The thermal behavior of the carbohydrazide complexes of certain metals (2)

— The isothermal decomposition —

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The carbohydrazide (hereafter, CDH) metal complexes, which are expected to be a new gas generant for the automobile air bags, were synthesied based on the method of Ivanov[1,4], and the isothermal decomposition behavior was investigated in the temperature range of 250−300℃.

With the Mg and Zn complexes, stable intermediates were formed in the course of the decomposition, unlike the others. The other metal complexes finally produced the divalent metallic oxide. The intermediates were predicted to be not in the form of $M(CDH)_m(NO_3)_n$ (M=Mg, Zn). As one possibility, the stable complex may be formed by re-coordination of substances evolved by the decomposition. In addition, by comparison of the activation energies for various CDH metal complexes during isothermal decomposition, it was found that the decomposition behavior depended largely on the complex stability[2,3].

On the other hand, in the Ca and Sr complexes, two CDH molecules were coordinated with a metal atom to form a more stable complex considering from the complex stability[2,3]. These complexes also formed stable intermediates in the course of the reaction, but it is very unlikely that they were formed by re-coordination because of the larger ionic radius of these coordinated metals. Perhaps, these complexes are very likely to have a different decomposition mechanism from that of the complexes coordinated by three CDH complexes.

1. Introduction

Recently, automobiles sold in Japan have been equipped with an air bag system for safer driving. Though NaN_3 is presently used as the main component of the gas generator, it has a treatment problem[4]. 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.

The 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 the previous report[4], in order to investigate the possibility of practical application of CDH, various CDH metal complexes were synthesized and the thermal analysis of them was carried out. In this report, for various CDH metal complexes $M(CDH)_3(NO_3)_2$; M=Mg, Zn, Mn, Co and $M(CDH)_2(NO_3)_2/(H_2O)_n$; M=Ca(n=1), Sr(n=0)), the behavior of the isothermal decomposition was investigated at various temperatures.

2. Experiment

2.1 Sample

CDH metal complexes were synthesized from various Wako pure chemical reagent grade metal nitrates ($M(NO_3)_2$; M=Mg, Zn, Mn, Ni, Co, Ca, Sr)
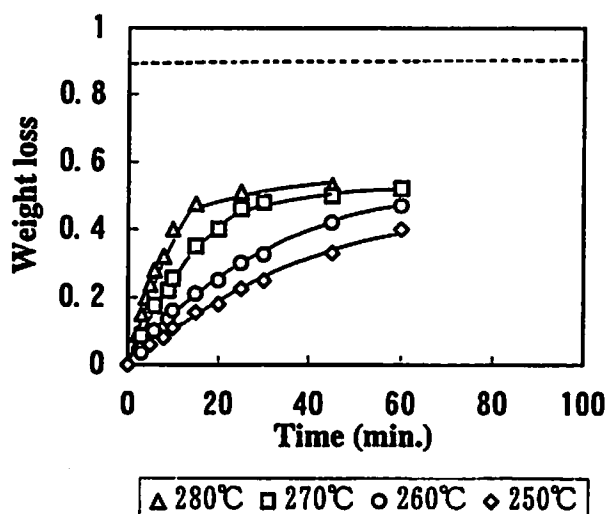
Fig. 1 The decomposition of $Mg(CDH)_3(NO)_2$ at various temperatures

Fig. 2 The decomposition of $Mn(CDH)_3(NO)_2$ at various temperatures
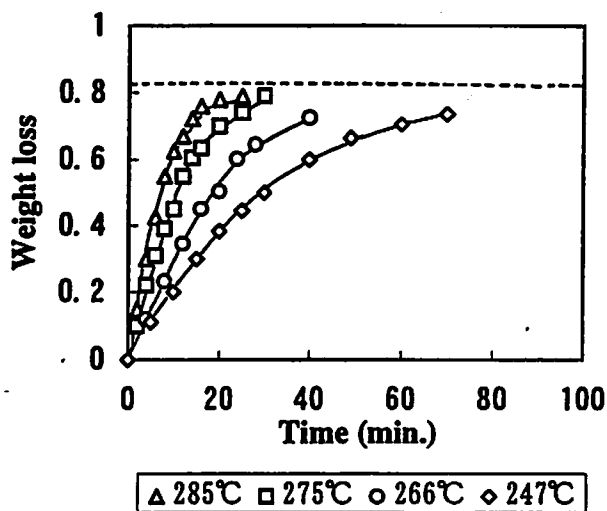

Fig. 3 The decomposition of $Ni(CDH)_3(NO)_2$ at various temperatures

and CDH from Japan Hydrazine Corporation, based on the method described in the previous report[4]. The obtained products were subjected to elemental analysis, analysis of $[NO_3]^{-1}$ concentration by conductometric titration (or absorptiometry) and analysis of the metallic ion by chelatometric titration. In the obtained complexes, three CDH molecules were coordinated with a metalatom except for the Ca and Sr complexes, in which two CDH molecules were coordinated with a metal atom.

2.2 Isothermal decomposition

Fifty 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

was inserted into an electric furnace kept at various temperatures. After being heated for a specified time, the weight of the sample was measured. The decomposition residue was analyzed by X-ray diffraction using a Rigaku Rotor Flex RU-200, by elemental analysis using a Yanagimoto CHN corder MT-3 type and by infrared spectroscopy using a Shimazu FTIR-8100 A.

3. Results and discussions

3.1 Isothermal decomposition of Mg, Mn, Co, Ni and Zn complexes

3.1.1 Change of weight loss against time

Figures 1, 2 and 3 show time versus the weight loss curves for Mg, Mn and Ni complexes as typical examples. In these figures, for reference the dotted line shows the weight loss that must have been reached if the decomposition residue is the divalent metallic oxide. In this regard, it has been confirmed that the residue in thermal analysis[4] is the divalent metallic oxide for various CDH metal complexes, and the decomposition can be presumed to be a reaction which generates gases such as N_2, CO, etc., and produces the metallic oxide as a residue.

The weight loss in isothermal decomposition of the Mg complex in the temperature range of 250−280 ℃ converged to 0.570, as shown in Figure 1. At lower experimental temperatures, the weight loss did not converge to a fixed value up to 100 minutes after the start of the reaction but converged to 0.570 after remaining at the same experimental temperature for several hours. This value of 0.570 is obviously dif-

Table 1 The results of elementary analysis of the residue

(Unit:wt.%)

M(CDH)$_3$· (NO$_3$)$_2$M=	C	H	N	M	O	Molecular formula
Mg	11.53	5.00	9.00	13.50*	61.00*	Mg(C$_2$H$_8$NO$_6$)
Zn	8.74	1.24	22.8	40.63*	26.59*	Zn(C H$_2$N$_2$O$_2$)

M ; metal
* ; calculated value

ferent from the calcd. value (0.9037) for the divalent metallic oxide (MgO) of the residue. Thus, it was predicted that in this experimental temperature range a stable intermediate was formed in the course of the reaction. The same phenomenon was also seen with the Zn complex : the weight loss converged to 0.630, whereas it should converge to 0.823 if the residue was ZnO. This is because the decomposition reaction may not be the elementary process. Furthermore, this is also strongly supported by the fact that several exothermic peaks are seen over a wide temperature range from 220 ℃ to 700 ℃ in the thermal analysis[4] of these complexes.

Assuming that stable intermediates are formed from these complexes, the molecular weight of the intermediates was calculated using the value of the final weight loss ; the results of the calculation were 179.98 for the Mg complex and 170.07 for the Zn complex. These values mean that significant amounts of organic components, other than the metals (Mg=24.31, Zn=65.37), still remain in the intermediates. The possibility that the CDH (the molecular formula : N$_4$H$_6$CO) remains undecomposed in the intermediates is not denied. Table 1 shows the results of the elemental analysis of these decomposition residues. The metal contents in the table were calculated based on the assumption that the metal contents remain unchanged throughout the decomposition ; the balance was regarded to be oxygen ([O%] =100−([C%]+[H%]+[N%]+[M%]). The ratio of the elements in the molecular formula derived from the elemental analysis denies the possibility that the CDH remains in the residues. The IR spectra of these decomposition residues did not show absorption by a new functional group, and no information enabling identification of the substance was obtained. An absorption attributable to nitrate ion was observed at 1390 cm^{-1}. However, in the Zn complex, the ex-

istence of nitrate ion is inconsistent with the ratio of the elements in the molecular formula, and in the Mg complex the balance of valence is not good. Consequently the intermdiates may be a mixture ; although their identification is difficult, it is inferred that the intermediates do not exist in the form of M(CDH)$_m$· (NO$_3$)$_n$ (M=Mg, Zn).

As shown in Figure 2, the weight loss for the Mn complex converged to the value (0.842) showing that the residue was the divalent metallic oxide (MnO). A similar result was also obtained for the Co complex. In both cases, the formation of the metal oxides was confirmed by X-ray diffraction analysis. Thus, stable intermediates were not confirmed to form during isothermal decomposition of these complexes in the temperature range of 240−300 ℃.

In the Ni complex, as seen in Figure 3, the curve of the weight loss has an inflection point. Some intermediate may be formed as in the case of the Mg and Zn complexes, but the reaction goes further. The weight loss finally converged to the value of 0.8350. The residue was NiO, which was confirmed by X-ray diffraction analysis.

Predictably, the Mg and Zn complexes will also be finally changed to the metallic oxides as the Ni complex (Figure 3), if isothermally decomposed at a higher temperature or for a longer time at the same experimental temperatures. Therefore, the temperature dependence of the reaction has to be investigated in the future.

3.1.2 Activation energies for decomposition

For various metal complexes, the fractional decomposition was derived from the weight loss finally obtained, and an applicable rate equation was investigated ; the result was that a first-order equation can best describe the reaction. Plots for the Mg complex, as a typical example, are shown in Figure 4, in which good linearity is seen over the range of the frac-
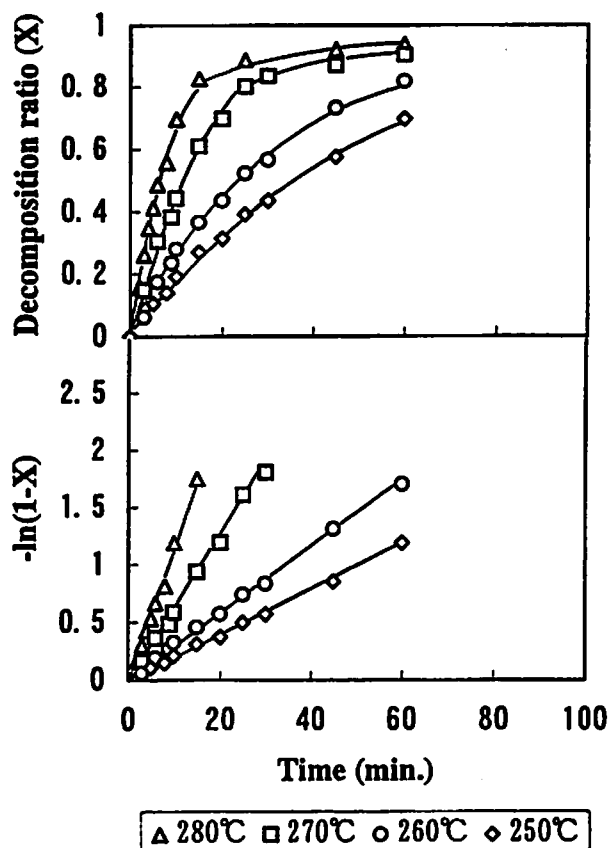
A 280℃ □ 270℃ o 260℃ ◇ 250℃

Fig. 4 Isothermal decomposition ratio(X) curves and linear plots for a first-order reaction for Mg(CDH)₃(NO₃)₂

tional decomposition from 10 to 85%. The rate constant at each temperature was obtained from the gradients of these straight lines. Arrhenius plots of the rate constants gives the activation energies (Fig. 5
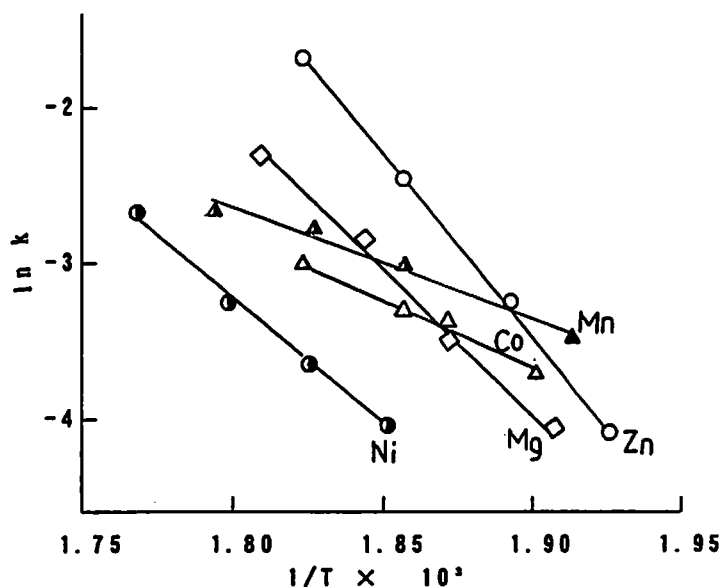
and Table 2) of the reactions. Figure 6 is a graphic representation of the activation energy data in Table 2, in which the initiation temperatures for the exothermic peaks in thermal analysis in the previous report[4] are also given for reference. The activation energy for CDH metal complexes increased in order of Mn, Ni, Co, and Zn in the same period of the periodic table ; this order is consistent with that in the Irving-Williams series[2] which describe the stability of metal complexes. This means that the more stable a complex is, the more difficult is the decomposition, in the experimental temperature range.

As for the rate constants (Figure 5), by the comparison among the Mn, Co and Ni complexes, it was revealed that their decomposition rates were in the descending order of Mn, Co and Ni at a temperature of 288 ℃ or lower. This is consistent with the tendency seen in their activation energies. However, the order of the decomposition rates was reversed at a temperature of 304 ℃ or higher. Probably this is attributed to a compensation effect. Therefore, it is difficult to discuss the order of their reactivities by comparing their rate constants only at a single temperature.

As for complexes having metals in the same period of the periodic table, there is a tendency that the more stable a complex is, the more easily it forms an intermediate. The CDH metal complexes generate gases, such as NH₃, CO, etc., which can be a ligand,

Fig. 5 Arrhenius plots of the decomposition of the carbohydrazide metal complexes

Table 2 Activation energy of decomposition for car-
bohydrazide metal complexes

Sample	ΔE (kJ/mol)
Mg(CDH)$_3$(NO$_3$)$_2$	146.9
Zn(CDH)$_3$(NO$_3$)$_2$	186.9
Mn(CDH)$_3$(NO$_3$)$_2$	50.2
Ni(CDH)$_3$(NO$_3$)$_2$	138.9
Co(CDH)$_3$(NO$_3$)$_2$	81.3
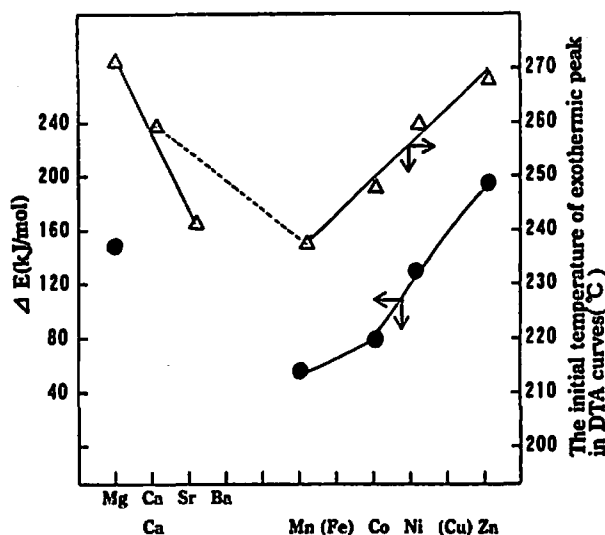
Fig. 6 Activation energies for the decomposition of
the carbohydrazide metal complexes

$\triangle$ 295℃ $\square$ 290℃ $\circ$ 281℃ $\diamond$ 263℃

Fig. 7 The decomposition of Ca(CDH)$_2$(NO$_3$)$_2 \cdot$ H$_2$O
at various temperatures

$\triangle$ 290℃ $\square$ 285℃ $\circ$ 271℃ $\diamond$ 261℃
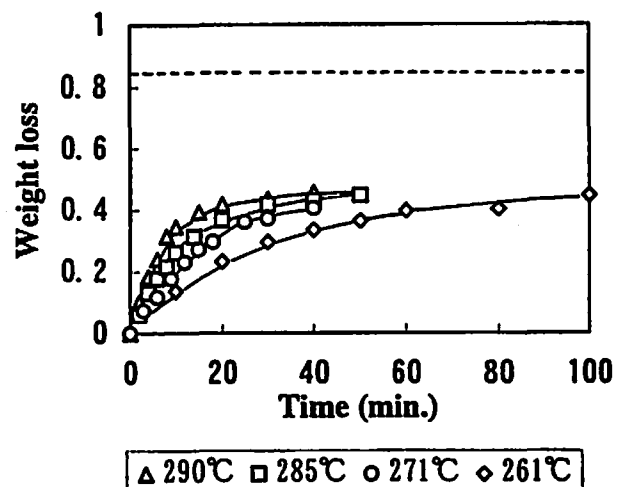
Fig. 8 The decomposition of Sr(CDH)$_2$(NO$_3$)$_2$ at
various temperatures

by decomposition. In the Mg and Zn complexes, there
is a possibility that these gases might be coordinated
again, because these metal complexes are relatively
stable as understood from the Irving-Williams series[2]
; that is, there is a possibility that the intermediate
might be a complex formed by re-coordination of
generated gases. In this regard, the authors are now
investigating what gases are generated and the rate of
generation for those gases and will report the results
in the next paper.

3.2 Decomposition of metal complexes coor-
dinated by two CDH molecules

3.2.1 Change in the weight loss with time

Figure 7 shows the weight loss vs. time curves for
the Ca complex. The dotted line in the figure shows
the calculated weight loss (0.845) based on the
assumption that the residue is CaO. As seen in the
figure, the weight loss converged to 0.450 in the ex-
perimental temperature range, indicating the forma-
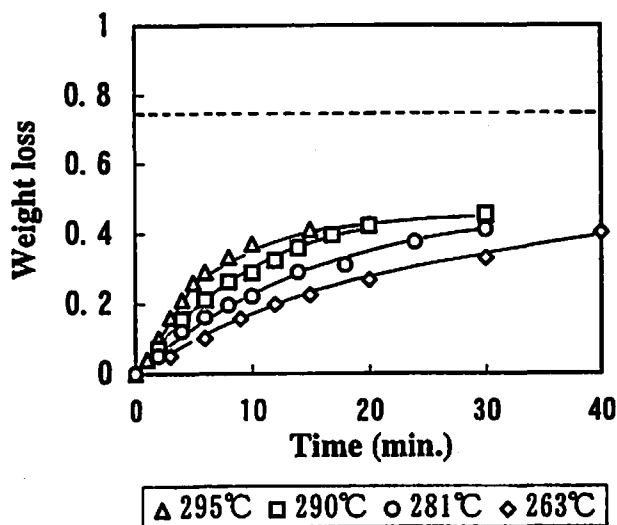tion of a stable intermediate in the course of the reac-

tion. Figure 8 shows the experimental result for the
Sr complex. The weight loss converged to 0.460,
while it should be 0.736 if SrO was formed. Table 3
shows the results of the elemental analysis of these
decomposition residues. From the ratio of the
elements obtained by the molecular formula in the
table, it is concluded that the intermediate in the Ca
complex does not have the form of Ca(CDH)$_m$(NO$_3$)$_n$.
The IR spectra did not provide information which
would enable the intermediateto be identified. Fur-
thermore, there is no absorption attributable to
nitrate ion, unlike the Mg and Zn complexes. Ca has
an larger ionic radius than Mn in the same period of
the periodic table, and predictably the Ca complex is

Table 3 The results of elementary analysis of the residue

(Unit: wt.%)

M(CDH)$_2$·(NO$_3$)$_2$M=	C	H	N	M	O	Molecular formula
Ca	6.59	2.12	21.47	23.50*	46.80*	Ca(C H$_4$N$_3$O$_5$)
Sr	0.62	0.18	17.59	41.40*	40.21*	Sr(NO$_3$)$_2$

M ; Metal
* ; calculated value

more difficult to form; therefore, unlike the Mg and Zn complexes, it is difficult for the gases generated by the decomposition to coordinate again. Considering from its molecular formula, the Ca complex exists in the form of a bridged complex, taking a structure clearly different from that of the complexes coordinated by three molecules ; therefore, the decomposition of the Ca complex might proceed by a different mechanism from that of the complexes coordinated by three CDH molecules. In this regard, further study has to be done. Figure 9 shows the results of X-ray diffraction of the decomposition residue for the Sr complex; the results revealed the existence of the diffraction pattern for strontium nitrate, which result is consistent with the molecular formula derived from the elemental analysis. Although the structure of this complex is not predicted from the molecular formula, nitrate ions might be coordinated as a ligand. The
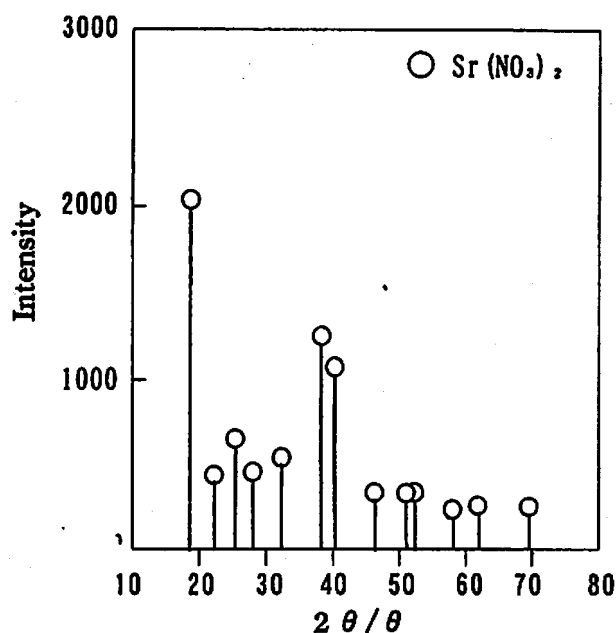

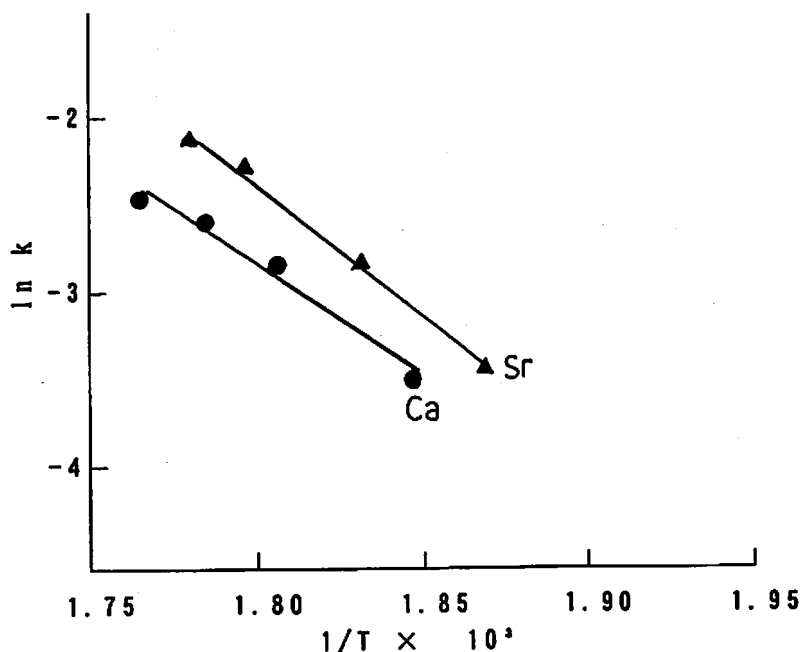Fig. 9 X-ray diffraction pattern of the decomposition residue of Sr(CDH)$_2$(NO$_3$)$_2$

Fig. 10 Arrhenius plots of the decomposition of the carbohydrazide metal complexes

Table 4 Activation energy of decomposition for carbohydrazide metal complexes

Sample	ΔE (kJ/mol)
$Ca(CDH)_2(NO_3)_2 \cdot H_2O$	88.0
$Sr(CDH)_2(NO_3)_2$	107.9

reaction mechanism of the Sr complex, like that of the Ca complex, is different from that of the other complexes.

3.2.2 Activation energies for the decomposition

For the Ca and Sr complexes, the fractional decomposition was derived from the weight loss obtained, and applicable rate equations were investigated. The result was that first-order equations are best applicable to both complexes. The rate constants at various temperatures were obtained from the gradients of these straight lines. Arrhenius plots of the rate constants give the activation energies for the reactions (Fig. 10 and Table 4). From the viewpoint of complex stability, the Ca complex has a larger value in the same period of the periodic table, and the Sr complex has larger value in the same group. This is consistent with the tendency seen in the activation energies obtained by the Kissinger method[6] and in the initial temperature of the exothermic peak by thermal analysis in the previous report[4]. However, it is inconsistent with the tendency of the complex stability. Presumably, in the Ca and Sr complexes, a more stable complex can be considered to form due to the lower complex stability compared with the others.

4. Conclusion

The CDH metal complexes, which are expected as a new gas generant for the automobile air bags, were synthesized based on the method of Ivanov[1], and their isothermal decomposition behavior was investigated in the temperatures range of 250—300 ℃.

The CDH metal complexes were predicted to generate gases by decomposition and to produce the bivalent metallic oxides. However, with the Mg and Zn complexes a different behavior was recognized : their final weight losses in isothermal decomposition were less than the expected values, and this revealed that stable intermediates were formed in the course of the reaction. Although their identification is difficult,

it is concluded that at least these are not in the form of $M(CDH)_m(NO_3)_n$ (M=Metal) from the results of the elemental analysis. As one possibility for the intermediates, stable complexes may be formed by re-coordination of substances generated by the decomposition reaction.

For the CDH metal complexes, a first-order equation would be most applicable to the isothermal decomposition reaction, and the activation energies were obtained based on the Arrhenius plots. By comparison of the obtained energies, it was found that the lower the complex stability was, the lower the activation energy for decomposition tended to be. Consequently, the behavior of the decomposition depended largely on the complex stability.

On the other hand, in the Ca and Sr complexes, two CDH molecules were coordinated with a metal atom to form a more stable complex considering the complex stability[2,3]. These complexes also formed stable intermediates the same as Mg and Zn complexes, but it is very unlikely that the intermediates are formed by re-coordination because of the larger ionic radius of these coordinated metals. Perhaps these complexes are very likely to have a decomposition mechanism different from that of the complex coordinated by three CDH complexes.

Reference

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5) for example, Michel Boudart ;Eiji Oshima, "The argument for the rate of reaction", Maruzen Co., LTD (1970), p 146

6) Kissinger, H. E. :"Reaction Kinetics in Differential Thermal Analysis", Analytical Chemistry, Vol. 29, p. 1702 (1957)

カルボノヒドラジド金属錯体の熱的挙動(2)

―等温下での熱分解―

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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および$M(CDH)_2(NO_3)_2(H_2O)_n$：M＝Ca（n＝1），Sr（n＝0））を合成し，250〜300℃の温度範囲での等温分解挙動を検討した。

　カルボノヒドラジド金属錯体は分解によりガスを発生し，2価の金属酸化物が残留することが予測されるが，Mg，Zn錯体は挙動が異なり，反応途中で安定な中間生成物を形成する。これらの分解残留物は元素分析の結果より，少なくとも$M(CDH)_m(NO_3)_n$の形ではない。同定は困難であるが，1つの可能性として分解により発生する物質が再配位し，安定な物質（錯体）を形成することがあげられる。さらに，等温分解における活性化エネルギーを比較することにより，錯体の安定性が，分解挙動に及ぼす影響が大きい事が判明した。

　一方，Ca，Sr錯体は，錯体の安定性が低いため，より安定な錯体，CDH 2分子配位錯体を形成することが推測された。これらの錯体も，反応途中で安定な中間生成物を形成するが，各々金属イオン半径が大きく，再配位錯体を形成する可能性は考えられない。従って，3分子配位錯体の分解とは機構が異なる可能性が高い。

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