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Behavior of Amine in Rhodium Complex–Tertiary Amine Catalyst System Active for Hydrogenation of Aldehyde under Oxo Reaction Conditions

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Synopsis. The title reaction was investigated to elucidate the reported disagreements on the kinetics. The concentration and the coordination stability of amine were found to affect the optimum pressure of carbon monoxide and the kinetics, and were suggested to control the reaction mechanism.

Rhodium complex is very active for the hydroformylation of olefin,[1–3] but not so effective for the hydrogenation of aldehyde under the hydroformylation conditions.[3,4] The addition of tertiary amine to the rhodium catalyst, however, markedly facilitates the hydrogenation to make possible one step synthesis of oxo alcohol.[5] With the system of rhodium complex and tertiary amine, the hydroformylation of olefin,[5–7] the hydrogenation of aldehyde,[6,7] and the selective hydrogenation of α,β-unsaturated aldehyde to alcohol[8,9] have been studied, but different optimum pressures of carbon monoxide,[5,9] and linear[6,7] and nonlinear[5,9] dependences on the pressure have been reported. It is accepted that anionic clusters of rhodium are formed in the presence of amine,[7] but the interaction of amine with the rhodium complex is not clear. In this paper we wish to clarify the behavior of amine in the system of rhodium complex and tertiary amine, and to describe a cause of disagreement on the effect of carbon monoxide.

Experimental

$[Rh_2Cl_2(CO)_4]$[10] and $[Rh(acac)(CO)_2]$[11] were prepared according to the procedures in the literatures. Amines were, on occasion, distilled from CaH_2, but typically used without further purification. Aminated polystyrene (Found: H; 9.0, C; 84.4, N; 5.5, Cl; 0.0%) was prepared as described in a previous paper.[9] Other reagents of guaranteed grade were used without further purification. The reactions of hydrogention and hydroformylation, and the reaction of $[Rh_2Cl_2(CO)_4]$ with aminated polystyrene were carried out as described in a previous paper.[9]

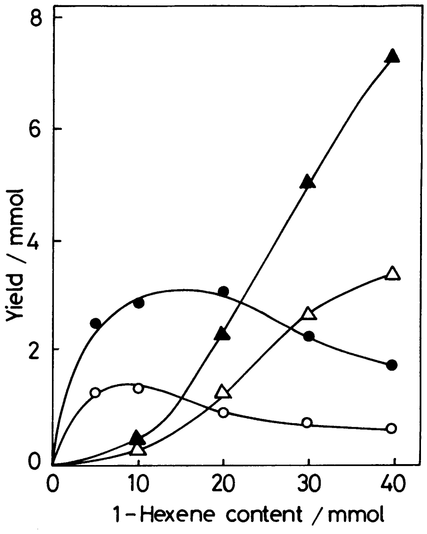

Fig. 1. Dependence of alcohol yields on 1-hexene content in hydroformylation of 1-hexene with $Rh_2Cl_2(CO)_4$ (0.05 mmol) and *N*-methylpyrrolidine (20 mmol) in benzene (20 ml) at 60 kg/cm² ($P_{H_2}/P_{CO}=1$) and 80 °C for 20 min.
▲: Heptanal, △: 2-methylhexanal, ●: 1-heptanol, ○: 2-methyl-1-hexanol.

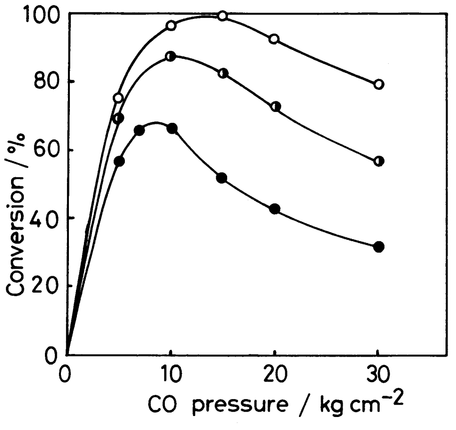

Fig. 2. Dependence of benzaldehyde conversion on pressure of carbon monoxide with $Rh_2Cl_2(CO)_4$ (0.05 mmol) and *N*-methylpyrrolidine in benzene (20 ml) at 30 kg/cm² (P_{H_2}) and 80 °C for 20 min.
N-Methylpyrrolidine; ●: 2.5 mmol, ◐: 5 mmol, ○: 10 mmol.

Results and Discussion

Figure 1 shows the dependence of the yield of heptanol in the hydroformylation on the content of 1-hexene. The obvious inhibition by olefin is seen on the hydrogenation, but not the hydroformylation. The similar inhibition by carbon monoxide is seen in Fig. 2. Since the yield of alcohol is independent of the concentration of aldehyde in spite of the high pressure of carbon monoxide as shown in Fig. 3, these inhibitions seem to indicate the competitive coordination of olefin and carbon monoxide with amine rather than aldehyde. The optimum pressure of carbon monoxide, P_{CO}(Max), where the highest yield of alcohol is obtained, seems to increase with an increase in the concentrtion of amine (Fig. 2). Figure 4 shows a good correlation between P_{CO}(Max) and the concentration of amine, including reported P_{CO}(Max)s.[5,9] This indicates that the coordination of amine on the rhodium complex is competitive with carbon monoxide, although Jurewicz *et al.*[7] proposed an equilibrum

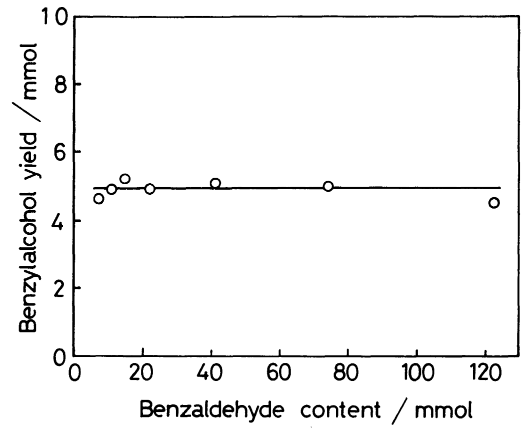

Fig. 3. Dependence of benzyl alcohol yield on content of benzaldehyde in hydrogenation of benzaldehyde with Rh(acac)$(CO)_2$ (0.05 mmol) and *N*-methylpyrrolidine (10 mmol) in benzene (20 ml) at 40 kg/cm² (P_{CO}) and 30 kg/cm² (P_{H_2}) and 60 °C for 30 min.

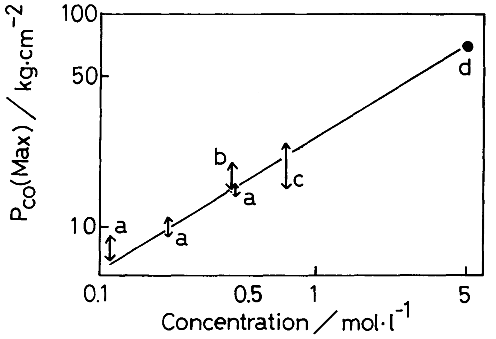

Fig. 4. Dependence of P_{CO}(Max) on concentration of *N*-methylpyrrolidine.
a) Hydrogenation of benzaldehyde at 30 kg/cm² (P_{H_2}) and 80 °C. b) Hydrogenation of benzaldehyde at 30 kg/cm² (P_{H_2}) and 60 °C. c) Hydrogenation of cinnamaldehyde at 40 kg/cm² (P_{H_2}) and 80 °C (Ref. 8). d) Hydroformylation of 1-hexene at 75 kg/cm² (P_{H_2}) and 90 °C (Ref. 5).

between $[HRh_x(CO)_y(NR_3)]$ and $[HNR_3^+ \cdot Rh_x(CO)_{\bar{y}}^-]$. Thus, it is concluded that the reported difference of P_{CO}(Max)s[5,9] is because of the different concentrations of amine. In the presence of carbon monoxide and amine, rhodium carbonyl complexes easily transform into anionic clusters,[7,13,14] suggesting that the interacton of amine with rhodium complex may be written as Eq. 1,

$$Rh_x(CO)_{y+1}^{n-} \underset{CO}{\overset{NR_3}{\rightleftharpoons}} Rh_x(NR_3)(CO)_y^{n-} \underset{NR_3}{\overset{olefin}{\rightleftharpoons}} Rh_x\,(olefin)(CO)_y^{n-}, \tag{1}$$

where $[Rh_x(NR_3)(CO)_y^{n-}]$ and $[Rh_x(olefin)(CO)_y^{n-}]$ may be active for the hydrogenation of aldehyde and the hydroformylation of olefin, respectively.

The results with the catalyst system of polymer amine are different from that of monomer amine. The hydroformylation of 1-hexene (10 mmol) in benzene (20 ml) at 80 °C and 60 kg/cm² ($P_{CO}/P_{H_2}=1$) for 60 min with $[Rh_2Cl_2(CO)_4]$ (0.05 mmol) and aminated polystyrene (0.75 matom-N) gave 1.0 mmol of heptanal, 0.9 mmol of 2-methylhexanal, 3.0 mmol of 1-heptanol, and 1.7 mmol of 2-methyl-1-hexanol. Further addition of the polymer (5 matom-N) resulted in no further increase in the yields. These results contrast with the cases of monomer amine where large amounts of amine are used.[5,7–9] It is known that $[Rh_2Cl_2(CO)_4]$ firmly interacts with aminated polystyrne.[6,7,9] $[Rh_2Cl_2(CO)_4]$ (0.05 mmol) was treated with aminated polystyrene (0.5 matom-N) in toluene (20 ml) to give colorless solution and brown polymer while evolving carbon monoxide. In N/Rh>10 the polymer-anchored rhodium complex showed no absorption band in ν(CO) region, while in N/Rh<5 three bands at 2060 (w), 1985 (s), and *ca.* 1800 cm^{-1} (w, broad) due to ν(CO)[9] were observed. These results indicate that polymer amine strongly interacts with rhodium complex to exclude carbon monoxide ligand, leading to a first order dependence on carbon monoxide.[6,7] Thus, it can be concluded that the kinetic disagreement of polymer amine system with monomer one comes from the difference of their coordination stability, though Jurewicz *et al.*[7] attributed the disagreement to the difference of reaction conditions.

The difference between polymer and monomer amines seems to bring about the different dependence on the concentration of aldehyde, *i.e.*, zero order with monomer amine system (Fig. 3) and first order with polymer one.[6] These kinetic difference might suggest different reaction mechanisms. Taking into account the first order dependence on the pressure of hydrogen,[5,6,9] the formation of rhodium hydride with monomer amine system may be a slow step followed by a fast reaction of the hydride with aldehyde, while the coordination of aldehyde or the reaction of a hydride with aldehyde on polymer-anchored rhodium complex may be slow.

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