

Catalytic Phenomena in Coordination Chemistry (1);
 Bis(dimethylglyoximato)bis(triphenylphosphine)cobalt(II)
 $\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2$ with hydrazobenzene in methanol

Kim, Sang Bock
 Dept. of Chemistry
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<Abstract>

Cobalt oxygen carrier complex bis(dimethylglyoximato)bis(triphenylphosphine) cobalt(II) was prepared in methanol at 25°C. U. V. and visible absorption spectra of the complex and hydrazobenzene were studied in the range of wavelength 200 nm—600 nm. The oxidation reaction of hydrazobenzene catalysed by the complex were compared with that of a catalyst N,N'-bis(3-methoxysalicylidene)ethylenediaminocobalt(II) $\text{Co}3\text{MeOSalen}$. $\text{Co}3\text{MeOSalen}$ was found that its catalytic effect was better than the $\text{Co}(\text{DMG})_2(\text{PPh}_3)_2$.

비수용액에서 비스(디메틸글리옥시마토) 비스(트리페닐포스핀)
 코발트(II) $[\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2]$ 착물의 제조와 하이드라조벤젠
 반응과의 촉매적 성질

김 상 복
 화 학 과
 (1983. 4. 19 접수)

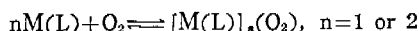
<요 약>

삼소운틴그라브트착물 비스(디메틸글리옥시마토)비스(트리페닐포스핀)코발트(II)를 25°C 메탄올에서 제조하였다. 이착물과 하이드라조벤젠과의 자외선 및 가시부범위 200~600 nm에서 흡수스펙트럼을 조사하였다. 상기착물이 촉매역할로서 하이드라조벤젠을 산화시킬때, 다른코발트착물 N,N'-비스(3-메톡시살리실리덴)에틸렌디아미나트코발트(II) $[\text{Co}3\text{MeOSalen}]$ 의 촉매역할과 비교하였다. $\text{Co}3\text{MeOSalen}$ 이 $\text{Co}(\text{DMG})_2(\text{PPh}_3)_2$ 보다 반응은 촉진시킴을 알았다.

I. Introduction

Cobalt oxygen carriers are able to catalyze the autoxidation of a number of organic compounds(1). To be classified as an oxygen carrier, it is necessary that the reverse reaction, i.e.,

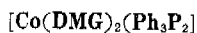
the dissociation of the dioxygen complex to give $\text{M}(\text{L})$ and O_2 , be observable. In practice this process can be observed by lowering the partial pressure of O_2 , by heating the complex, or by the addition of a ligand capable of replacing the bound O_2 (2).



Bis(dimethylglyoximato)cobalt(II), referred to also as cobaloxime(II), and its derivatives are known to react reversibly with molecular oxygen in aprotic solvents (3). $\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2$ and $\text{Co}(\text{3MeOSalen})(\text{Ph}_3\text{P})$ catalyze the oxidation of hydrazobenzene(4). The catalytic activity of those complexes seems to depend on their concentrations.

II. Experimental

1. Preparation of Bis(dimethylglyoximato)bis(triphenylphosphine) cobalt(II)



(1) Purification of Methanol (5)

About 10 g of magnesium turnings was added to 1 l of methanol and the resulting mixture was allowed to stand for one day. It was refluxed for two hours, and then distilled. About 10 g of dried magnesium sulphate was added and the resulting mixture was kept for one day. After filtering it, it was dried over molecular sieves for one day and filtered.

(2) Preparation of $\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2$ (3)(6)

Dry N_2 gas was passed through into 200 ml of dry methanol. As cobaltacetate tetrahydrate $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ 12.5 g (0.05 moles) was added, the colour of the solution was changed into pink. When dimethylglyoxime 11.5 g (0.1 mole) was added to the solution and stirred, the pink colour was changed into yellowish green. After dissolving dimethylglyoxime completely, triphenylphosphine 27.5 g (0.1 mole) was added, and then the colour of the solution changed to black. After stirring continuously for one hour, the dark black product was collected by quick

filtration in the air, and then the product was transferred to a vacuum desiccator and dried for one day at room temperature at 0.2 mmHg. After taking out the sample from the desiccator, it was crushed into a powder and put it into the desiccator again and dried it for two hours. The black product was transferred to the dry nitrogen filled glove bag. The dry complex was relatively stable on storage if protected against humidity and oxygen. The yield is 95%.

(3) Analysis of $\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2$

Elemental analysis of two preparations are shown in Table 1. The differences between theoretical and experimental values of preparation 1 are given as 0.18 of C, 0.03 of H, and 0.08 of N. In the case of H and N, they seem to be available, but C has a little error. Preparation 2, which has 1.81 of C, has larger error than preparation 1, but 0.03 of H and 0.33 of N are available. The reason seems to be that the preparation 2 has been done with no recrystallisation and probably some excess dimethylglyoxime giving the high % N.

III. Spectroscopic properties of UV and visible spectra

As Figure 1 shows, hydrazobenzene ($1.85 \times 10^{-3} \text{ M}$) has an optical density of 0.77 ($\epsilon = 747 \text{ (M}^{-1}\text{Cm}^{-1})$) at 242 nm, and 0.12 ($\epsilon = 233 \text{ (M}^{-1}\text{Cm}^{-1})$) at 288 nm. There is also a shoulder (0.66 Abs.) at 325 nm.

In Figure 7 we found that hydrazobenzene has a weak band at 440 nm. Figure 2 shows that

Table 1. Analysis of $\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2$ at 25°C

Sample number	Theoretical	C	H	N	Remarks
		64.96	5.41	6.89	
1	Found	64.78	5.44	6.81	with recrystallisation
2	Found	63.15	5.57	7.14	with no recrystallisation

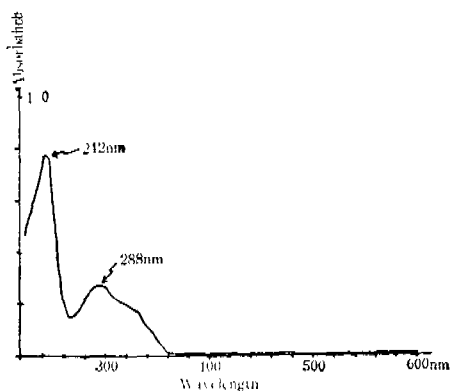


Fig. 1. UV and Visible absorption spectrum of hydrazobenzene ($1.03 \times 10^{-3} \text{ M}$) in methanol at 25°C

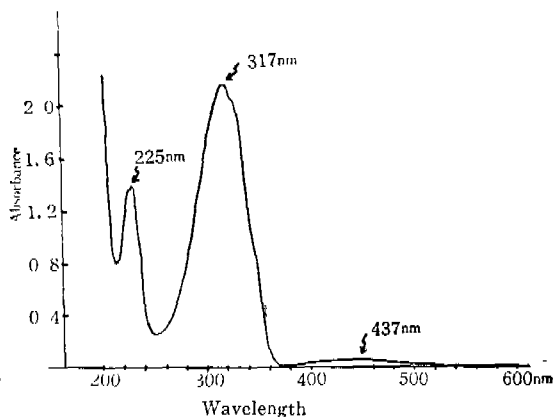


Fig. 2. Absorption spectrum of azobenzene ($1.02 \times 10^{-3} \text{ M}$) in methanol at 25°C

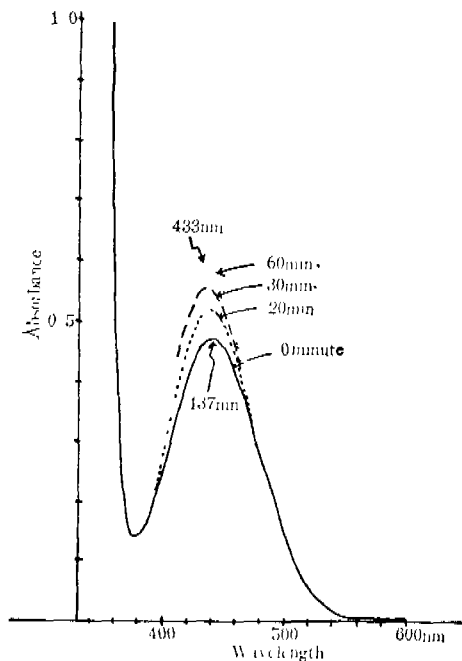


Fig. 3. Absorption spectra of azobenzene ($1.02 \times 10^{-3} \text{ M}$) irradiated in methanol at 25°C

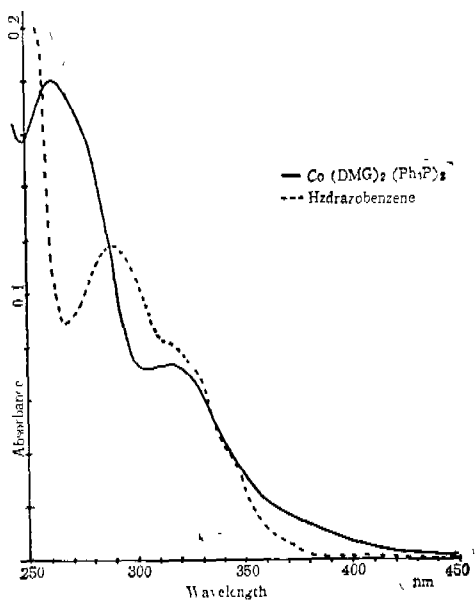


Fig. 4. Absorption spectra of $\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2$ and hydrazobenzene in methanol at 25°C
 $[\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2] = 1.03 \times 10^{-5} \text{ M}$
 $[\text{Hydrazobenzene}] = 1.85 \times 10^{-3} \text{ M}$

azobenzene (7) ($1.02 \times 10^{-3} \text{ M}$) has an optical density of 2.174 ($\epsilon = 2131 \text{ M}^{-1}\text{cm}^{-1}$ at 317 nm and 1.4 ($\epsilon = 1373 \text{ M}^{-1}\text{cm}^{-1}$ at 225 nm. Figure 3 shows a weak band of azobenzene at 437 nm. After one hour being irradiated, the weak band

was shifted to the left from 437 nm (0.52 Abs.) to 433 nm (0.60 Abs.) and the absorbance was increased. Azobenzene (trans) has $\epsilon = 500 \text{ M}^{-1}\text{cm}^{-1}$ at 443 nm and $\epsilon = 2131 \text{ M}^{-1}\text{cm}^{-1}$ at 317 nm, but cis-azobenzene has a $1500 \text{ M}^{-1}\text{cm}^{-1}$

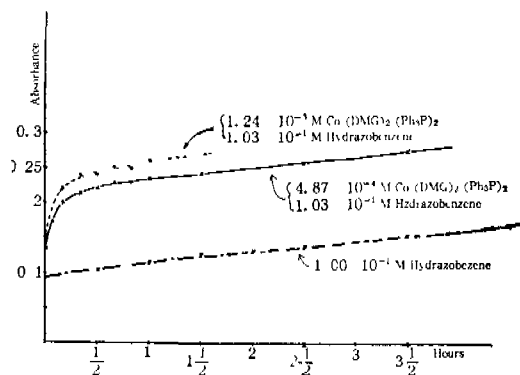


Fig. 5. Plot of absorption of substrates and catalysts against time at $\lambda = 440$ nm.

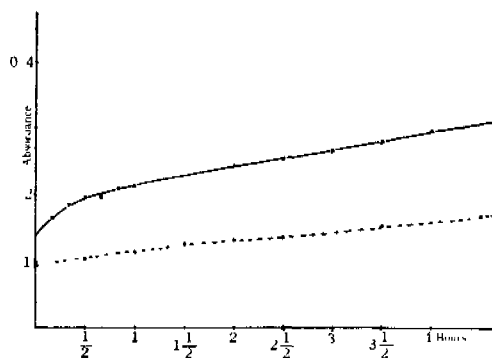


Fig. 6. Plot of absorbance against time in methanol at 25°C
 $[\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2] = 4.40 \times 10^{-4} \text{ M}$
 $[\text{Hydrazobenzene}] = 1.00 \times 10^{-1} \text{ M}$

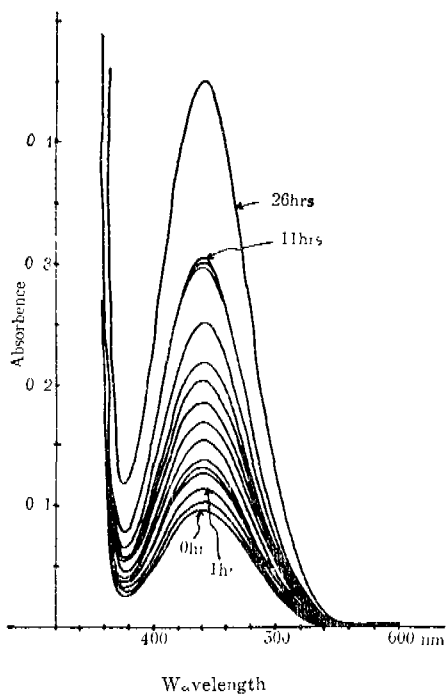


Fig. 7. Absorbance changes of autoxidation of hydrazobenzene ($1.00 \times 10^{-1} \text{ M}$) in methanol at 25°C

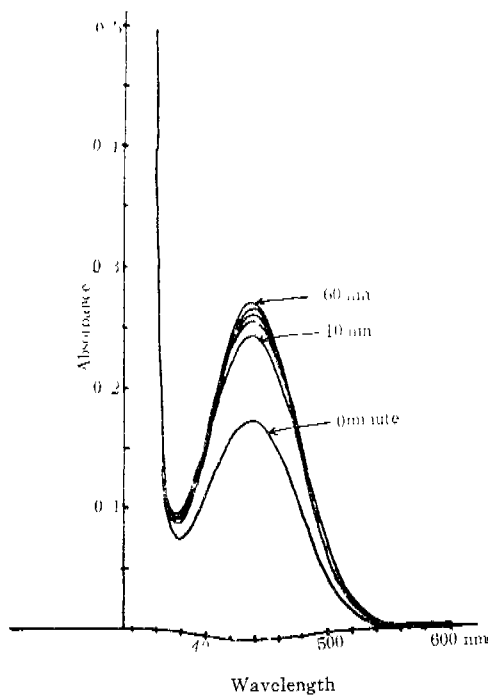


Fig. 8. Absorbance changes of oxidation reaction of hydrazobenzene ($1.03 \times 10^{-1} \text{ M}$) catalysed by $\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2$ ($1.24 \times 10^{-3} \text{ M}$) in methanol at 25°C

extinction coefficient at 433 nm and $5,200 \text{ M}^{-1}\text{cm}^{-1}$ at 281 nm⁽⁷⁾. In Figure 4 $\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2$ complex has an optical density of 0.18 ($\epsilon = 17,476 \text{ M}^{-1}\text{cm}^{-1}$ at 260 nm and 0.74 ($\epsilon = 71,845 \text{ M}^{-1}\text{cm}^{-1}$ at 315 nm. An absorbance

band of hydrazobenzene at 288 nm was shown as a dotted line. As shown in Figure 5, the rate of increase of hydrazobenzene at 440 nm is linear without catalyst. The plot of reaction of substrate hydrazobenzene ($1.03 \times$

10^{-1} M) and a catalyst $\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2$ (4.87×10^{-4} M) shows that, for about thirty minutes, hydrazobenzene at 440 nm increases rapidly, but after half an hour, the rate of increase is the same as that in the absence of catalyst. A higher concentration of the catalyst (1.24×10^{-1} M) shows higher absorbance but not in proportion. In Figure 6, $\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2$, which was not recrystallised, is shown that it is not so sharp curve for thirty minutes compared with the catalyst which was recrystallised in Figure 6.

After twelve hours an absorbance reaction curve line was reached 0.45 of absorbance.

In Figure 7,8, we can see the absorbant spectra of oxidation reaction of the substrate and the catalyst. Figure 7 shows that the rate of autoxidation of hydrazobenzene to azobenzene is slow, but, with catalyst in Figure 8, oxidation reaction of hydrazobenzene looks fast within twenty minutes.

7. Discussion

In preparation of $\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2$, the product was produced by the method of G. N.

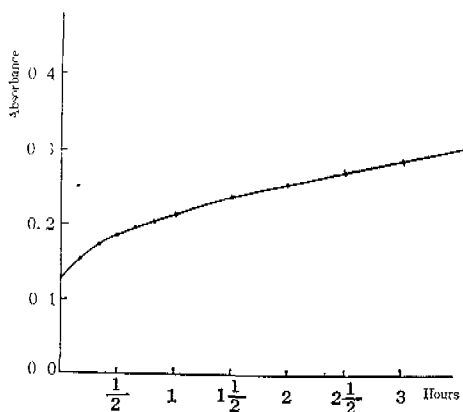


Fig.9. Plot of absorbance against time
 $[\text{CoSalen}] = 3.52 \times 10^{-4}$ M and $[\text{Hydrazobenzene}] = 1.02 \times 10^{-1}$ M; $[\text{Co}(3\text{MeOSalen})] = 2.51 \times 10^{-3}$ M and $[\text{Hydrazobenzene}] = 1.03 \times 10^{-1}$ M in methanol at 25°C

Schrauzer and L.P.Lee(3). Attempts to make solutions of dimethylglyoxime and Ph_3P in dry methanol failed because dimethylglyoxime and triphenylphosphine were not dissolved in dry methanol, so $\text{Co}(\text{DMG})_2(\text{Ph}_3\text{P})_2$ could not produce by combining each solutions of the compounds. The yield 95% was very good.

Azobenzene has been shifted from 437 nm to 433 nm and also increased absorbance when azobenzene was irradiated in Figure 4. Trans-azobenzene has a weak optical density in 443 nm⁽⁷⁾, but cis-azobenzene in 433nm. Therefore azobenzene seems to be changed from trans form to cis form when it was irradiated. Cis-azobenzene has also a band at 281 nm (7)(8). As hydrazobenzene is oxidised to azobenzene by catalyst in Figure 4, a band at 288 nm has shifted to 275 nm. The effect of varing the reaction curve deviation and concentration is shown in Figure 5. As the concentration of catalyst increases, the curve seems to be sharper, and in the case of $\text{Co}(3\text{MeOSalen})$ in Figure 9 and 10, higher concentration of catalyst has sharper reaction curve than lower one. So catalytic activity of oxidation reaction is supposed to depend on the catalytic concentration.

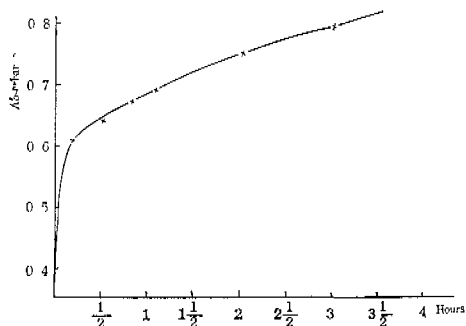


Fig.10. Plot of absorbance against time.
 $[\text{Co}(3\text{MeOSalen})] = 2.51 \times 10^{-3}$ M
 $[\text{Hydrazobenzene}] = 1.03 \times 10^{-1}$ M
 in methanol at 25°C

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