The thermal behavior of the carbohydrazide complexes of certain metals (3)

The gas evolved in the decomposition of the Mg complex

by Miyako AKIYOSHI*, 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 gas evolution behavior of the Mg complex during the decomposition was investigated in the isothermal decomposition at 240−270℃ and at 400℃.

Main evolution gases was N_2, NH_3 and N_2O during isothermal decomposition at 240−270℃. The rate equation for the evolution of these gases was first-order for every kind of gas. The rate constant of N_2O evolution was smaller than that of N_2 and NH_3. The rate equation for the decomposition of the complex was also first-order. The rate constant of the decomposition shows the same tendency as that of N_2 and NH_3. The evolution of N_2 and NH_3 is supposed to be the main reaction in the temperature range of 240−270℃.

Furthermore, the decomposition at 400℃ proceeded so rapidly that ignition occurred. The gases evolved in the case of ignition were different from that during the decomposition at 240−270℃.

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. 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 ex-

Received on 1996. 11. 29

*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

pected to be one of the new gas generators. In the previous reports[1,2], in order to investigate the possibility of practical application of CDH, various CDH metal complexes were synthesized and their thermal decomposition behavior was investigated.

In this report, for the Mg complex nitrate ($Mg(CDH)_3(NO_3)_2$), the evolution behavior of the gas during the isothermal decomposition was investigated at various temperatures.

2. Experiment

2.1 Sample

The Mg complex of CDH was synthesized from Wako pure chemical reagent grade metal nitrate ($Mg(NO_3)_2$) and CDH from Japan Hydrazine Corporation, based on the method of Ivanov et al.[3]. 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.

2.2 Qualitative analysis of the evolution gas

The gas evolved during the decomposition was

Table 1 The analytical conditions in gas chromatography

	N_2	CO	CO_2	N_2O
Length of column		$3\,mm\phi \times 1.5\,m$		
Packing material	molecular sieve 5 A	active carbon		silica gel
Col.temp (℃)	40		35	
Carrier gas (mℓ/min.)	30		20	70

analyzed qualitatively using EGA (evolved gas analysis) (a Rigaku TAS-200 Thermal Analyzer, a Yokogawa HP5972 mas spectrometer). Five mg of the sample was weighed into the aluminum container and was heated to 500℃ at a heating rate of 20℃/min. in an atmosphere of He.

2.3 Evolution behavior of the gas during the isothermal decomposition

2.3.1 Decomposition at 240−270℃

The pyrolysis apparatus, which the glass tube (A) (18 mm in inside diameter and 200 mm in length) was fixed into the electric furnace, was connected to a gas chromatograph (hereafter, GC ; a Shimazu GC-4C). Fifty mg of sample was weighted into a quartz glass container (the boat shape : 5 mm in height and 30 mm in length) and this container was inserted into a glass tube (A). The decomposition was carried out at various temperatures (240−270℃) under a He gas (0.5% O_2) flow of 20 mℓ/min. The flow course of the carrier gas in the GC was changed to the pyrolysis apparatus at specified intervals, and the gas evolved by the decomposition was introduced to the GC. By repeating this operation, the amount of the gas evolved was measured continuously. Table 1 shows the measurement conditions for GC. The pyrolysis apparatus was connected to an absorption tube and a fixed amount of the water absorbed with NH_3 was withdrawn at specified intervals. NH_3 was quantified by the indophenol method [4].

Furthermore, after being heated for a specified time, the weight of the sample was measured.

2.3.2 Decomposition at 400℃

The sample was decomposed using the pyrolysis apparatus at 400℃ under a He flow of 20 mℓ/min. The gas evolved by the decomposition was collected in a collection bag (Tedlar Bags; 100 mm × 150 mm). The gas was analyzed using GC. The detailed measurement conditions are mentioned above (Table 1). In
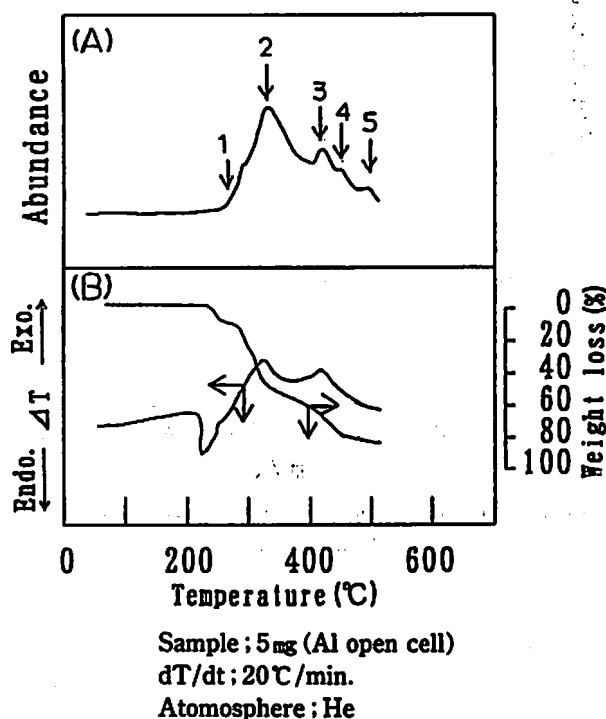

Sample ; 5 mg (Al open cell)
dT/dt ; 20℃/min.
Atomosphere ; He

Fig. 1 The amount of total ions of the gas evolved (A) and DTA-TG (B) for the Mg complex

addition, NH_3 was also quantified.

3. Results and discussion

3.1 Qualitative analysis of the gas evolved

Fig. 1(a) shows the change in the total ionic amount of the gas evolved during the decomposition. In contrast with the results of thermal analysis (Fig. 1(b)), the gas began to evolve as soon as the exothermic reaction started. In addition, the amount of the gas evolved had a maximum value at 310℃. Fig. 2 shows the mass spectrum of the gas evolved at each point in Fig. 1. Table 2 lists fragment values and the kinds of gases evolved. N_2, NH_3, CO, CO_2, N_2O, H_2O and O_2 were assumed to evolve, and the kind of the gas scarcely changed during the reaction process. N_2 may be main product, considering the intensity of the peak at m/e = 28 and the structure of the Mg complex $(Mg(N_4H_6CO)_3(NO_3)_2)$. Under an excess

× 10⁴
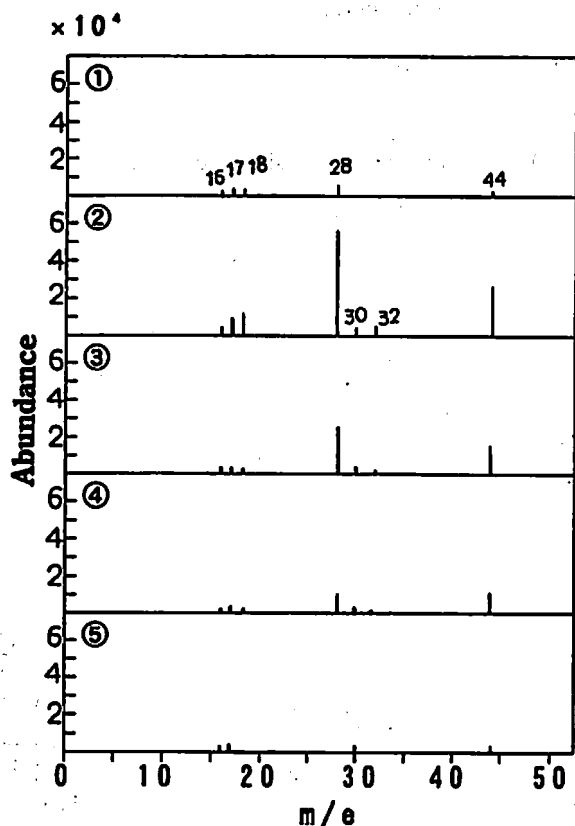

Fig. 2 The mass spectrum of the gas evolved at various points in Fig. 1

Table 2 The fragment values for evolved gases

m/e	components
17	NH_3, H_2O
18	H_2O
28	N_2, CO, CO_2
30	NO, N_2O
32	O_2
44	CO_2

oxygen atmosphere, the carbon, hydrogen and nitrogen elements change to CO_2, H_2O and N_2, respectively, due to decomposition. In the CDH metal complex, NH_3 and CO gas may evolve because of the negative oxygen balance $(-0.229 g/g)$. N_2O was assumed to evolve considering the peak at $m/e = 30$ and 44, though its evolution mechanism were unknown. In addition, the amount of N_2O or CO_2 increased with the temperature, because the peak intensity at $m/e = 44$ became large.

3.2 Change in the evolution amount of gases

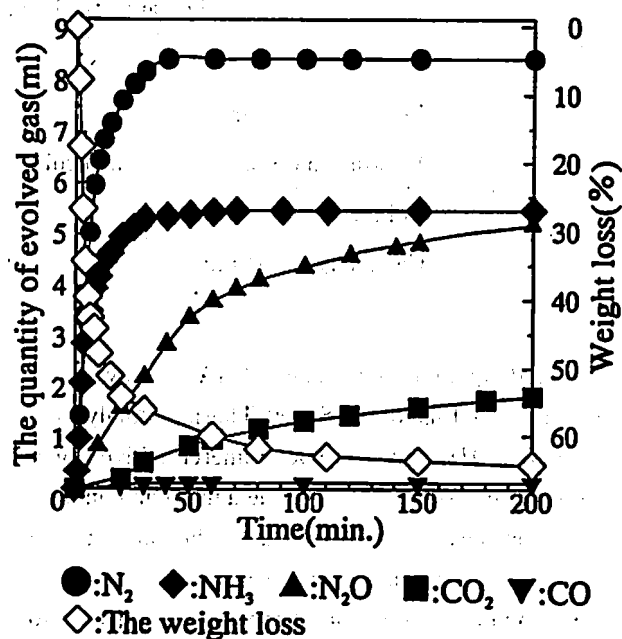The evolution behavior of the gases, which were assumed in the TG-MS analysis, was investigated

●:N_2 ◆:NH_3 ▲:N_2O ■:CO_2 ▼:CO
◇:The weight loss

Fig. 3 The gas evolved in the decomposition of $Mg(CDH)_3(NO_3)_2$ at 260°C

Table 3 The amounts of the gas evolved

	Amount of the gas evolved	
	mℓ/g(MgCDH*¹)	mol/mol(MgCDH*¹)
N_2	170	3.17
NH_3	110	2.06
N_2O	90	1.7
CO	2.4	0.05
CO_2	42	0.75
the total	414.4	7.73

calculated values at Standard State
*1 : Mg CDH ; $Mg(CDH)_3(NO_3)_2$

quantitatively in the isothermal decomposition.

Fig. 3 shows the evolved amount of N_2, NH_3, N_2O, CO and CO_2 and the weight loss of the Mg complex versus time curves at 260°C. O_2 evolution, which was assumed in TG-MS analysis, was not confirmed by the gas chromatographic method. The evolution of N_2, NH_3 and CO finished at 20～30 minutes after the start of the reaction. After these gases stopped evolving, N_2O and CO_2 evolved gradually with slow decomposition. Table 3 shows the evolution amount of gases per 1 mol of Mg complex. The evolution ratio of NH_3 and N_2O to all gases was 26.5% and 21.7%, respectively. Therefore, in addition to N_2, it is possibile that the evolution of these gases is main reaction.

Table 4 The elemental analysis of the decomposition residue

element(wt.%)					molecular formula
C	H	N	Mg	O	
15.44	2.76	31.35	15.70	34.75	$Mg(C_2N_3H_4O_3)$

Table 5 The mass balance of nitrogen and carbon atom(unit:%)

		N content[*1]	C content[*2]
the evolved gas	N_2	45.3	
	NH_3	14.7	—
	N_2O	24.3	—
	CO	—	1.7
	CO_2	—	25.0
the residue($Mg(C_2N_3H_4O_3)$)		21.4	66.7
the total		105.7	93.4

[*1] content : (N in the product)/(N in the $Mg(CDH)_3(NO_3)_2$)
[*2] content : (C in the product)/(C in the $Mg(CDH)_3(NO_3)_2$)

The balance of both nitrogen and carbon atoms was examined before and after the reaction. The metal complex contains fourteen nitrogen and three carbon atoms. In the evolved gas, there were twelve atoms and one atom, respectively. As seen in Fig. 3, the final weight loss of the sample converged to 0.630. Clearly, the organic substance remains in the sample, because the convergence value is different from the calcd. value for MgO(0.9037), which is the final residue in the thermal analysis. Table 4 shows the results of the elemental analysis of the decomposition residue. Including the nitrogen and carbon atoms in the decomposition residue, the mass balance of those atoms is approximately good. For reference, Table 5 lists the results of the mass balance of nitrogen and carbon atoms. There may be small errors, because the residue may be a mixture of a various products, as described in the previous report[2].

3.3 Gas evolution rate

As mentioned above, the evolution of N_2, NH_3 and N_2O gases was the main reaction during the isothermal decomposition, and the evolution rate of these gases was investigated. Figs. 4—6 show the change in the evolved amounts of the three gases during the isothermal decomposition in the temperature range of 240—270°C.

The fractional evolution was calculated from the final gas amounts evolved. In investigating the evolution rate equation for the gases, a first-order equation can best describe the reaction for every kind of gas. As a representative example, Fig. 7 shows the evolution ratio(X) versus time curve and the ($-\ln X$) versus time line for N_2 gas evolution. In the $\ln X$ against time plots, good linearity was seen over the range of the fractional evolution from 10 to 90%. Fig. 8 shows an Arrhenius plot for the evolution of N_2, NH_3 and N_2O gases. The rate constant of N_2O evolution was small compared with that of N_2 and NH_3.

On the other hand, Fig. 9 shows the weight loss of the sample versus time curve at various temperatures under He flow. As mentioned above, the final weight loss converged to 0.630. However, this value was different from the convergence value (0.570) under the atmosphere, as described in the previous report[2]. In that report[2], the authors suggested the possibility that the gas evolved during the decomposition participates in the reaction again and that a stable intermediate (complex) was formed. It is consided that under the He flow, the decomposition progressed further due to the diffusion of the evolved gas around the sample. The fractional decomposition was derived from the final weight loss, and a rate equation was investigated. As with the gas evolution rate, a first-order equation can best describe the reaction. Fig. 10
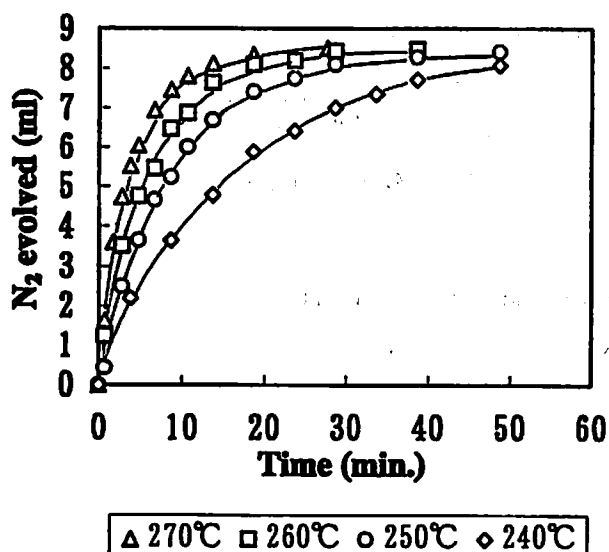
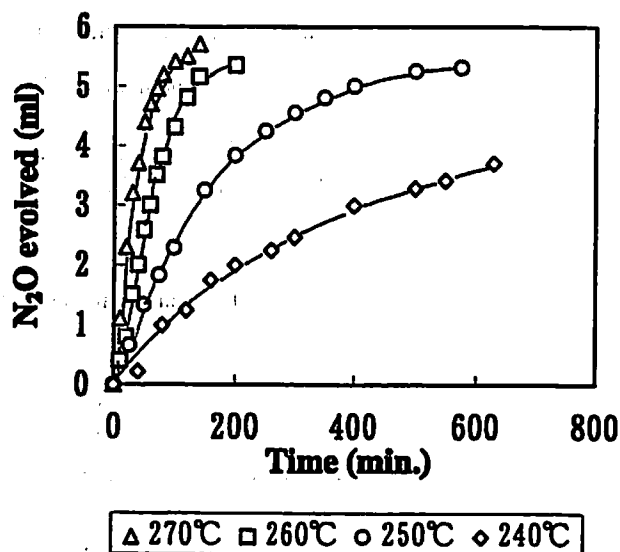Fig. 4 The amount of N_2 evolved in the decomposition at various temperatures

△ 270℃ □ 260℃ ○ 250℃ ◇ 240℃

Fig. 6 The amount of N_2O evolved in the decomposition at various temperatures

△ 270℃ □ 260℃ ○ 250℃ ◇ 240℃
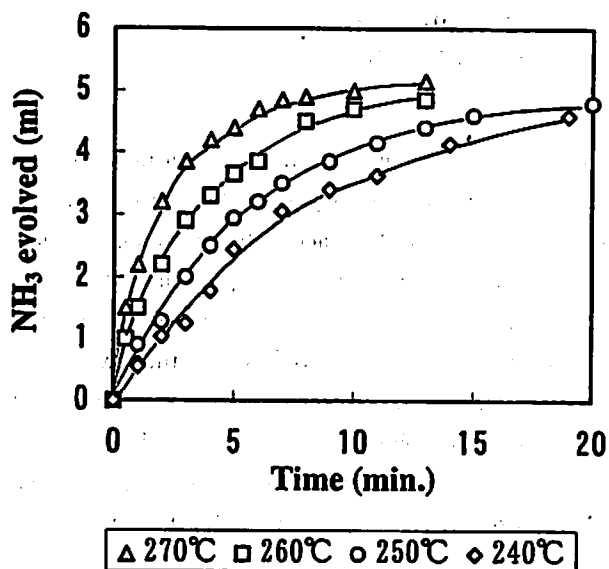
Fig. 5 The amount of NH_3 evolved in the decomposition at various temperatures

△ 270℃ □ 260℃ ○ 250℃ ◇ 240℃
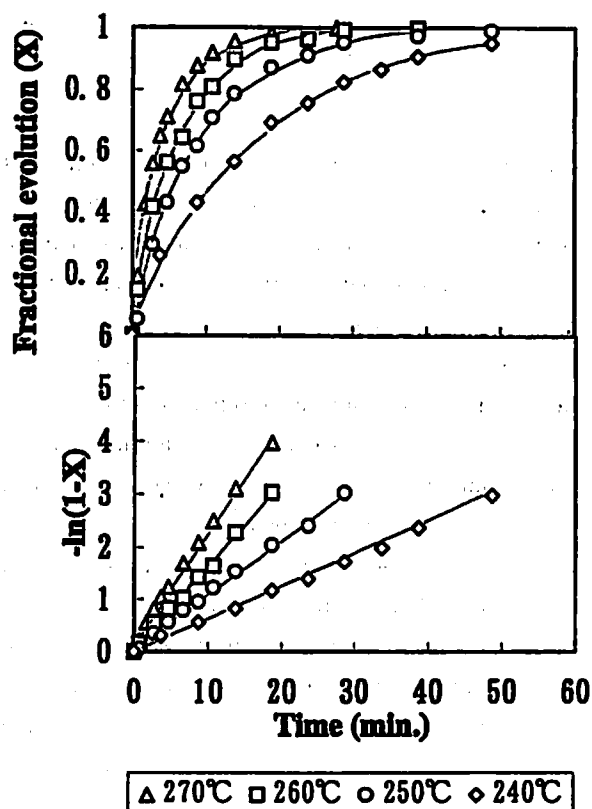
Fig. 7 N_2 fractional evolution (X) versus time curves and linear plots for a first-order reaction

△ 270℃ □ 260℃ ○ 250℃ ◇ 240℃

shows the fractional decomposition (X) versus time curve and the (−lnX) versus time plots. In the (−lnX)−time plots, good linearity was seen over the range of fractional decomposition from 10 to 85%. Moreover, Fig. 11 shows the results of the Arrhenius plot. Compared with Fig. 8, the rate constant of the decomposition shows the same tendency as that of N_2, NH_3, but clearly different from that of N_2O. Therefore, the evolution of N_2 and NH_3 is main reaction in the temperature range of the isothermal decomposition, as suggested from Fig. 3.
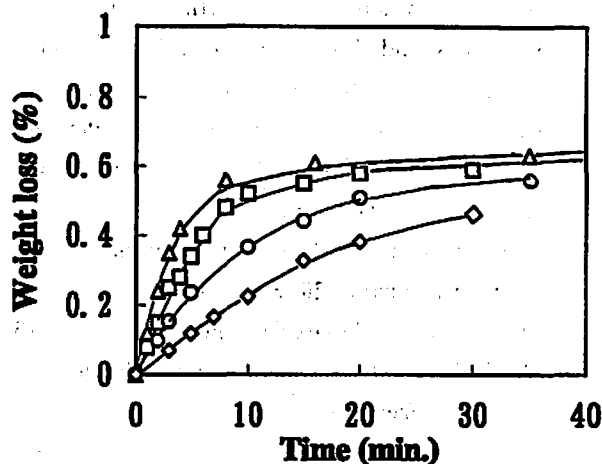
3.4 Decomposition at a temperature higher than that of the isothermal decomposition

At 400℃ or above, the Mg complex decomposes so rapidly that ignition occurs. Because the probability of ignition becomes high at 300℃ or above, the isothermal decomposition was carried out in the temperature range of 240−270℃. From the results of the X ray deffraction of the decomposition residue in the case of ignition, the diffraction pattern of MgO
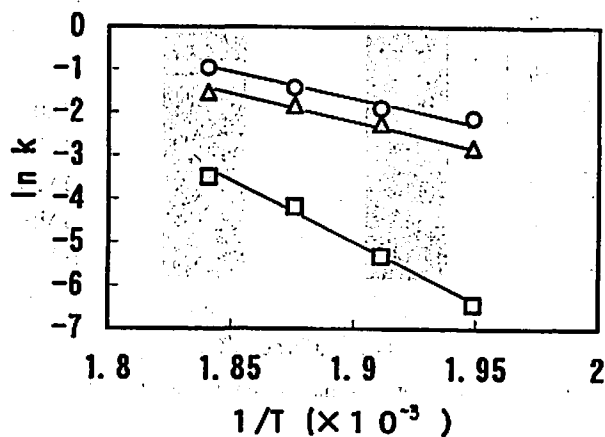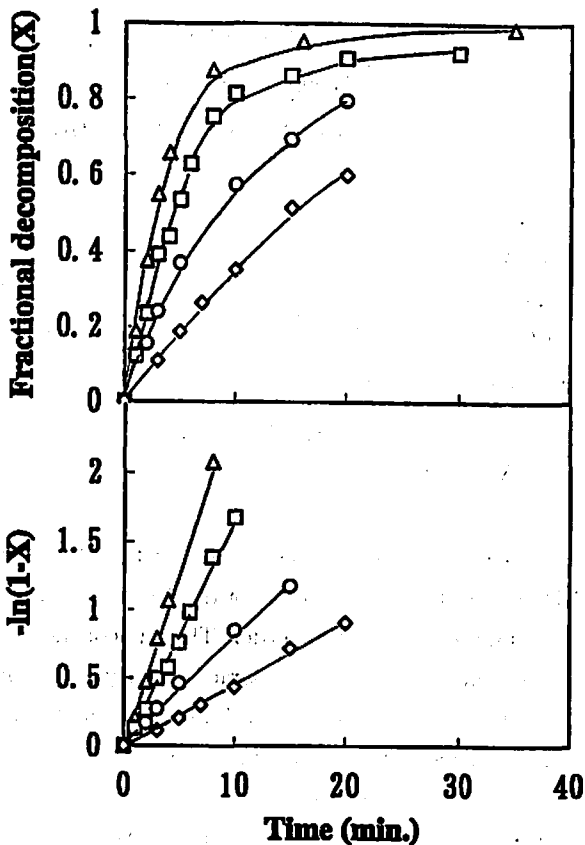
Fig. 8 Arrhenius plots for the gases evolved

o N_2 △ NH_3 □ N_2O

Fig. 9 The decomposition of $Mg(CDH)_3(NO_3)_2$ at various temperatures under He flow

△ 270℃ □ 260℃ o 250℃ ◇ 240℃

Fig. 10 Fractional decomposition (X) versus time curves and linear plots for a first-order reaction for the $Mg(CDH)_3(NO_3)_2$
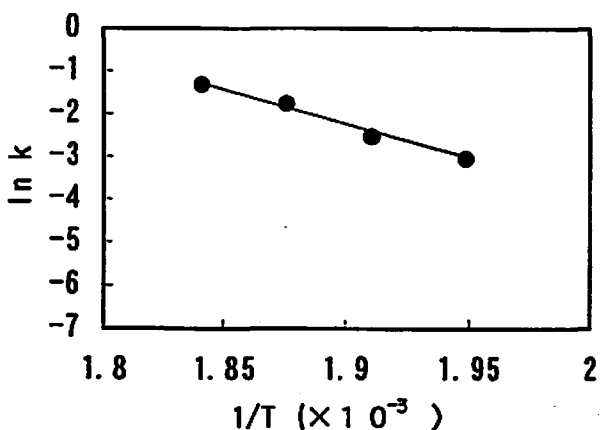
△ 270℃ □ 260℃ o 250℃ ◇ 240℃

Fig. 11 Arrhenius plots of the decomposition of $Mg(CDH)_3(NO_3)_2$ under He flow

was confirmed. Therefore, in the case of ignition, the decomposition apparently progresses without forming the intermediate in the course of the reaction. Table 6 shows the evolved amounts of various gases collected in the case of ignition. Moreover, Fig. 12 shows the distribution of the gases evolved at 400℃. For reference, the result of the decomposition at 270℃ is also shown in Fig. 12. In the case of ignition (at 400℃), the evolution ratio of N_2 increases and that is different from the result at 270℃. The mass balance of carbon atoms is not good before and after the reaction, and further analysis is needed.

4. Conclusions

For the Mg CDH complex, the evolution behavior was investigated in the isothermal decomposition at

240−270℃ and at 400℃.

Main evolved gas was N_2, NH_3 and N_2O during the isothermal decomposition at 240−270℃. The evolution ratio of these gases was 3:2:2 in mole ratio. The rate equation for the evolution of these gases was first-order for every kind of gas. The rate

Table 6 The amount of gas evolved

	Amount of gas evolved	
	mℓ/g(MgCDH) *¹	mol/mol(MgCDH) *¹
N₂	297	5.55
NH₃	52.4	0.97
N₂O	25.8	0.5
CO	2.2	0.05
CO₂	62.5	1.15
the total	439.9	8.22

calculated values at Standard State

*1 : Mg CDH ; Mg(CDH)₃(NO₃)₂

Fig. 12 The proportional of each gas to all gases evolved

constant of N_2O evolution was smaller than that of N_2 and NH_3 gases. The rate equation for the decomposition of the complex was also first-order. The rate constant of the decomposition shows the same tendency as that of N_2 and NH_3. Therefore the evolution of N_2 and NH_3 is supposeed to be the main reaction in the temperature range of 240−270℃.

At 400℃, the decomposition of the Mg complex progresses so rapidly that ignition occurs. Clearly, the gases evolved in the case of ignition were different from those in the case of the decomposition at 240−270℃. The evolved amount of N_2O was small, and the evolution ratio of N_2 and NH_3 was 5:1 in mole ratio. In the future, further investigation is needed.
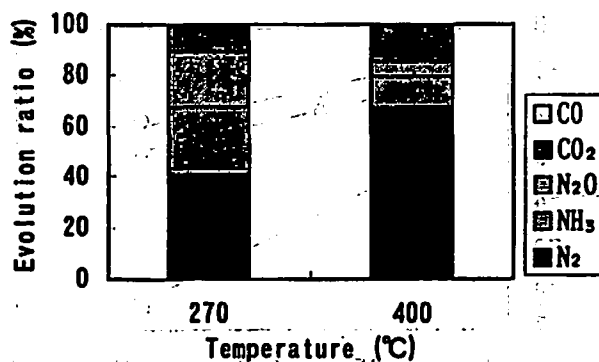
Reference

1) Miyako Akiyoshi, Norimasa Hirata, Hidetsugu Nakamura and Yasutake Hara, J. Expl. Soc. Japan, 57 (6), 238 − 243 (1996)

2) Miyako Akiyoshi, Norimasa Hirata, Hidetsugu Nakamura and Yasutake Hara, J. Expl. Soc. Japan, 57 (6), 244 − 251 (1996)

3) M. G. Ivanove et al., Russian Journal of Inorganic Chemistry, 26 (8), 1150 (1981)

4) "The chair of the experimental chemistry 15 (Analysis)", ed. by The Chemical Society of Japan, Maruzen (1991), p 188.

カルボノヒドラジド金属錯体の熱的挙動(3)
―Mg錯体の熱分解時のガス発生挙動―

秋吉美也子*，平田哲正**，中村英嗣*，原　泰毅*

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($Mg(N_4H_6CO)_3(NO_3)_2$)の熱分解時ガス発生挙動を明確にするべく，Mg錯体について240〜270℃での等温分解実験を行った。

構造上主体と考えられる窒素に加えて，アンモニア，亜酸化窒素の発生が確認された。錯体の分解速度およびガスの発生速度はガスの種類に限らず，1次式に最もよく適合した。ただし，亜酸化窒素の発生速度定数は他のものに比べて小さく，実験温度範囲の分解では，窒素，アンモニアの発生が主体である。

さらに，より高温（400℃）では，試料の分解が急激に進行して発火するが，この際に発生するガスは等温実験（240〜270℃）とは異なる結果が得られた。今後更なる検討を要する。

（*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）