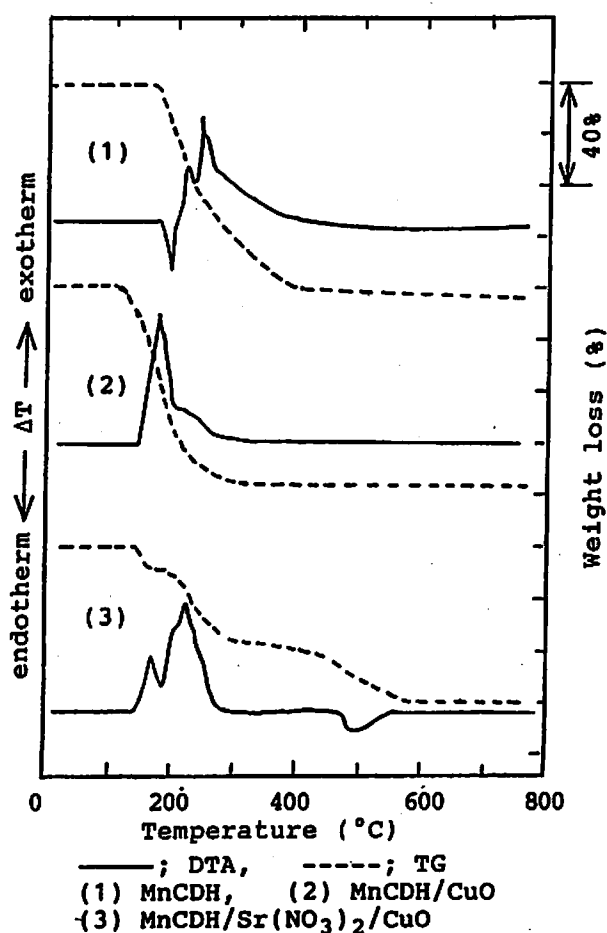


Fig.1 DTA and TG curves of the Mn complex and mixtures

mixtures with CuO and with Sr(NO<sub>3</sub>)<sub>2</sub> and 10% CuO. The initial temperature of the decomposition for the Mn complex of CDH was the lowest of all the CDH metal complexes<sup>4,5)</sup>. The decomposition reaction gradually occurred after the melting as in the case of the other metal complexes of CDH. In the binary system with CuO, the Mn complex nitrate of CDH started to exothermally decompose at a lower temperature than the melting point of the complex, which was consistent with the tendency in the Mg and Zn complexes. The decomposition reaction fin-

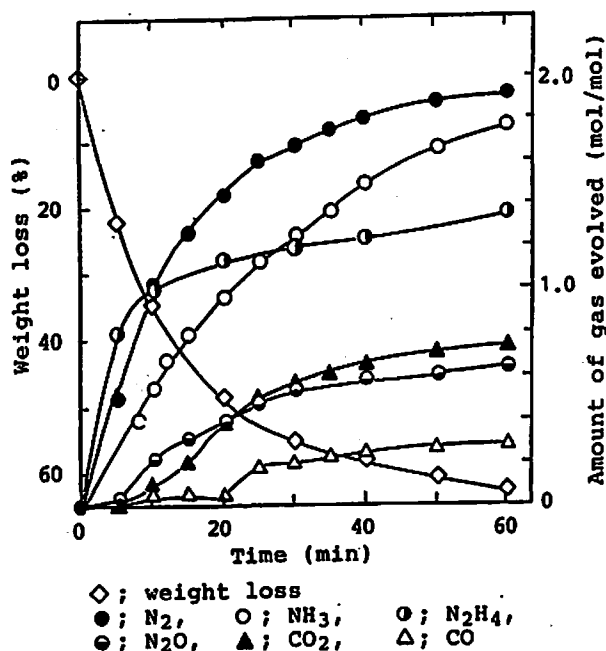


Fig. 2 Amount of gas evolved at 260°C for the Zn complex

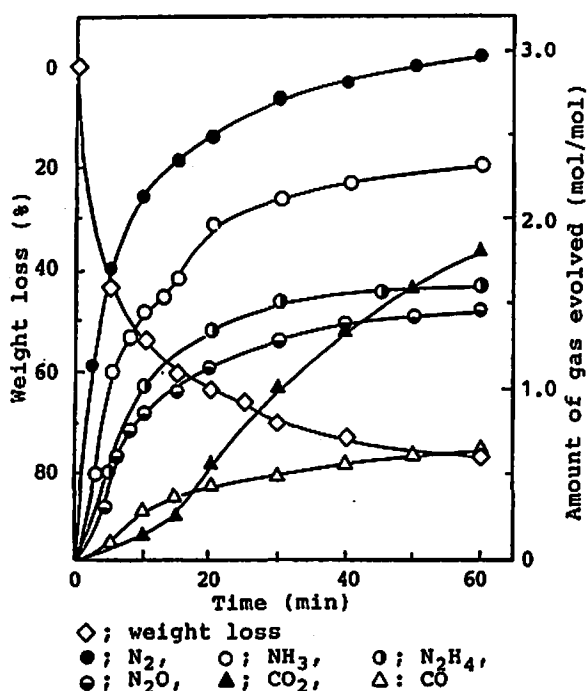


Fig. 3 Amount of gas evolved at 260°C for the Mn complex

ished at a lower temperature than the one for the Mn complex only.

When using  $\text{Sr}(\text{NO}_3)_2$  as the oxidizing agent with  $\text{CuO}$ , a part of the  $\text{Sr}(\text{NO}_3)_2$  remained unreacted and it decomposed above 500°C (temperature of the decomposition, 570°C<sup>(12)</sup>). However, the reactivity with the Mn complex increased with the addition of  $\text{CuO}$ .

### 3.2 Analysis of the evolved gas

#### 3.2.1 Quantitative analysis of the evolved gas during the isothermal decomposition

The evolved gas behavior for the Mg complex corresponded to the tendency in the DTA curve, and mainly  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$  gases were evolved during the decomposition<sup>(6)</sup>. Furthermore, the kind of the evolved gas was unchanged for the stoichiometric mixture with various oxidizing agents<sup>(12)</sup>. The same tendency was seen in the Zn and Mn complexes based on the TG-MS analysis; these results are not shown in this report, because they were consistent with the tendency in the Mg complex<sup>(12)</sup>. For the Zn and Mn complexes, Figs. 2 and 3 show, respectively, the amount of the gas evolved versus time during these isothermal decompositions at 260°C. Carbon monoxide and carbon dioxide evolved after the evolution of the gases including the nitrogen atom except for  $\text{N}_2\text{O}$  gas, such as nitro-

Table 3 Amount of gas evolved at 260°C for 1 hour (unit: mol/mol)

Gases	Mixtures		
	MgCDH	MgCDH	MnCDH
$\text{N}_2$	1.99	1.96	2.98
$\text{NH}_3$	1.89	1.85	2.32
$\text{NH}_2\text{NH}_2$	1.46	1.49	1.64
$\text{N}_2\text{O}$	0.75	0.70	1.12
$\text{NO}_2$	0.0011	0.0007	0.0023
$\text{CO}$	0.05	0.29	0.52
$\text{CO}_2$	0.75	0.81	2.28
N number	10.29	10.15	13.80
%	73.5	72.5	98.6
C number	0.80	1.10	2.80
%	26.7	36.7	93.3

\*MCDH= $\text{Mg}(\text{CDH})_3(\text{NO}_3)_2$ , M=Mg, Zn, Mn

gen and ammonia gases.  $\text{N}_2\text{O}$  gas evolved after the evolution of the other gases including the nitrogen atom, and the evolution of  $\text{N}_2\text{O}$  was thought to be caused by the decomposition of the nitrate.

The evolved amount of all gases during the decomposition of the Mn complex was larger than that for the Mg and Zn complexes. Table 3 lists the amount of the evolved gas at 260°C for

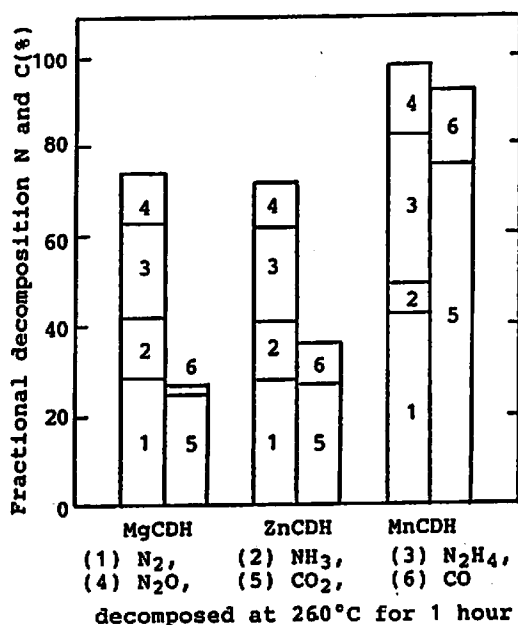


Fig. 4 Fractional evolution of gas evolved during the isothermal decomposition at 260°C for 1 hour

1 hour, and Fig. 4 shows the results in Table 3 with converting the amount of the gas evolved into the fractional evolution. In this table, the results for the Mg complex of CDH are also shown, because hydrazine was not analyzed in the third report. The mass balance of nitrogen and carbon atoms in the gas was fairly good, above 90%, for the Mn complex might be more unstable than the other complexes of CDH, as

reported in the first study. The fractional evolution of nitrogen gas was 42.6% even in the Mn complex.

### 3. 2. 2 Gas evolved upon igniting under the isothermal conditions

At 400°C, the decomposition of the sample progressed so rapidly that ignition occurred. Tables 4 and 5 show the analysis results of the evolved gas upon ignition at 400°C for the Zn and Mn complexes, respectively. The amount of the nitrogen gas evolved significantly increased compared to the results during the isothermal decomposition at 260°C. With the addition of the oxidizing agent, the amount of nitrogen gas increased, while that of ammonia and hydrazine decreased. The efficiency of the addition of the oxidizing agent when using KBrO<sub>3</sub> was the largest of all systems in both complexes. In this case, the fractional evolution of nitrogen gas was 97.4% in the Zn complex and 96.3% in the Mn complex.

The low mass balance of the nitrogen atom when Sr(NO<sub>3</sub>)<sub>2</sub> was used was obtained as a phenomenon common to the three complexes, Mg, Zn and Mn complexes. Sr(NO<sub>3</sub>)<sub>2</sub> did not seem to sufficiently react with the complex when used as the oxidizing agent. Furthermore, the low fractional evolution of the carbon dioxide gas

Table 4 The amount of gas evolved for the Zn complex and mixtures (unit: mol/mol)

Gases	Mixtures of Table 1				
	ZnCDH*	(2)	(3)	(4)	(5)
N <sub>2</sub>	4.56	5.72	6.82	6.37	6.72
NH <sub>3</sub>	0.94	1.09	0.42	1.06	6.0×10 <sup>-5</sup>
NH <sub>2</sub> NH <sub>2</sub>	1.22	0.14	0.017	0.13	0.00
N <sub>2</sub> O	0.47	0.00	0.00	0.00	0.00
NO×10 <sup>-2</sup>	0.49	2.1	0.36	1.48	4.1
NO <sub>2</sub> ×10 <sup>-4</sup>	9.0	2.7	0.5	2.9	0.38
CO	2.28	0.14	0.29	0.67	0.89
CO <sub>2</sub>	0.47	1.76	2.57	0.94	1.02
N number	13.45	12.83	14.15	14.07	13.48
%	96.1	91.7	101.1	91.4	88.7
C number	2.75	1.90	2.86	1.61	1.91
%	91.7	63.3	95.3	53.7	63.7

\*ZnCDH = Zn(CDH)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>

Table 5 The amount of gas evolved for the Mn complex and mixtures  
(unit: mol/mol)

Gases	Mixtures of Table 1				
	MnCDH*	(7)	(8)	(9)	(10)
N <sub>2</sub>	5.18	5.62	6.74	6.12	6.53
NH <sub>3</sub>	1.74	1.29	0.28	0.97	0.8
NH <sub>2</sub> NH <sub>2</sub>	0.66	0.24	0.011	0.09	0.09
N <sub>2</sub> O	0.21	0.00	0.00	0.16	0.09
NO×10 <sup>-2</sup>	8.6	2.3	2.6	4.22	3.27
NO <sub>2</sub> ×10 <sup>-4</sup>	25.0	2.3	693	0.0	16.8
CO	1.98	0.12	0.77	0.66	0.90
CO <sub>2</sub>	0.68	1.85	1.89	1.20	1.14
N number	13.85	13.03	13.88	13.75	14.25
%	98.9	93.1	99.1	89.3	93.7
C number	2.66	1.97	2.66	1.86	2.04
%	88.7	65.7	88.7	62.0	68.0

\*MnCDH = Mn(CDH)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>

was caused by fixation as SrCO<sub>3</sub>. SrCO<sub>3</sub> was formed by the reaction of SrO with the H<sub>2</sub>O and CO<sub>2</sub> decomposition products, as previously reported<sup>7)</sup>.

The amount of NOx gas evolved for the Mn complex, for the mixture system with KBrO<sub>3</sub> in particular, was larger compared with that in the Zn and Mg complexes, though the cause has not been determined yet.

#### 4. Conclusion

The evolved amount of all gases and nitrogen gas during the decomposition of the Mn complex was larger than that for the Mg and Zn complexes, for the Mn complex might be more unstable than the other complexes of CDH, as reported in the first study. The fractional evolution of nitrogen gas was 42.6% even in the Mn complex.

The amount of evolved nitrogen gas during the ignition at 400°C significantly increased compared with the results during the isothermal decomposition, and that increased further with the addition of CuO.

When KBrO<sub>3</sub> was used as the oxidizing agent, the amount of evolved nitrogen gas evolved was the largest of all the systems. KBrO<sub>3</sub> reacted the most completely with the complex of CDH of all the oxidizing agents used in these experiments.

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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7報)

—亜鉛, マンガン錯体のガス発生挙動—

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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亜鉛およびマンガン錯体を取り上げ, その性能を評価する目的で, 第5報では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。本報告では錯体単体及び過塩素酸カリウム, 臭素酸カリウム及び硝酸ストロンチウムの酸化剤と両錯体との混合物に一部酸化銅を加えた系のガス発生挙動を比較検討した。

前報に報告したマグネシウム錯体および今回の亜鉛, マンガン錯体の中ではマンガン錯体が最も不安定で, 全ガス発生量および窒素ガス発生量が大きい。

亜鉛錯体およびマンガン錯体に対する酸化剤の効果は臭素酸カリウムが最も大きく, 低い反応温度で激しく反応した。また, 窒素および二酸化炭素の発生量も最も大きくなった。硝酸ストロンチウムを用いた系では, 窒素の発生量は最も少なかったが, 酸化銅を添加することにより増大した。

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