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PROMOTING EFFECT OF ACIDS ON THE FORMATION OF ETHYLENE GLYCOL FROM SYNTHESIS GAS CATALYZED BY THE RHODIUM–TRICYCLOHEXYLPHOSPHINE SYSTEM

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Summary

Carboxylic acids, pentafluorophenol and phosphoric acid (HX) facilitate the formation of ethylene glycol from synthesis gas catalyzed by the rhodium–tricyclohexylphosphine (TCP) system. Complexes recovered from the resultant solutions were identified as $RhX(CO)(TCP)_2$, which are stable to repeated use. The catalytically active species or its immediate precursor is proposed to be $HRh(CO)_2(TCP)_2$ from IR spectroscopic analysis under synthesis gas pressure of 280 bar.

Introduction

The direct conversion of synthesis gas to ethylene glycol is known to be effectively catalyzed by rhodium complexes [1 - 3]. The reaction has been enhanced with promoters, such as alkali salts or tertiary amines [4], or by the use of basic solvents, such as 1,3-dimethylimidazolidin-2-one (DMI) [5] or 1-alkyl pyrrolidin-2-one [6 - 8]. The rhodium species recovered from the resultant solutions have been shown to be $[Rh_{12}(CO)_{30}]^{2-}$, $[Rh_6(CO)_{15}]^{2-}$, $[Rh(CO)_4]^-$ etc. Catalytic activity to ethylene glycol has been enhanced by the use of tertiary alkyl phosphines, such as triisopropylphosphine [9, 10] or tri-n-butylphosphine [11]. Orange crystals were isolated from the reaction solutions with PPr^i_3, and identified as $[Rh(CO)_3(PPr^i_3)]_2$ [12]. This compound is stable only under CO atmosphere; it decomposes even under N_2 and even in the solid state [13]. Thus a more stable and active catalyst is needed for practical application. The catalytically active species in this system was presumed to be $HRh(CO)_3(PPr^i_3)$ based on hydrogenolysis of the $[Rh(CO)_3(PPr^i_3)]_2$ complex [12].

In this study, we have examined the effect of organic acids on the rhodium–tricyclohexylphosphine (TCP) catalyst system in order to improve the catalytic activity and stability of the complex.

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Results and discussion

Effect of TCP concentration in the Rh–TCP system

Table 1 shows the effect of the TCP concentration on the rates to ethylene glycol and methanol with the Rh–TCP catalyst system in DMI or tetraglyme (TGM) solvents. In the absence of TCP, the rate to glycol of 9.63 h^{-1} was more than twice as high as the rate to methanol of 4.12 h^{-1} in DMI (Exp. 1). The rate to glycol barely increases and the rate to methanol increases remarkably with an increase in the TCP concentration. Increasing the concentration of TCP diminishes the selectivity to glycol (ratio of glycol/methanol), while the rate of CO hydrogenation (sum of the rates to glycol and methanol) reaches its maximum value at a molar ratio TCP/Rh = 2. From IR analysis of the reaction solutions, rhodium was found to exist mainly as $[Rh_6(CO)_{15}]^{2-}$ (2040, 1985 and 1960 cm^{-1}) [14] in the absence of TCP. The absorption at 1952 cm^{-1} assigned to $[Rh(CO)_3(TCP)]_2$ (1) [12, 15], and the weak absorption at 1900 cm^{-1} assigned to $[Rh(CO)_4]^-$ [14] are observed by adding <2 equiv TCP. Only the latter absorption is observed at TCP/Rh = 4. The formation of $[Rh(CO)_4]^-$ may be understood as follows. The complex 1 is converted to $HRh(CO)_3(TCP)$ by the oxidative addition of H_2 under the reaction conditions, and this hydride complex reacts with excessive amounts of TCP to afford $[TCP{\cdot}H]\,[Rh(CO)_4]$ through $[TCP{\cdot}H]\,[Rh(CO)_3(TCP)]$, as indicated in eqn. 1.

$$HRh(CO)_3(TCP) \xrightarrow{TCP} [TCP{\cdot}H][Rh(CO)_3(TCP)] \xrightarrow{CO} [TCP{\cdot}H][Rh(CO)_4] \qquad (1)$$

TABLE 1

Catalytic activities of Rh–tricyclohexylphosphine (TCP) system[a]

Expt.	Solvent	TCP/Rh[b]	Rate (h^{-1})[c]		EG/MeOH[b]
			EG	MeOH	
1	DMI[d]	–	9.63	4.12	2.34
2		1	10.68	10.68	1.00
3		2	10.14	25.17	0.40
4		4	6.12	20.79	0.29
5	TGM[e]	2	0.90	17.36	0.05
6		4	2.43	24.44	0.10
7		10	4.92	18.40	0.27
8		20	7.28	13.05	0.56
9		50	5.39	13.64	0.40

[a] [Rh] = 0.013 M, solvent 7.5 ml, CO/H_2 (1/1) 550-500 bar, 220 °C, 2 h.
[b] Molar ratio.
[c] Turnover number for ethylene glycol (EG) or methanol (MeOH).
[d] 1.3-Dimethylimidazolidin-2-one.
[e] Tetraglyme.

On the other hand, no reactions occur without TCP in TGM solution because of the decomposition of the catalyst to rhodium metal. The rates to ethylene glycol and methanol increase with an increase in the concentration of TCP, and the rate to glycol reaches a maximum value of 7.28 h^{-1} at TCP/Rh = 20. The rhodium species observed after the reaction is assigned to 1, and $[Rh(CO)_4]^-$ is not found upon addition of excess TCP. The reason may be the large dielectric constant of DMI, which stabilizes the rhodium species by solvation, compared to that of TGM.

Effect of acid concentration on the catalytic activity

Table 2 shows the effect of 3-fluorobenzoic acid (FBA) and TCP concentrations on the formation of ethylene glycol and methanol in DMI or TGM. The following generalizations were deduced:

(1) the rate to glycol is enhanced with an increase in FBA concentration;

(2) the rate to methanol decreases with an increase in FBA concentration;

(3) no esters originating from FBA are found in the products;

(4) the maximum glycol rate is observed at TCP/Rh = 2, whereas in the absence of FBA it is observed at TCP/Rh = 1;

(5) the band at 1946 cm^{-1} is observed in every reaction solution in Table 2, and this absorption does not change in air at room temperature for as long as a few weeks.

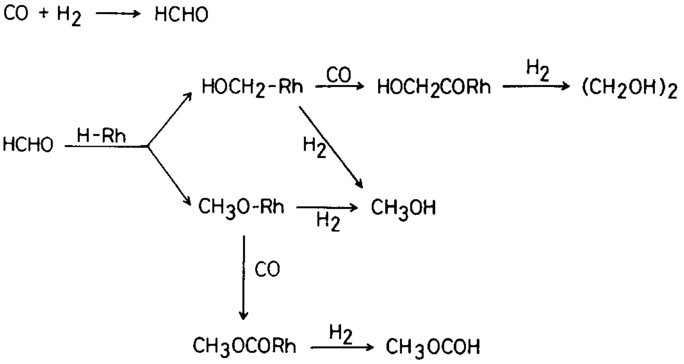
A generalized mechanism for the homogeneous hydrogenation of CO [16] is shown in Scheme 1. The presence of the hydroxymethyl intermediate is required for ethylene glycol production [17]. Whether the methanol is formed by this route or by the methoxide route, or both, is not known in the Rh–TCP–acid system. The rate to methanol correlates well with the

TABLE 2

Effect of 3-fluorobenzoic acid (FBA) and TCP[a]

Expt.	TCP/Rh[b]	FBA/Rh[b]	Solvent	Rate (h^{-1})		EG/MeOH
				EG	MeOH	
10	2	1	DMI	9.72	25.48	0.38
11	2	2		11.12	24.67	0.45
12	2	10		14.27	23.41	0.61
13	2	20		15.87	18.11	0.87
14	2	50		18.31	10.59	1.73
15	1	50		12.60	12.52	1.01
16	3	50		16.58	27.16	0.61
17	2	1	TGM	2.56	20.50	0.13
18	2	10		4.65	21.45	0.22

[a] Reaction conditions as in Table 1.
[b] Molar ratio.



Scheme 1. Generalized mechanism for the homogeneous hydrogenation of CO [16].

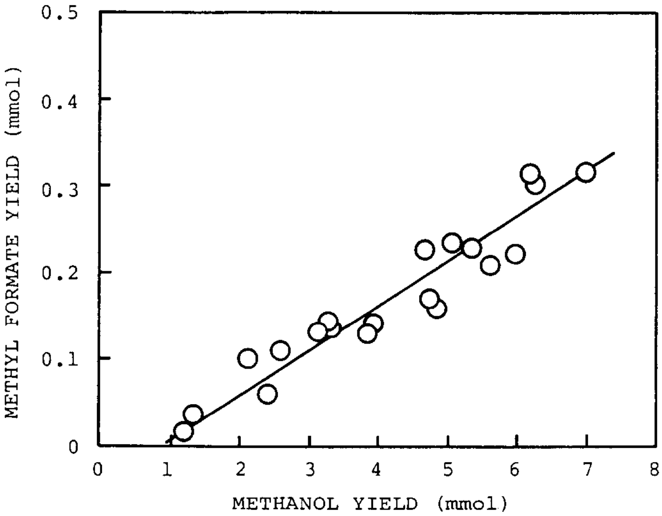


Fig. 1. Relation between yields of methanol and methyl formate. [Rh] = 0.013 M, [TCP] = 0.026 M, varying concentrations of various carboxylic acids, CO/H_2 (1/1) 550 - 500 bar, 220 - 230 °C, 2 h.

rate to methyl formate in 20 experiments with a correlation coefficient of 0.955, as shown in Fig. 1. This correlation suggests that methanol and methyl formate are obtained from the same intermediate by the methoxide route. A linear correlation is found between the selectivity to glycol and the ratio of FBA/Rh with a correlation coefficient of 0.998 (Exp. 3, 10 - 14). The acid may affect the mode of addition of formaldehyde to the Rh—TCP system and the Rh—TCP—FBA system, the TCP/Rh ratio of the two active species may be 1 and 2 in the Rh—TCP system and in the Rh—TCP—FBA system, respectively. A possible active species is discussed below.

We examined the promoting effect of various acids on the hydrogenation of CO with the Rh—TCP system. The results are summarized in Table 3.

TABLE 3

Effect of various acids on Rh—TCP system[a]

Expt.	Acid	Rate (h^{-1})		EG/MeOH
		EG	MeOH	
19	benzoic acid	16.62	15.73	1.06
20	pentafluorophenol	15.91	13.00	1.22
21	*p*-phthalic acid	15.19	19.23	0.79
22	acetic acid	13.71	16.42	0.83
23	4-fluorophenol	10.25	28.23	0.36
24	phenol	6.58	30.04	0.22
25	phosphoric acid[b]	13.92	9.77	1.42
26	hydroiodic acid[b]	0	0	—

[a] [Rh] = 0.013 M, [TCP] = 0.026 M, [acid] = 0.65 M, DMI 7.5 ml, CO/H_2 (1/1) 550 - 500 bar, 220 °C, 2 h.
[b] [Acid] = 0.065 M.

The promoting effect of carboxylic acids and pentafluorophenol is found in DMI solvent. The other phenols do not affect the rate to ethylene glycol. Rates and selectivities to glycol in the phosphoric acid system are comparable to those in the FBA system, but no reactions occur in the hydroiodic acid system. A single band is observed in the region of 1950-1940 cm^{-1} in each case, but bands at 2051 and 1981 cm^{-1}, assigned to $[RhI_2(CO)_2]^-$ [18], are observed in the hydroiodic acid system.

Identification and catalytic activity of the complex recovered from the Rh—TCP—FBA system

An air-stable yellow complex is isolated from the resultant solutions of TGM or DMI with the Rh—TCP—FBA system. This compound is identified as $Rh(3\text{-}F\text{—}C_6H_4CO_2)(CO)(TCP)_2$ (**2**). In order to examine whether this compound exists or not at elevated pressures of synthesis gas, we conducted an investigation to obtain the IR spectra of the reaction solutions in DMI under 280 bar pressure at room temperature. In the Rh—TCP—FBA system, strong bands at 1952 and 1900 cm^{-1}, which are assignable to **1** and $[Rh(CO)_4]^-$, are mainly observed. A single band at 1952 cm^{-1} is observed in the Rh—TCP system under the same conditions. By depressurization of synthesis gas, compound **1** is retained in the absence of FBA, but in the presence of FBA, the two species which are observed at 280 bar are converted to **2**. As **2** is more stable than **1**, the Rh—TCP—FBA system is better suited to repeated use in practical application. As seen in Table 4, catalytic activities of the recovered complex are comparable to those of the Rh—TCP—FBA system in DMI or TGM solvent (*cf.* Expts. 10 and 17). A single band assigned to **2** is observed in the IR spectra of both reaction solutions. Accordingly, acids play an important role in the stabilization of the rhodium complex after reaction by the oxidation of Rh(0) leading quantitatively to Rh(I).

TABLE 4

Catalytic activities of complex recovered from the reaction solution[a]

Expt.	Solvent	Rate (h^{-1})	
		EG	MeOH
27	DMI	9.45	31.83
28	TGM	3.68	32.37

[a] [Rh] = 0.013 M, solvent 7.5 ml, CO/H_2 (1/1) 550 - 500 bar, 220 °C, 2 h.

Catalytically active species

The reaction of 1 with 1 equiv bis(triphenylphosphine)iminium acetate (PPNOAc) in the presence of 1 equiv TCP was found to form the complexes $Rh(OAc)(CO)(TCP)_2$ and $[PPN][Rh(CO)_3(TCP)]$, as represented in eqn. 2 [19].

$$1 + PPNOAc + TCP \longrightarrow Rh(OAc)(CO)(TCP)_2 + [PPN][Rh(CO)_3(TCP)] + 2CO \quad (2)$$

Thus $RhX(CO)(TCP)_2$ (X = anionic ligand) and an unstable $HRh(CO)_3(TCP)$ (3) may be obtained from 1, HX and TCP, as is shown in eqn. 3.

$$1 + HX + TCP \longrightarrow RhX(CO)(TCP)_2 + HRh(CO)_3(TCP) + 2CO \quad (3)$$

The synergistic effect of varying additives on the catalytic activities using $Rh(PhCO_2)(CO)(TCP)_2$ (4) as the catalyst precursor in TGM is shown in Table 5, in which comparative data with the Rh—TCP system are added. The rate and selectivity to glycol increase on addition of excess benzoic acid. The acid facilitates the formation of 3 (eqn. 3). This nucleophilic reaction (eqn. 3) would also be enhanced by the effect of alkali salts etc. It is noted that the addition of equimolar salts, such as cesium salts or PPN salts, increases the rate and selectivity to glycol.

Infrared spectra of the resultant solutions were obtained under synthesis gas pressure of 280 bar at room temperature, as shown in Fig. 2. As the band at 1955 cm^{-1} is observed in the Rh—TCP system, rhodium exists mainly as 1 (Fig. 2a). In the reaction solution with 4, the bands at 2041, 1972, 1955 and 1944 cm^{-1}, which are assigned to $HRh(CO)_2(TCP)_2$ (5) [20] and 1, are observed (Fig. 2b). In the reaction solution with 4 and an equimolar amount of CsI, the concentration of 5 increases remarkably (Fig. 2c). The catalytic activity and selectivity correlate well with the concentration of 5 (Expts. 29 and 31). Formation of an analogous rhodium hydride complex $HRh(CO)_2(PPh_3)_2$ has been found in the reaction products of $Rh(3\text{-}F\text{—}C_6H_4CO_2)(CO)(PPh_3)_2$ under atmospheric pressure of synthesis gas [19].

A possible reaction pathway of the rhodium compound is shown in Scheme 2. The initially charged 4 is reduced with synthesis gas to afford

TABLE 5

Catalytic activities of $Rh(PhCO_2)(CO)(TCP)_2$ with or without additives[a]

Expt.	Salt	Rate (h^{-1})		EG/MeOH	IR[b] curve
		EG	MeOH		
5	—[c]	0.90	17.36	0.05	(a)
29	—	2.81	35.18	0.08	(b)
30	—[d]	5.73	24.45	0.23	
31	CsI	13.88	18.20	0.76	(c)
32	CsBr	13.98	18.23	0.76	
33	CsCl	13.88	14.94	0.93	
34	CsF	12.52	12.65	0.99	
35	PPNOAc[e]	14.58	34.19	0.43	

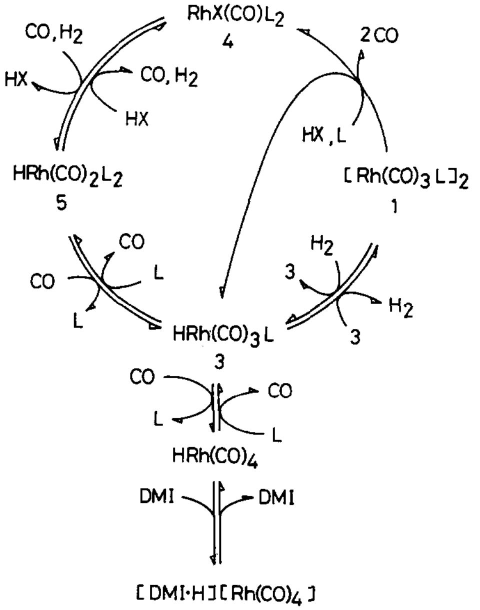
[a] [Rh] = 0.02 M, [Cs] or [PPN] = 0.02 M, TGM 5 ml, CO/H_2 (1/1) 550 - 500 bar, 220 °C, 2 h.

[b] See Fig. 2.

[c] Refer to Table 1.

[d] $[PhCO_2H] = 0.2$ M was employed.

[e] Bis(triphenylphosphine) iminium acetate.



Scheme 2. Possible reaction pathway of rhodium compound ($X = PhCO_2$ and $L = TCP$).

5, 3 and 1. The anionic ligand X may be separated as HX under these conditions. This acid HX reacts with 1 to afford 4 and 3. Compound 3 reacts with TCP to afford 5. The maximum rate and selectivity to ethylene glycol are found at TCP/Rh = 2 (Table 2) in the Rh—TCP—FBA system. The

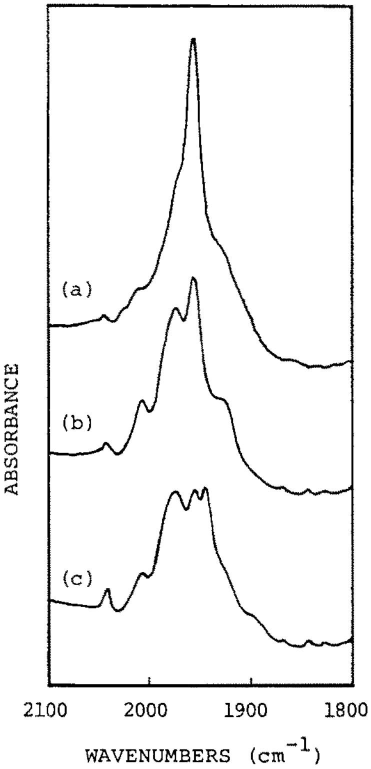


Fig. 2. IR spectra of the reaction solutions. Employed catalyst precursors are: (a) $Rh_4(CO)_{12}$/TCP = 1/2, (b) $Rh(PhCO_2)(CO)(TCP)_2$ (5), (c) 5/CsI = 1/1. Reaction conditions as in Table 5; spectral measurement conditions: CO/H_2 (1/1) 280 bar, room temperature.

rhodium hydride species 5 may be a plausible active species or its immediate precursor.

Experimental

Materials

The rhodium compound used as the catalyst precursor was tetrarhodium dodecacarbonyl, purchased from Nippon Engelhard. Benzoatocarbonyl bis(tricyclohexylphosphine)rhodium was prepared from $Rh_4(CO)_{12}$, tricyclohexylphosphine and benzoic acid by our method [19]. Tricyclohexylphosphine was obtained from Strem. Tetraglyme was distilled from NaH under N_2 and DMI was distilled under N_2 before use.

Analytical methods

Analyses of the reaction products were carried out on a Shimadzu model GC-R1A gas chromatograph, using a 3 mm × 2 m glass column packed with 2% PEG-20M on Chromosorb 101. Identities of major products were confirmed by GC–MS. The IR spectra of the reaction solutions were recorded on a Jasco model A-102 with a data processor for routine use, and IR spectra at elevated pressure were recorded on a Nicolet 170SX FT–IR spectrometer with a CaF_2 cell window, which is similar to the method proposed in a recent report [3].

Synthesis gas reactions

All reactions with synthesis gas were run in a 40 ml autoclave constructed of Hasteloy C stainless steel, fitted with heating and agitation means. Typically, the autoclave was loaded in air with solvent, catalyst precursor and additives. The reactor was sealed, flushed with CO/H_2 (1/1) several times, charged with CO/H_2 pressure of 370 bar at room temperature and heating was commenced. After the reactor had reached operating temperature, the reaction was run over a period of an appropriate reaction time. The reactor was cooled, vented to atmospheric pressure and opened. The liquids were collected and analyzed. Identified products were ethylene glycol, methanol, methyl formate, ethanol, n-propanol, ethylene glycol monoformate, 1,2-propylene glycol and glycerine.

Identification of the recovered complex

The synthesis gas reaction was run with [Rh] = 0.065 M, [TCP] = 0.13 M, [FBA] = 0.325 M in 7.5 ml of TGM under pressure of 500 bar at 220 °C for 2 h. A yellow homogeneous solution was obtained. Yellow crystals were obtained by allowing the solution to stand overnight at 0 °C, giving 70% yield. IR (KBr; cm^{-1}): 1945 (CO), 1630 (CO_2), 760d (3-F—$C_6H_4CO_2$). NMR ($CDCl_3$; ppm): 1.0-2.5 (cyclohexyl; 66H), 7.0-8.0 (C_6H_4; 4H). ESCA (eV) 307.8 (*cf.* $Rh_4(CO)_{12}$, 306.2; $RhCl(CO)(PPh_3)_2$, 307.6). FD–MS (M^+) 830 (calculated for $C_{44}H_{70}FO_3P_2Rh$ 830). Microanalysis (%), found: C, 63.10; H, 7.96; F, 1.93; P, 7.01; Rh, 12.50% (calcd.: C, 63.60; H, 8.49; F, 2.29; P, 7.46; Rh, 12.40%).

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