

The thermal behavior of the carbohydrazide complexes of certain metals (1)

— The synthesis and the thermal analysis —

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The carbohydrazide (hereafter, CDH) metal complexes expected to be a gas generant for the automobile air bags were synthesized on the basis of the method by Ivanov¹⁾. For CDH metal complexes, it appeared that water affected the crystal stability. So the cause of this required investigation.

The thermal reactivity increased on coordination of CDH to a metal compared with CDH. The influence of the coordinated metal on the thermal reactivity was investigated by the initial temperature of decomposition and the activation energy of decomposition evaluated using Kissinger's equation²⁾. It was predicted that the reactivity of CDH metal nitrate complexes decreased in the order of Mn, Mg, Co, Ni and Zn. This tendency was reflected in the tendency of complex stability³⁾, and the correlation between complex stability and thermal stability was recognized in CDH metal complexes. The reactivity for perchlorate was higher than that for nitrate in the same metal complex.

1. Introduction

Recently, automobile sold in Japan have been equipped with an air bag system for safety drive. Though NaN_3 has been used as the main component of the gas generator at present, it has a treatment problem⁴⁾. Consequently, a new gas generator, which offers high thermal stability and which evolves a large amount of harmless gas on decomposition, has been desired as a substitute for NaN_3 .

CDH, which is composed of four nitrogen atoms, a carbon atom and an oxygen atom, is expected to be one of the new gas generators.

In this research, in order to investigate the possibi-

ty of practical application of CDH, various CDH metal complexes ($\text{M}(\text{CDH})_3(\text{NO}_3)_2$, $\text{M}(\text{CDH})_3(\text{ClO}_4)_2$; M =bivalent metal) were synthesized and thermal analysis was performed.

2. Experiments

2.1 Synthesis of CDH metal nitrate complex

For the CDH metal nitrate complex, hot aqueous solutions of various Wako pure chemical reagent grade metal nitrates ($\text{M}(\text{NO}_3)_2$, M =Mg, Zn, Mn, Ni, Co, Ca, Sr) and CDH from Japan Hydrazine Corporation were mixed in a mole ratio of 1:3. When ethanol was added to the cooled mixture, part of the product crystallized out of solution. The product was washed with ethanol and dried after filtration.

The CDH metal perchlorate complex was synthesized using various Wako pure chemical reagent grade metal perchlorates ($\text{M}(\text{ClO}_4)_2$, M =Mg, Zn) and CDH from Japan Hydrazine Corporation as well as nitrates.

The product was used after confirmation by elemental analysis, conductimetric titration (or absorptiometry) and chelatometric titration.

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Table 1 The identification of CDH complex of calcium

	found (%)	calcd. (%) $\text{Ca}(\text{CDH})_1(\text{NO}_3)_m(\text{H}_2\text{O})_n$	
		$l=3, m=2, n=0$	$l=2, m=2, n=1$
C*	6.68	8.29	6.63
H*	4.04	4.18	3.90
N*	38.68	45.15	38.67
$[\text{NO}_3]^{-**}$	34.35	28.55	34.23
$[\text{Ca}]^{2+***}$	11.06	9.23	11.06

*elemental analysis

**conductimetric titration

***chelatometric titration

Table 2 The identification of CDH complex of strontium

	found (%)	calcd. (%) $\text{Sr}(\text{CDH})_1(\text{NO}_3)_m(\text{H}_2\text{O})_n$	
		$l=3, m=2, n=0$	$l=2, m=2, n=0$
C*	6.11	7.48	6.12
H*	3.09	3.77	3.09
N*	35.91	40.70	35.75
$[\text{NO}_3]^{-**}$	31.54	25.74	31.65
$[\text{Sr}]^{2+***}$	22.60	18.19	22.36

*elemental analysis

**conductimetric titration

***chelatometric titration

2.2 Thermal analysis

Thermal analysis was carried out using a Rigaku TAS-200 thermal analyzer. The sample container was an open alumina cell and the amount of sample was 5 mg. The sample was heated to 600 °C in Ar atmosphere at a heating rate of 20 °C/min..

Furthermore, the heating rate was also changed to 2, 5, 10 and 20 °C/min., and we evaluated the activation energy of decomposition using Kissinger's equation²⁾.

2.3 Identification of decomposition residue

50 mg of each sample was weighed into a glass tube sealed at one end (6 mm in inside diameter and 60 mm in length) and placed in an iron block having a hole 8 mm in diameter and 50 mm in length. This block inserted into a electric furnace was heated at a heating rate of 1 °C/min, until the sample completely decomposed (see the results of thermal analysis). After cooling, the obtained decomposition residue was analyzed by X-ray diffraction using a Rigaku Rotor Flex RU-200.

3. Results and Discussion.

3.1 Synthesis of CDH complexes of certain metals

3.1.1 Nitrates of CDH metal complexes

The formation of metal nitrate complexes was confirmed by the above-mentioned analysis except for the Sr and Ca complexes. As for the Ca and Sr complexes, because of the lack of a description in the report by Ivanov et al., Tables 1 and 2 show the results of elemental analysis, etc.. The third and fourth columns of these tables show the theoretical values for $\text{M}(\text{CDH})_1(\text{NO}_3)_m(\text{H}_2\text{O})_n$ ($\text{M}=\text{Ca}$ and Sr) for comparison. There was good agreement between the calculated values for $\text{Ca}(\text{CDH})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and for $\text{Sr}(\text{CDH})_2(\text{NO}_3)_2$ and the found values, thus indicating that only two CDH molecules were coordinated to the metal.

Regarding this, the stability of the complex tend to be proportional to charge and be inversely proportional to ion radius³⁾. That is to say, the stability of the Ca and Sr complexes is lower than that of the other metal complexes, and it was thought that more

stable complex was formed because of steric hindrance, etc.. Furthermore, regarding the water of crystallization in the Ca complex, its existence was confirmed by infrared spectrum and thermal analysis. Because the crystal structures of these complexes are yet unknown, we intend to carry out structural analysis of these complexes in the future. Regarding the Ca complex, it was assumed to form a bridged complex considering from its molecular formula. Ivanov et al. reported¹⁾ that the structure of these complexes, except for Ca and Sr complexes, was a six-coordinated octahedron, in which both the terminal nitrogen atoms of CDH were coordinated to the metal.

Recrystallization from water was performed to increase the purity of the products, but the Mn and Co complexes showed a difference before and after the recrystallization. For the Mn complex, two types of crystals were yielded at the same time : $\text{Mn}(\text{CDH})_3 \cdot (\text{NO}_3)_2$ and $\text{Mn}(\text{CDH})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. The former showed a change in color from a transparency and evolved the smell of NH_3 with time. This was ascribed to gradual decomposition. CDH also displayed the same behavior of NH_3 evolution sometimes after recrystallization, although the mechanism of reaction was unexplained in this study. As the one of the possibility, the presence of water was thought to accelerate the decomposition.

On the other hand, the Co complex caused the hydration after recrystallization and a change in physical characteristics (i.e., a decrease in solubility in water) was observed. However, no decomposition with time was noted. Based on these facts, it was estimated that water affected the stability of the CDH metal complexes.

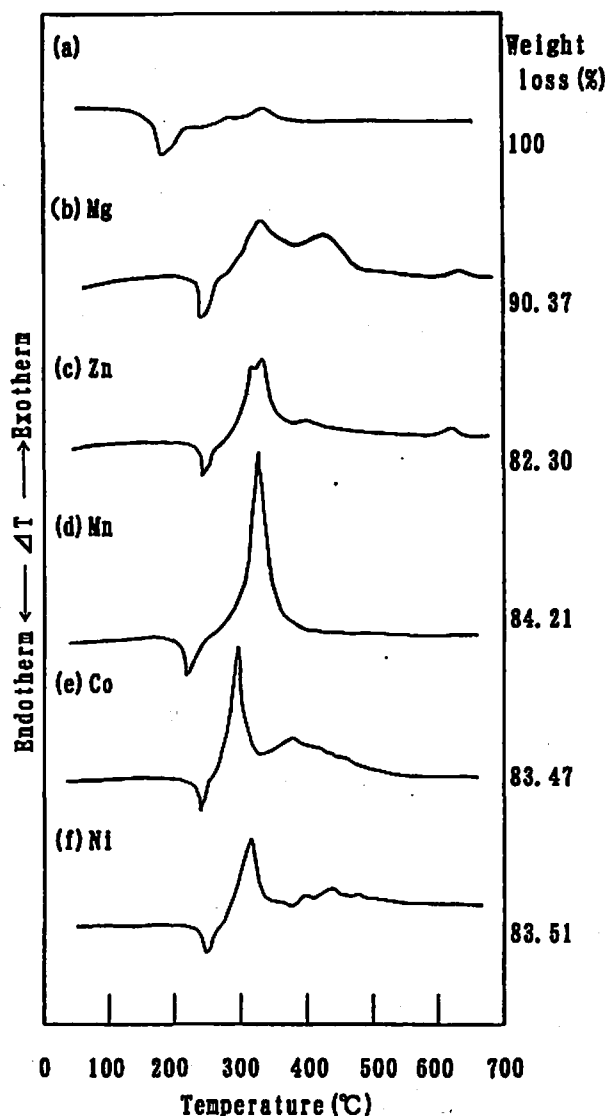
3.1.2 CDH metal perchlorate complexes

The formation of Mg and Zn perchlorate complexes ($\text{M}(\text{CDH})_3(\text{ClO}_4)_2$) was confirmed by the analysis mentioned in 2.1.3. Recrystallization from water was performed to increase the purity of the products, and both complexes didn't show a difference before and after the recrystallization.

3.2 Behavior of CDH metal complexes

3.2.1 Metal nitrate complexes

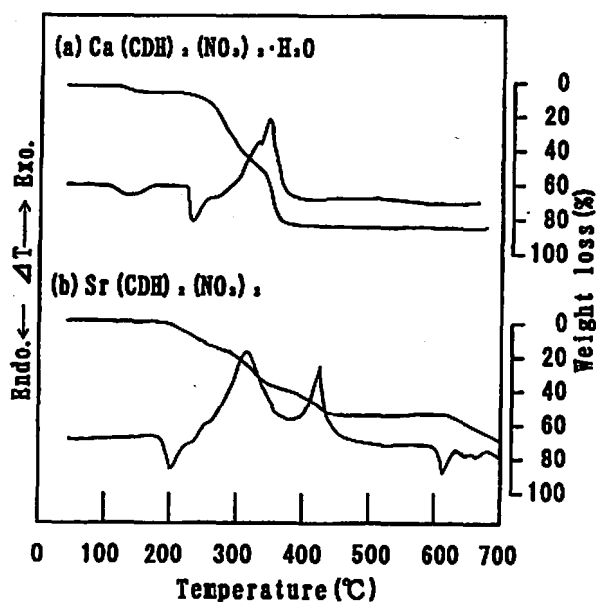
Fig. 1(a) shows the result of the thermal analysis for CDH itself, and Fig. 1(b)~(f) shows those for various CDH metal nitrate complexes. The final



Sample : 5mg , dT/dt : 20°C/min.
Atmosphere : Ar
(a) CDH, (b) ~ (f) : $\text{M}(\text{CDH})_3(\text{NO}_3)_2$, N=

Fig. 1 DTA curves of the carbohydrazide complexes of certain metals.

weight loss ratio is shown in Fig. 1 with omission of thermal gravimetric results. CDH caused a small exothermic reaction after melting at 156.7 °C (melting point: 154 °C⁴⁾). In metal complexes coordinated by three CDH molecules, the initial temperature of the endothermic peak was 200 to 230 °C and an exothermic peak occurred soon after melting. CDH showed an endothermic reaction including melting ; however, the main reaction of the metal complexes was exothermic decomposition. Consequently, it was concluded that the reactivity increased due to the coordination of CDH to the metal. However, the exothermic peak separated into several peaks, and thus the reactivity was complicated in the metal complex compared with



Sample ; 5mg (Alumina open cell)
dT/dt ; 20°C/min.
Atmosphere ; Ar

Fig. 2 TG-DTA curves of the carbohydrazide complexes of certain metals

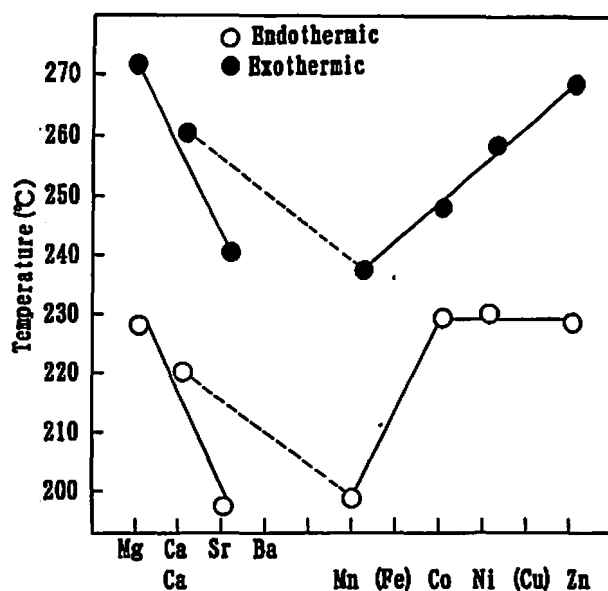


Fig. 3 The initial temperature of the endothermic and exothermic peaks in the DTA curves

that of CDH.

The final product at 600 to 700 °C in thermal analysis was confirmed to be a bivalent metallic oxide from the weight loss ratio shown in Fig. 1 and X-ray diffraction analysis.

Fig. 2 shows the results of the thermal analysis of the Ca and Sr complexes in which two molecules of CDH are coordinated. The Ca complex released water

Table 3 Activation energy of decomposition evaluated from Kissinger's equation

Sample	ΔE (kJ/mol)
Mg(CDH) ₃ (NO ₃) ₂	134.1
Zn(CDH) ₃ (NO ₃) ₂	214.0
Mn(CDH) ₃ (NO ₃) ₂	98.3
Ni(CDH) ₃ (NO ₃) ₂	189.1
Co(CDH) ₃ (NO ₃) ₂	173.1
Ca(CDH) ₂ (NO ₃) ₂ ·H ₂ O	133.8
Sr(CDH) ₂ (NO ₃) ₂	148.4

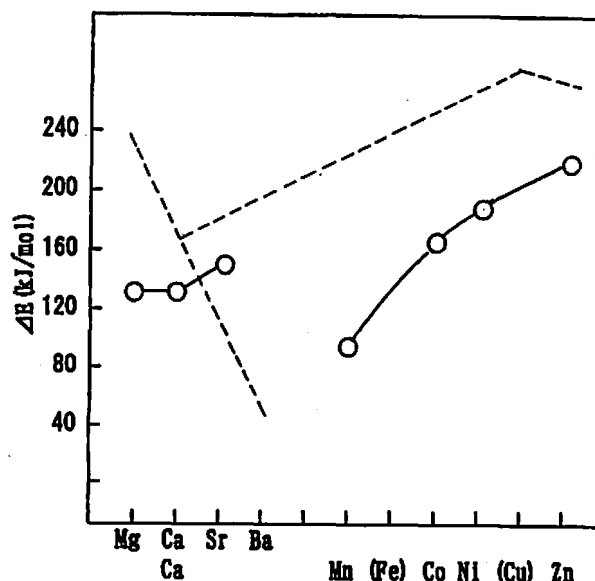


Fig. 4 Activation energies for the decomposition of carbohydrazide complexes of certain metals

at about 80 °C and caused exothermic reaction soon after melting at 220 °C. On the other hand, the Sr complex showed several exothermic peaks just after melting at 195 °C. In these cases, the final product in thermal analysis was confirmed to be a bivalent metallic oxide, CaO and SrO, respectively.

Fig. 3 shows the initial temperature of the endothermic and exothermic peaks obtained from thermal analysis of various metal nitrate complexes. For most of the metal complexes, the initial temperature of melting was about 220 to 230 °C and no distinct difference appeared. However, the Mn and Sr complexes showed a lower initial temperature of 200 °C lower than others. On the other hand, the tendency of the initial temperature of exothermic decomposition was reflected in order of the Irving-William system⁶⁾ in the same period except for the Ca complex and in

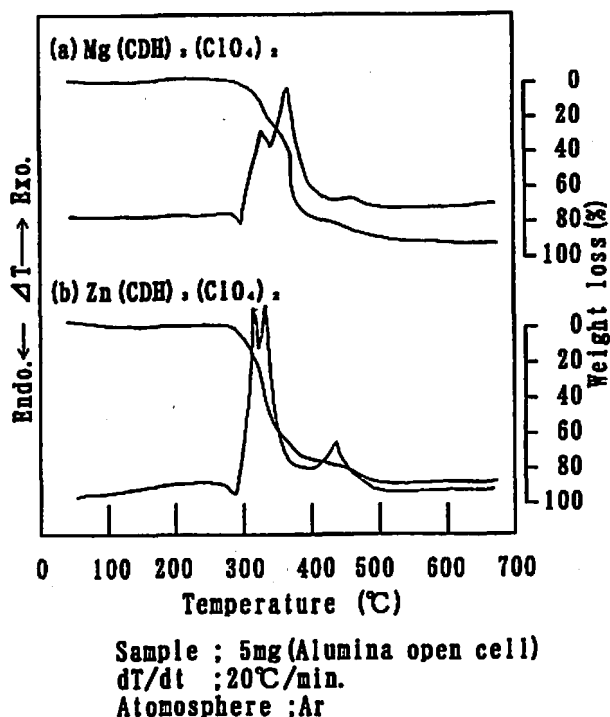


Fig. 5 TG-DTA curves of the carbohydrazide complexes of certain metals

creased in the order of ionic radius reduction in the same group. That is to say, it can be concluded that the initial temperature of the exothermic peak tended to be in good agreement with the tendency of the metal complex stability relative to any ligands.

Furthermore, in one evaluation, Table 3 and Fig. 4 show the activation energies of decomposition evaluated using Kissinger's method²⁾ based on the dependence of the reaction on the heating rate. Fig. 4 shows the tendency of complex stability schematically (the dotted line) in the same figure for comparison. Based on the tendency of the activation energies, it was estimated that decomposition was likely to proceed in the order of Zn, Ni, Co, Mg, Sr, Ca and Mn and this tendency agreed with the stability of the complex except for the Ca and Sr complexes. Because the initial temperature of the exothermic peak in the DTA curves showed the same tendency, the correlation between stability and thermal stability was recognized in the CDH metal complexes. The activation energy of the Ca and Sr complexes was high, though the stability of these complexes was low among the metal complexes. This may be due to the fact that two molecules of CDH were coordinated, resulting in a different structure from that of other metal complexes. In other words, the formation of a

more stable structure could be considered because the stability was low as mentioned above. Similarly, in a comparison of the Ca complex and the Sr complex, the Ca complex was less thermally stable than the Sr complex, the cation of which is lower in the Periodic Table. Perhaps, the mechanism of coordination was different considering the molecular formula.

However, there is a possibility that the water of crystallization in the Ca complex had an effect on the decomposition, assuming that decomposition was accelerated by water as described above.

3.2.2 Metal perchlorate complex

Fig. 5 shows the results of thermal analysis of the perchlorate of the Mg complex and Zn complex: The initial temperature of melting of the perchlorates was higher than those of the nitrates as shown in Fig. 1. An exothermic peak caused by decomposition occurred soon after melting, and the temperature range of the peak was narrow compared with those of the nitrates. Consequently, it can be concluded that the decomposition rate of the perchlorate was greater than that of the nitrate. However, for the Mg complex, the activation energy of the perchlorate evaluated using Kissinger's method²⁾ was larger than nitrate (Table 4) and did not agree with the results of thermal analysis. This may originate from the fact that the decomposition was not an elementary reaction. Thus, it is necessary to carry out a detailed analysis, such as the isothermal decomposition, in order to clarify the reaction mechanism. The decomposition residue was confirmed to be MgO and ZnO based on weight loss data and X-ray diffraction as in the case of the nitrate.

4. Conclusions

The carbohydrazide metal complex, expected to be a new gas generator, was synthesized based on the method by Ivanov et al.¹⁾ For the Ca and Sr complexes, which are relatively low in complex stability as a six-coordinated octahedron, the production of $\text{Ca}(\text{CDH})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Sr}(\text{CDH})_2(\text{NO}_3)_2$ was confirmed by many analyses. It appeared that water affected the crystal stability in the CDH metal complex. So the cause of this required investigation. The thermal reactivity increased on coordination of CDH to a metal compared with CDH. It was predicted that the reactivity decreased in the order of Mn, Mg, Co, Ni and Zn. This tendency was reflected in the

tendency of complex stability^{3), 5)}, and the correlation between complex stability and thermal stability was recognized in the CDH metal complex. It was also found that the reactivity of the perchlorate was higher than that of the nitrate in the same metal complex.

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カルボノヒドラジド金属錯体の熱的挙動(1)

— 合成と熱分析 —

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新規のガス発生剤として期待されるカルボノヒドラジド金属錯体 ($M(CDH)_3(NO_3)_2$: $M = Mg, Zn, Mn, Ni, Co$, $M(CDH)_2(NO_3)_2(H_2O)_n$: $M = Ca (n=1), Sr (n=0)$, $M(CDH)_3(ClO_4)_2$: $M = Mg, Zn$) を Ivanov ら¹⁾の方法に基づき合成した。カルボノヒドラジド金属錯体においては水分が結晶安定性に影響を及ぼす事が懸念されるため、その原因解明が必要である。

また示差熱分析より、カルボノヒドラジド単独より金属に配位させることで反応性が高まる事を確認した。熱反応性への配位金属の影響を熱分解開始温度および Kissinger 法²⁾(非定温)より求めた分解の活性化エネルギーから比較検討した結果、 $Zn < Ni < Co < Mg < Mn$ の順に反応性が高まる事が予測された。これは錯体の安定性の傾向と一致しており、カルボノヒドラジド金属錯体では錯体の安定性と熱安定性とに相関性が認められた。また、同じ金属錯体でも、過塩素酸塩の方が硝酸塩より反応性が高いことがわかった。

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