Mechanistic Studies on Direct Ethylene Glycol Synthesis from Carbon Monoxide and Hydrogen

1. Homogeneous Rhodium Catalyst

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Mechanistic studies on direct syngas conversion to ethylene glycol by a homogeneous Rh catalyst combined with a trialkylphosphine were performed. High-pressure IR studies showed that when a bulky trialkylphosphine, such as $P^iPr_3(L)$, was added to the Rh catalyst, it gave $HRh(CO)_3L$, rather than Rh carbonyl cluster anions, whereas PPh_3 and P^nBu_3 tended to decompose under the reaction conditions, forming an inactive Rh phosphidocarbonyl cluster anion, $[Rh_9P(CO)_{21}]^{2-}$. Kinetic studies by means of complete-mixing flow-reaction experiments revealed that the formation of formaldehyde (FAL) from CO and H_2 was rate-determining, and a bulky trialkylphosphine accelerated both the formation and the hydrogenation of FAL. It was suggested that these acceleration effects were connected with enrichment of the mononuclear hydride species and improvement of the CO insertion abilities to the hydride and the hydroxymethyl complexes by the phosphine ligand. The studies on the catalyst concentration dependencies by means of batchwise reaction revealed the involvement of dinuclear mechanisms in the formation of FAL and the reductive elimination of the hydroxymethyl and the hydroxyacetyl complexes. © 1992 Academic Press, Inc.

INTRODUCTION

The direct conversion of synthesis gas to ethylene glycol (EG) is known to be catalyzed by various carbonyl complexes of transition metals such as Co, Rh, Ru, Ir, and Re (*1–7*). Among these metals, Rh and Ru are the most effective. We previously reported that a bulky trialkylphosphine (with large cone angles around the P atom), such as P^iPr_3, prominently enhances the activity and the stability of the Rh carbonyl catalyst (*2*). Considering the well-known hydroformylation of formaldehyde (FAL) (*8, 9*), FAL and glycolaldehyde (GAL) have been regarded as important possible intermediates for this reaction (*10, 11*). Its mechanistic studies, however, have been scarce because of the complexities due to the multistep/multi-species nature of the catalysis. In this paper, high-pressure IR studies and kinetic studies were performed to clarify the

mechanism for the Rh/phosphine catalysts more specifically (*12*).

EXPERIMENTAL

Reagents

$Rh_4(CO)_{12}$ and $Rh(CO)_2acac$ were used as the catalyst precursors, dissolved in a solvent.

High-Pressure IR Studies

The high-pressure and high-temperature IR apparatus, which was originally made by our laboratory, consists of an IR cell, a 100-cc autoclave made of SUS-316 stainless steel, and a Hitachi IR-730 spectrometer. The IR cell, which is connected to the autoclave by a stainless tube wrapped with heating tape, consists of a stainless-steel body, a window (10 mm in diameter) made of CaF_2 with a Teflon O-ring packing, and a heating coil. In general, part of the reaction solution in the autoclave was introduced into the IR

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cell under high pressure and high temperature through a manual valve, and the IR spectrum was instantly recorded. The IR spectra recorded in absorption mode after subtracting the background bands due to a solvent are shown in the text.

Kinetic Studies

The complete-mixing flow-reaction (CMFR) experiments were carried out by using an 80-cc reactor made of SUS-316 stainless steel equipped with a mechanical stirrer. FAL was handled in the form of an ethanol solution to dissolve in the catalyst solution. A sufficient amount of CO/H_2 gas was supplied to the reactor so that no substantial change in the CO/H_2 ratio occurred during the reaction. The effluent solution was cooled rapidly to ambient temperature. The amount of reaction solution filled in the reactor was measured after the reactor was cooled and all the calculations were carried out based on the concentrations at ambient temperature. The batchwise reactions were carried out in a 50-cc autoclave made of Hastelloy C-276 stainless steel. The liquid products were analyzed by programmed temperature (80 to 240°C at 8°C/min) GLC with a 1-m column packed with 10% PEG–20 M TPA on Chromosorb-102 and were identified by GLC/mass spectral analysis.

RESULTS AND DISCUSSION

High-Pressure IR Studies

Figure 1 shows the IR spectra of phosphine-promoted Rh catalysts in N-methyl-2-pyrrolidone (NMP) solvent at 180°C under a pressure of 180 atm (CO/H_2 = 1). In the absence of phosphine, a large amount of Rh mononuclear anion, $[Rh(CO)_4]^-$ (A), with a specific band at 1900 cm^{-1} and a small amount of Rh hydride carbonyl cluster anions with a broadband at 1990 cm^{-1} were observed (*13, 14*). The ratio of the mononuclear complex (A) was increased with increasing CO pressure. A small amount of N-methylpyrrolidine (NMPD), which was produced by the hydrogenation of NMP, was
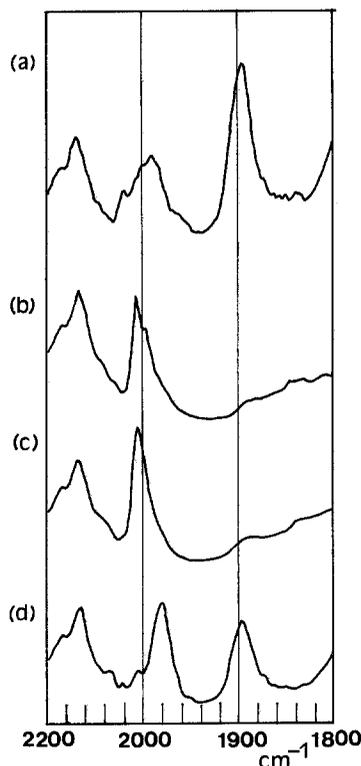
FIG. 1. High-pressure IR spectra for Rh catalysts; [Rh] 0.01 g-atom/liter, NMP solvent, CO/H_2 (1/1) 180 atm, 180°C, 1 h. (a) No additive; (b) PPh$_3$, 0.01 mol/liter; (c) P^{n}Bu$_3$, 0.01 mol/liter; (d) P^{i}Pr$_3$, 0.01 mol/liter. The broad absorption at 2135 cm^{-1} is based on dissolved CO gas.

detected in the solution. Therefore, protonated NMPD must be the countercation of the anionic complexes. Vidal and Waller (*13*) reported that EG formation is connected with Rh hydride carbonyl cluster anions. Equimolar addition of PPh$_3$ or P^{n}Bu$_3$ to the Rh catalyst gave irreversibly a strong band at 2010 cm^{-1}, which corresponds to the characteristic absorption of $[Rh_9P(CO)_{21}]^{2-}$. This phosphidocarbonyl cluster anion was confirmed by ^{31}P NMR spectra. Little activities of the Rh catalysts with these phosphines for CO hydrogenation are attributable to the formation of the inactive phosphidocarbonyl cluster. On the other hand, the P^{i}Pr$_3$-promoted Rh catalyst gave a new band at 1980 cm^{-1}. When cooled

and depressurized, the band at 1980 cm^{-1} shifted reversibly to 1950 cm^{-1} and a red precipitate was deposited. Tomotake *et al.* (*15*) isolated the red complex and assigned it $Rh_2(CO)_6(P^iPr_3)_2$ by spectral analyses. Considering the interconversion of the corresponding Ir complexes (*16*), $Ir_2(CO)_6$ $(PPh_3)_2$ and $HIr(CO)_3PPh_3$, the species with absorption at 1980 cm^{-1} was assigned to $HRh(CO)_3P^iPr_3$ (B). Rh carbonyl clusters were not observed in the Rh/P^iPr_3 catalyst system under these conditions. Above inferences are summarized in the following equations:

$$Rh_4(CO)_{12} \xrightarrow[P^iPr_3]{CO/H_2}$$

$$P''Bu_3 \downarrow \text{ or } PPh_3$$

$$[Rh_9P(CO)_{21}]^{2-}$$
$$[Rh(CO)_4]^- + HRh(CO)_3L \quad (L = P^iPr_3)$$

$$-H_2 \downarrow \text{cooling}$$

$$Rh_2(CO)_6L_2$$

The complex, $HRh(CO)_4$, which is considered to exist in equilibrium with the complexes (A) and (B), could not be detected. Temperature dependencies of the IR spectra under the conditions of Fig. 1 revealed that the formation of the Rh phosphidocarbonyl cluster anion occurs at 180°C (PPh_3), 200°C ($P''Bu_3$), and 260°C (P^iPr_3). This fact indicates that the degree of difficulty for the decomposition of the phosphines increases in the order $PPh_3 < P_nBu_3 \ll P^iPr_3$, coinciding with the increasing order of the activities of the Rh/phosphine catalysts (*2*). In the case of the $Rh/P''Bu_3$ catalyst, Watanabe *et al.* (*17*) found that a large excess addition of $P''Bu_3$ enhances the activity for CO hydrogenation. We confirmed spectroscopically that the presence of excess $P''Bu_3$ suppresses the formation of the phosphidocarbonyl cluster. These results revealed that addition of a bulky trialkylphosphine such as P^iPr_3 effectively stabilizes the Rh mononuclear hydride carbonyl (B) by its coordination to Rh metal, rather than Rh carbonyl cluster anions. It is also suggested that complex (B)

FIG. 2. High-pressure IR spectra for Rh catalysts under reaction conditions; [Rh] 0.01 g-atom/liter, NMP solvent, CO/H_2 (1/1) 300 atm, 200°C 2 h. (a) No additive; (b) P^iPr_3, 0.01 mol/liter; (c) P^iPr_3, 0.03 mol/liter; (d) P^iPr_3, 0.01 mol/liter, and N-ethylimidazole, 0.03 mol/liter. The absorptions based on dissolved CO gas were canceled by subtraction in these spectra.

plays an important role for enhancement of the activity for CO hydrogenation.

Figure 2 and Table 1 show, respectively, the IR spectra and the CO hydrogenation activities of the Rh/P^iPr_3 catalysts under the reaction conditions (200°C, 300 atm), including an additive effect of N-ethylimidazole as a second promoter. The Rh/NMP system (Fig. 2a) gave mainly the mononuclear anion (A) under a CO pressure higher than that of Fig. 1a. The Rh/P^iPr_3 catalysts gave mainly complexes (A) and (B), similar to Fig. 1, as well as a small amount of the phosphidocarbonyl cluster. Excess addition of P^iPr_3 (Fig. 2c), which increased complex (B), increased

TABLE 1

Activities of Rh/P^{i}Pr$_3$ Catalysts

Catalyst[a]	Activity (mol/liter)	
	EG	MeOH
(a)	0.015	0.029
(b)	0.035	0.026
(c)	0.038	0.15
(d)	0.055	0.034

[a] Catalysts and reaction conditions are given in the legend to Fig. 2.

FIG. 3. P_O/V vs F/V for Rh/NMPD/NMP catalyst; Rh(CO)$_2$acac 0.04 g-atom/liter, NMPD 0.05 mol/liter, CO/H$_2$ (1/1) 500 atm, 220°C, catalyst solution feed rate 90 g/h. Sel. = 100 × EG/(EG + MeOH) (no GLY and little GAL were detected).

the total activity of (EG + MeOH), but decreased EG selectivity with an increase in MeOH formation. On the other hand, addition of the amine as a second promoter, which balanced both complexes, increased the EG formation with high EG selectivity. These facts suggest that complex (B) is responsible for the total activity for CO hydrogenation.

Kinetic Studies by CMFR Experiments

The overall reaction is illustrated in Scheme 1. Although the FAL concentration is too low to be determined under the reaction conditions, the reaction rates relating to FAL can be analyzed by means of CMFR experiments, in which FAL is supplied together with the catalyst solution and CO/H$_2$ gas continuously to the reactor. Provided that the reaction rates of FAL are propor-

tional to the FAL concentration in the reactor, the overall production rate P_O is given by Eq. (1) based on the FAL balance.

$$P_O/V = (F/V)/(1 + k_{-1}/k_2) + k_1/(1 + k_{-1}/k_2) \quad (1)$$

Figure 3 shows the relationship between the overall production rate (P_O) and the FAL feed rate (F) in the case of the Rh/NMPD/NMP catalyst system, in which NMPD is added in an amount sufficient to offer to the countercation. V represents the volume of the reaction mass in the reactor. As can be seen in the figure, P_O/V increased with the increase in F/V in such a manner that the
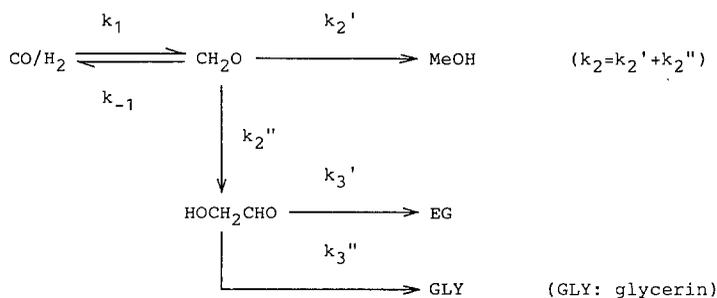
SCHEME 1

TABLE 2

Kinetic Data for Rh Catalysts[a]

No. additives[b] (mol/liter)	Rate constants[c]				Formation ratio	
	k_1	k_{-1}/k_2	Kk_2'	Kk_2''	EG/MeOH	GLY/EG
1 NMPD (0.05)	9	0.04	170	56	0.33	0.00
2 P^{i}Pr$_3$ (0.04)	30	0.20	75	75	0.86	0.12
3 P^{i}Pr$_3$ (0.04) NMPD (0.14)	30	0.30	24	76	2.6	0.17

[a] Rh(CO)$_2$acad 0.04 g-atom/liter, N-methyl-2-pyrrolidone solvent, CO/H$_2$ (1/1) 500 atm, 220°C.

[b] NMPD, N-methylpyrrolidine.

[c] k_1, Kk_2', and Kk_2'': in mol/g-atom/h, $K = k_1/k_{-1}$.

slope of the straight line was close to 45°, showing the small k_{-1}/k_2 value. This implies that the rate-determining step is the CO hydrogenation to form FAL. Figure 3 also shows that the EG/MeOH formation ratio was unchanged by the addition of FAL, implying that the added FAL behaved in the same manner as the FAL formed from CO and H$_2$. Similar relationships were obtained in the case of the Rh/P^{i}Pr$_3$ catalyst systems. Table 2 shows the kinetic data for several Rh catalysts. IR spectra of the catalyst solutions under the conditions had the same patterns as those in Fig. 2. Since the reaction conditions (temperature, pressure, and CO/H$_2$ ratio) are fixed, k_1/k_{-1} ($= K$) is constant, and consequently, the values of Kk_2' and Kk_2'' in the table show the relative magnitude of k_2' and k_2'', respectively. In the case of the Rh/P^{i}Pr$_3$ catalyst system, the formation of FAL is also rate-determining, since the k_{-1}/k_2 value is smaller than 1. The enhancement of the activity by addition of P^{i}Pr$_3$ can be attributed to improvement of the activity for the CO hydrogenation to form FAL. The activity for the hydroformylation of FAL to form GAL is also improved, whereas that for the hydrogenation of FAL to form MeOH is depressed. This is in accordance with the results for the hydroformylation of FAL by the PPh$_3$-promoted Rh catalyst under much milder conditions (9, 18). On the basis of kinetic and IR studies, it is suggested that the phosphine ligands enrich the mononuclear hydride species that

are more effective than hydride carbonyl cluster anions for the CO hydrogenation to form FAL and also enhance the CO insertion ability of Rh kinetically or thermodynamically.

$$HRh(CO)_3L \xrightarrow{CO}$$
$$HCORh(CO)_3L \rightarrow CH_2O \quad (2)$$

$$HOCH_2Rh(CO)_3L \xrightarrow{CO}$$
$$HOCH_2CORh(CO)_3L \rightarrow HOCH_2CHO \quad (3)$$
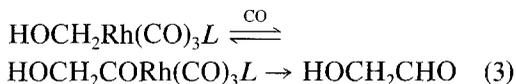
Addition of an amine as a second promoter also depressed the hydrogenation of FAL to form MeOH and gave a higher EG/MeOH ratio as shown in Table 2. The synergistic effect of the phosphine ligand and the amine additive with respect to the FAL hydroformylation is also in accordance with the case of the PPh$_3$-promoted Rh catalyst (18). Chan et al. (18) suggested that an amine accelerates the formation of the hydroxymethyl species coordinated by the phosphine, and this is also considered to be the case for the direct conversion of syngas to EG under much severer conditions.

$$HRh(CO)_3L \xrightarrow{B} Rh(CO)_3L^- \xrightarrow{CH_2O}$$
$$^-OCH_2Rh(CO)_3L \xrightarrow{BH^+}$$
$$HOCH_2Rh(CO)_3L \quad (4)$$
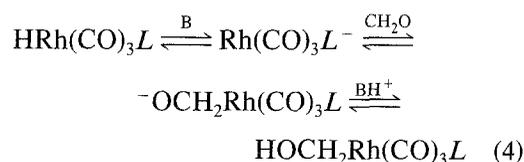
Dependency on the Catalyst Concentration

We studied the catalyst concentration dependencies to clarify the involvement of dinuclear mechanisms in the elementary reactions. Collman et al. (19), by using a silica-supported Rh catalyst, obtained evidence that the hydrogenolysis of the metal acyl in the Rh-catalyzed hydroformylation of olefins proceeds by dinuclear reductive elimination.

$$RCO-ML_m + H-ML_n \rightarrow$$
$$L_mM - ML_n + RCHO \quad (5)$$

As for the direct CO/H$_2$ conversion, on the

FIG. 4. Influence of Rh concentration; NMPD, 0.5 mmol; NMP, 10 ml; CO/H_2 (1/1) 500 atm; 220°C. Turnover shows the turnover frequency for (EG + MeOH).

other hand, Dombek and Harrison (20) suggested that the formation of the formyl complex also proceeds by a dinuclear mechanism.

$$L_mM-CO + H-ML_n^- \rightarrow$$
$$L_mM^--CHO + ML_n \quad (6)$$

Figure 4 shows the dependencies of the catalyst activity and the selectivity on the Rh concentration in the Rh/NMPD/NMP catalyst system, which gave mainly the sole complex (A) in a low Rh concentration. As seen in the figure, the kinetic order of the overall reaction with respect to the Rh changed from 1 to 2 as the Rh concentration was lowered. Since Rh exists substantially only as mononuclear species in this low Rh concentration region under the high CO pressure, it is concluded that a dinuclear mechanism is involved in the catalysis. Taking into account the results by the CMFR experiments, it is plausible that this second-order reaction is involved in the formation of FAL. Both the formation of the formyl complex and the elimination of FAL can, in principle, proceed by dinuclear mechanisms. Considering the IR studies, we propose the following equation in which complex (B) plays essential roles.

$$HRh(CO)_3L \xrightarrow{CO}$$

$$HCORh(CO)_3L \xrightarrow{HRh(CO)_3L}$$
$$CH_2O + Rh_2(CO)_6L_2 \quad (7)$$
$$\Big\updownarrow H_2$$
$$2HRh(CO)_3L$$

The dependency of the selectivity on the Rh concentration also suggests the involvement of a dinuclear mechanism, which is, however, related to the subsequent reaction of FAL, as shown by Eq. (8). When the Rh concentration is very low, it is plausible that the CO insertion step is at equilibrium and hence the selectivity is controlled by the competition between the bimolecular hydrogenolysis of the hydroxymethyl and the acyl species. When the Rh concentration becomes higher, the competition between the hydrogenolysis and the CO insertion to the hydroxymethyl species is considered to prevail, resulting in an increase in the MeOH selectivity.

$$HOCH_2-M \xrightarrow{HM'} CH_3OH \quad (8)$$
$$\searrow$$
$$HOCH_2CO-M \xrightarrow{HM'}$$
$$HOCH_2CHO$$

CONCLUSION

On the basis of high-pressure IR and kinetic studies, we propose the mechanism represented by Scheme 2 for the direct conversion of CO/H_2 to EG by the phosphine-promoted Rh catalysts. The formation of FAL from CO and H_2 is rate-determining. A bulky trialkylphosphine ligand effectively stabilizes the Rh mononuclear hydride carbonyl rather than Rh carbonyl clusters and hence increases the concentration of the metal hydride, which is essential for CO hydrogenation. Furthermore, the phosphine ligand facilitates the CO insertion to the metal hydride to accelerate the FAL formation. The subsequent reactions of FAL proceed mainly via the hydroxymethyl species, which give MeOH by dinuclear elimination

$$H-M$$

$$H-M + CO \rightleftharpoons HCO-M \rightleftharpoons CH_2O + M-M$$

$$H-M$$

$$H-M + CH_2O \rightleftharpoons HOCH_2-M \longrightarrow CH_3OH + M-M$$

$$CO \Big\Updownarrow \qquad H-M$$

$$HOCH_2CO-M \longrightarrow HOCH_2CHO + M-M$$

$$(H-M: \ HRh(CO)_3L \ or \ HRh(CO)_4)$$

SCHEME 2

and GAL by CO insertion followed by di-nuclear elimination. The phosphine ligand also enhances the CO insertion ability to the hydroxymethyl species, and the amine base activates the phosphine complex to facili-tate the formation of the hydroxymethyl species.

ACKNOWLEDGMENTS

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