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Oxidation by Transition Metal Complexes. III. Oxidation of Cinnamaldehyde Catalyzed by Rhodium Compounds

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The catalytic activity of $RhCl(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$ for oxidations of styrene and cinnamaldehyde has been studied. Under oxygen atmosphere, these complexes can cause catalytically oxidation of cinnamaldehyde to give benzaldehyde, glyoxal, benzene and styrene. The reaction is complicated because decarbonylation reaction takes place with oxidation, and the carbonyl complex formed plays a catalytic role for the oxidation.

In previous papers,[1,2] we reported on the catalytic oxidation of styrene and methylstyrenes with some rhodium compounds under oxygen stream to produce the corresponding aldehydes and ketones.

In connection with this work, the catalytic oxidation of cinnamaldehyde by the rhodium complexes was investigated. It was found that some rhodium complexes have catalytic functions for oxidation, but the reaction is complicated because decarbonylation reaction also takes place at the same time. Cinnamaldehyde gave benzaldehyde and glyoxal by oxidation, and styrene and benzene by decarbonylation. It becomes apparent that the oxidation reaction might proceed *via* the carbonyl complex, $RhCl(CO)(PPh_3)_2$ formed by decarbonylation of the starting aldehyde. In the present paper we wish to report on the oxidation of cinnamaldehyde with rhodium complexes.

Results and Discussion

Catalytic oxidation of styrene with iridium and rhodium complexes under oxygen atmosphere[1,2] give benzaldehyde and acetophenone. The complex $RhCl(PPh_3)_3$ is known to be an efficient catalyst for decarbonylation of aldehydes.[3-6]

In order to investigate the relation between oxidation and decarbonylation, the relation between product concentrations and the time for the oxidation of styrene in toluene was examined.

The result is given in Fig. 1. We see that the concentration of benzaldehyde increases with reaction time very slowly during the first hour and then increases rapidly. After 8 hr, the yield of benzaldehyde became almost constant and reached 213%.[7]

Acetophenone was also formed in 13% yield. A 3% yield of benzene was attained by the decarbonylation of benzaldehyde.

From the fact that both oxidation and decarbonylation reactions take place simultaneously, we examined the decarbonylation of cinnamaldehyde with a $RhCl(PPh_3)_3$ catalyst before studying the oxidation of cinnamaldehyde.

Mixtures of the reactant cinnamaldehyde and $RhCl(PPh_3)_3$ in toluene were heated at 80°C for 8 hr under nitrogen stream.

Figure 2 shows that cinnamaldehyde easily undergoes decarbonylation to give styrene.

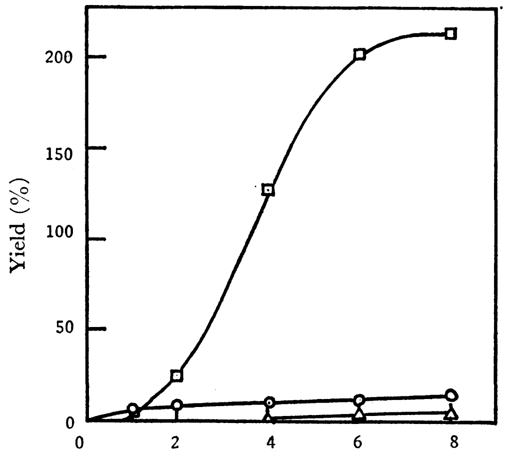

Fig. 1. Oxidation of styrene with $RhCl(PPh_3)_3$ in toluene: □: Benzaldehyde, ○: Acetophenone, △: Benzene

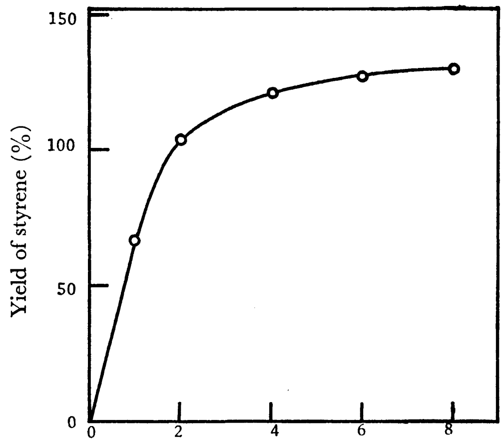

Fig. 2. Decarbonylation of cinnamaldehyde with $RhCl(PPh_3)_3$ in toluene under nitrogen stream.

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[3] J. Tsuji and K. Ohno, *Tetrahedron Lett.*, **1965**, 3969.

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[5] K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, **90**, 99 (1968).

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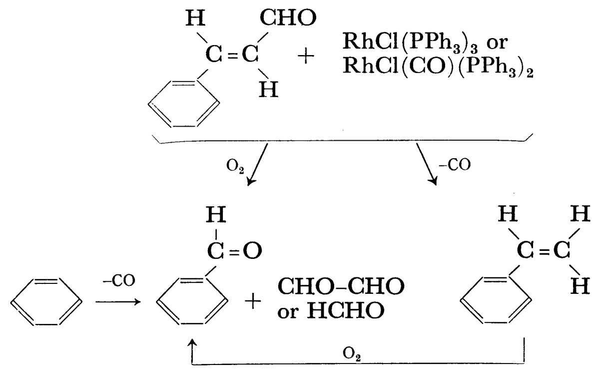
[7] Yields are based on the catalyst used.

TABLE 1. OXIDATION OF CINNAMALDEHYDE (Reaction temp. 80°C, Reaction time 8 hr)

Catalyst	Solvent	Products and yields,[a] %			
		Benzene	Styrene	Benzaldehyde	Acetophenone
$RhCl(PPh_3)_3$	Toluene	45	97	248	trace
$RhCl(PPh_3)_3$	Ethanol	trace	127	trace	8
$RhCl(CO)(PPh_3)_2$	Toluene	9	30	968	trace

a) Yields are based on the catalyst used.



Scheme 1. Reaction scheme in the oxidation of cinnamaldehyde.

Oxidation reaction of cinnamaldehyde was then carried out under constant bubbling of oxygen (Table 1 and Scheme 1). The products were benzaldehyde (248%), styrene (97%), benzene (45%), glyoxal, and formaldehyde. The relation between the product concentration and the time for the oxidation reaction is given in Fig. 3.

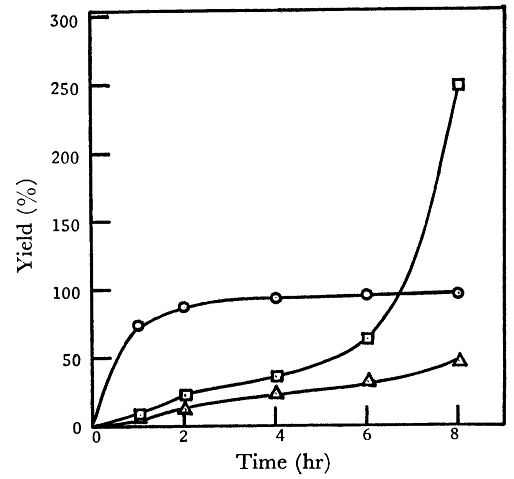


Fig. 3. Oxidation of cinnamaldehyde with $RhCl(PPh_3)_3$ in toluene.
□: Benzaldehyde, ○: Styrene, △: Benzene

It can be said that benzaldehyde is produced from the C=C double-bond cleavage of both cinnamaldehyde and styrene derived from the decarbonylation of cinnamadehyde. The fact that oxidation of both styrene and cinnamaldehyde has an induction period and involves decarbonylation reaction suggests that some rhodium carbonyl complexes formed play an important role for the oxidation catalyst. $RhCl(CO)(PPh_3)_2$ was obtained from the reaction mixtures. We therefore, examined the catalytic activity of the rhodium complex $RhCl(CO)(PPh_3)_2$ for oxidation reaction. Oxidation of cinnamaldehyde was carried out in the presence of $RhCl(CO)(PPh_3)_2$ under similar conditions. It was found that the carbonyl complex has remarkably high activity for the oxidation catalyst. A plot of the yields of products *versus* reaction time is given in Fig. 4.

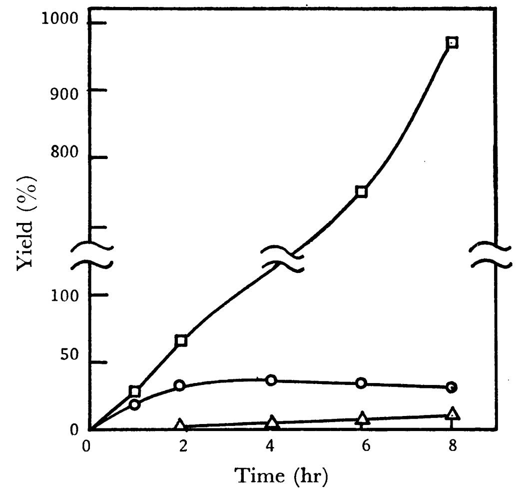


Fig. 4. Oxidation of cinnamaldehyde with $RhCl(CO)(PPh_3)_2$ in tolune.
□: Benzaldehyde. ○: Styrene. △: Benzene

The yield of benzaldehyde increased with reaction time and reached 968% after 8 hr.

On the other hand decarbonylation of aldehydes is very slow. The yield of styrene (30%) hardly changed with time and benzene derived from benzaldehyde was obtained in only 9% yield. The product distribution in the $RhCl(PPh_3)_3$ catalyst after the induction period (one hour) is very similar to that in the $RhCl(CO)(PPh_3)_2$ catalyst.

These results show that the $RhCl(PPh_3)_3$ catalyzed oxidation might proceed *via* the carbonyl complex, $RhCl(CO)(PPh_3)_2$.[8]

We reported that the catalytic oxidation of styrene with rhodium complexes undergoes a remarkable solvent effect.[2] Such an effect was also observed in the oxidation of cinnamaldehyde.

The catalytic oxidation of cinnamaldehyde with $RhCl(PPh_3)_3$ in ethanol gave styrene (127%) and acetophenone (8%).

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[8] $RhCl(CO)(PPh_3)_2$ liberates carbon monoxide during the catalytic decarbonylation.[5]

Alcohol is not a good solvent for the C=C double-bond cleavage.

Experimental

Materials and Analysis. All temperatures were uncorrected. Vpc analysis was made by a Yanagimoto G-8 gas chromatograph using Apiezon-L, Silicone OV-17 or Diethyl phthalate columns. Toluene and ethanol were purified as mentioned previously.[1] Cinnamaldehyde was dried over anhydrous magnesium sulfate and distilled.

Preparation of Rhodium Complexes. Chlorotris(triphenylphosphine)rhodium(I), $RhCl(PPh_3)_3$ and chlorocarbonylbis(triphenylphosphine)rhodium(I), $RhCl(CO)(PPh_3)_2$ were prepared by the method of Osborn *et al.*[9]

General Procedure for Oxidation by the Rhodium Complexes. The rhodium complex and cinnamaldehyde were dissolved in a solvent such as toluene. Under constant bubbling of oxygen the solution was heated at 80°C for 8 hr. After evaporation of the solvent, isolation of the products was carried out by gas or column chromatography.

Oxidation of Cinnamaldehyde by Rhodium Complexes. In a flask similar to that described previously[1] was placed a mixture containing 2.83 g (3.06 mmol) of $RhCl(PPh_3)_3$, 15.5g (0.117 mol) of cinnamaldehyde and 150 m*l* of toluene as a solvent. The oxidation reaction was carried out at 80°C with constant bubbling of oxygen for 8 hr. At appropriate intervals, a portion of the solvent was analyzed as usual. After evaporation of the solvent under reduced pressure, the residual material was chromatographed on a silica-gel column (30 g). Elution with one liter of ether gave triphenylphosphine oxide. In addition, elution with 500 m*l* of methanol gave dark brown complexes. The complexes were further chromatographed on a silica-gel column to give a considerable amount of carbonyl complex $RhCl(CO)(PPh_3)_2$ and unidentified complexes (mp 210—213°C (decomp.)) which gave no carbonyl absorption. From vpc analysis and isolation of the solvent cinnamaldehyde, 0.97 g (248%) of benzaldehyde, 0.31 g (97%) of styrene, 0.11 g (45%) of benzene, glyoxal, and formaldehyde were obtained. From vpc analysis (activated carbon column) of the outlet gas, carbon monoxide was determined. In the case of the reaction in ethanol as solvent, we obtained cinnamaldehyde, 0.39 g (127%) of styrene and 0.03 g (8%) of acetophenone. The complex $RhCl(CO)(PPh_3)_2$ was isolated from the reaction mixtures.

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9) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, *C*, **1966**, 1711.