CHEMISTRY LETTERS, pp. 1935-1938, 1986.

Effect of Alkyl-Substituted Pyrrolidones on the Formation of Ethylene Glycol from Synthesis Gas

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Synthesis of ethylene glycol from synthesis gas via rhodium catalysis in the presence of a pyrrolidone, which has a stronger electron donative substituent than methyl or has two 2-oxopyrrolidinyl groups in the molecule was examined. These compounds facilitate the formation of ethylene glycol.

Production of ethylene glycol is one of the most important targets in the utilization of synthesis gas.[1,2) It is already known that rhodium catalyzes the formation of ethylene glycol in N-methylpyrrolidone solvent at pressures of about 2000 bar.[3) Solvent must be playing an important role like amine promoters.[4) But selectivity to ethylene glycol has not been sufficient, and the basicity level of the solvents have not hitherto been discussed.

We have examined the hydrogenation of carbon monoxide catalyzed by $Rh_4(CO)_{12}$ in various N-alkyl pyrrolidones at relatively low pressures (ca. 400 bar). Considerable amounts of ethylene glycol and methanol were obtained with smaller quantities of methyl formate and ethanol. The result is summarized in Table 1. Unexpectedly, the selectivity to ethylene glycol has been found to vary to a great extent with varying alkyl substituents.

Table 1. Hydrogenation of carbon monoxide in substituted pyrrolidones a)

No.	Substituents of solvent b)		σ^* of R	Turnover number/h^{-1}		
	R	R'		EG c)	MeOH	EG+MeOH
1	Me	H	0.00	0.72	2.55	3.27
2	Et	H	-0.10	0.91	2.20	3.11
3	^{n}Bu	H	-0.13	1.16	2.02	3.18
4	^{i}Pr	H	-0.19	1.88	1.52	3.40
5	^{t}BuMeCH	H	-0.28	1.19	0.96	2.15
6	^{t}Bu	H	-0.30	1.56	0.90	2.46
7	Me	Me	0.00	1.26	2.11	3.37

a) $Rh_4(CO)_{12}$ 0.8 mg-atom, solvent 20 cm^3, CO/H_2(1/1) 400-390 bar, 200 °C, 4 h. b) 1-R-5-R'-Pyrrolidone. c) Ethylene glycol.

Anions such as $Rh_6(CO)_{15}^{2-}$ (2040, 1985, and 1960 cm^{-1}) and $Rh(CO)_4^-$ (1900 cm^{-1})[5)] were observed in the IR spectra of the reaction solutions. This indicates the formation of the unstable intermediates such as $H_2Rh_6(CO)_{15}$ and $HRh(CO)_4$, which react with solvent molecules to form the salts as shown in Eq. 1. A similar reaction of Et_3N and $HRh(CO)_3(Ph_3P)$ has been shown to afford $Et_3NH^+Rh(CO)_3(Ph_3P)^-$.[6)]

$$HRh_n(CO)_m + Solv. \rightleftharpoons \underset{\mathbf{1}}{[Solv.\cdot H^+ \ Rh_n(CO)_m^-]} \qquad (1)$$

In the next step, the influence of bispyrrolidones on the hydrogenation of carbon monoxide was examined. As they are solid at the room temperature, they were used as the solutions in γ-butyrolactone. The dependence of reaction rates on the ratio of additive/Rh are illustrated for 1,2-bis(2-oxopyrrolidinyl)cyclohexane (CHBP) and 1,2-bis(2-oxopyrrolidinyl)ethane (EBP) in Fig. 1. The maximum glycol rate is observed at the ratio of 10 (CHBP/Rh) and 20 (EBP/Rh) respectively. In the later case formation of $Rh_6(CO)_{15}^{2-}$ is noted from the IR spectra of the solutions as seen in Fig. 2A. But $Rh(CO)_4^-$ becomes the main species at the ratio of 40 as is shown in Fig. 2B. The analogous change has been found for CHBP (CHBP/Rh; 10 and 20). The excessive addition of bispyrrolidones may lead to the excessive reduction of the rhodium complexes as is deduced from the change in the

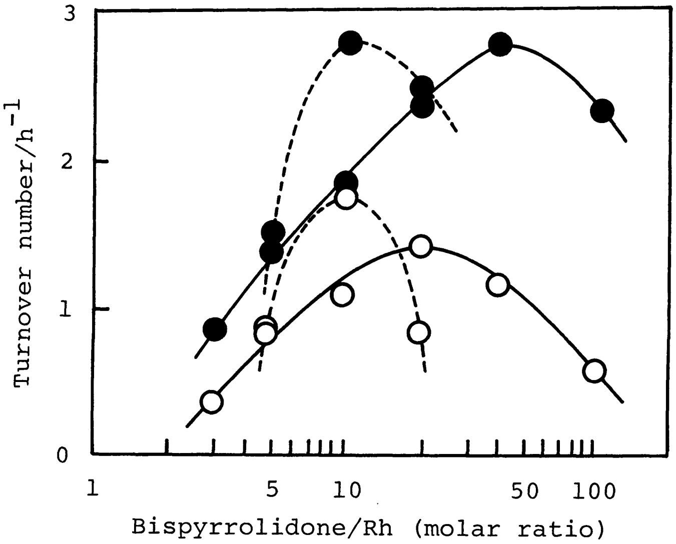


Fig. 1. Relation between catalytic activities and amounts of bispyrrolidones
Reaction conditions; [Rh]=0.013 M in 7.5 cm^3 of solvent, CO/H_2(1/1) 400 bar, 200 °C, 4 h.

—○— EG(EBP), —●— EG+MeOH(EBP)
--○--- EG(CHBP), --●--- EG+MeOH(CHBP)

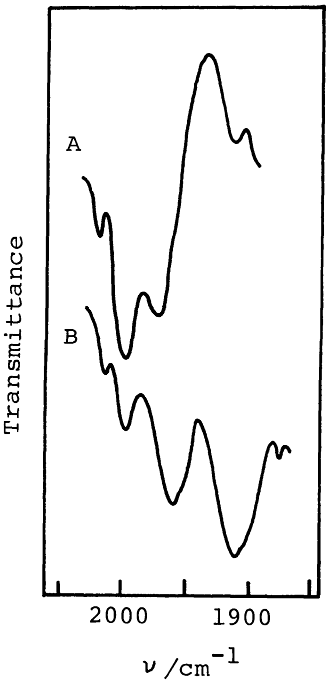
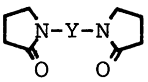


Fig. 2. IR spectra in the presence of EBP
A; EBP/Rh=20, B; EBP/Rh=40.

IR spectra. The change of the rhodium compound results in the decrease in the rate to ethylene glycol with the increase in the rate to methanol. We cannot explain at present the difference of the maximum additive/Rh ratio between CHBP and EBP clearly. The reason of the higher maximum glycol rate of the former than the later is discussed below. The order of the maximum glycol rate is given as, CHBP > $QCHMeCH_2Q$ > EBP > $Q(CH_2)_3Q$ (Q=2-oxopyrrolidinyl group) as is shown in Table 2. These values are approximately comparable to those in alkyl pyrrolidone solvents where the ratio to rhodium (ca. 230) are almost ten times greater.

Table 2. Hydrogenation of carbon monoxide with bispyrrolidones a)

No.	Y of 	Additive/Rh (molar ratio)	Turnover number/h^{-1}	
			EG	MeOH
8	none	-	0.02	0.11
9	1,2-C_6H_{10} b)	10	1.72	1.05
10	-$CHMeCH_2$-	20	1.56	1.05
11	-$(CH_2)_2$-	20	1.37	1.07
12	-$(CH_2)_3$-	20	1.16	1.21

a) Reaction conditions; $Rh_4(CO)_{12}$ 0.3 mg-atom, γ-butyrolactone 7.5 cm^3, CO/H_2(1/1) 430-395 bar, 200 °C, 4 h.

b) cis/trans=2/3.

In the reaction in pyrrolidone solvents with ^{t}BuMeCH and ^{t}Bu substituents, we have found the products which are identified as the hydroformylated forms of the alkenes that may be formed by the cleavage of alkyl-N bond of the pyrrolidone and subsequent β-hydrogen elimination of the alkyl group. Glycol and methanol rates in these solvents are considerably lower, probably due to the poisoning effect of the decomposition products or the steric effect of the solvent molecules. In the reaction in the pyrrolidone solvents with Me, Et, ^{n}Bu, and ^{i}Pr substituents, a linear relationship between glycol or methanol rates and Taft's substitution constant of the substituent is found with the correlation coefficient -0.945 and 0.947 respectively (Table 1). The increase in the electron density on the nitrogen atom of pyrrolidones causes the increase in the glycol rates and the decrease in methanol rates. The sum of the two is considered to be equal to the rate to the formaldehyde intermediate,7) which is almost constant with different alkyl substituents as seen in Table 1. Higher electron donative substituents improve the selectivity to ethylene glycol without changing the rate to the formaldehyde intermediate.

The dissociation of **1** to rhodium complex anions and the positively charged counterions is considered as the key process in the formation of ethylene glycol as shown in Eq. 2, similar to the promoting effect of amines.4)

$$\mathbf{1} \rightleftharpoons [\mathrm{Solv.}\cdot\mathrm{H}]^{+} + \underset{\mathbf{2}}{[\mathrm{Rh}_{n}(\mathrm{CO})_{m}]^{-}} \tag{2}$$

The cluster anion **2** ($n > 1$) and the mononuclear anion $\mathrm{Rh(CO)_4}^-$ (**3**) have been proposed to be the catalyst or its immediate precursor for glycol and methanol formation respectively.4) The change of the proportion of **2** and **3** with various pyrrolidone solvents may be caused by the electronic effect or the steric effect of the substituent. The linear relationship between glycol or methanol rates and the substitution constant suggests that the electronic effect predominates over the steric effect. Similarly the order of the maximum glycol rate in bispyrrolidones is explained by relation between the concentration of **2** and the electron donative effect of the group Y in Table 2. The active species for the formaldehyde production is not established, but the formation of this intermediate is proportional to the amounts of total rhodium.

This work is a part of "$\mathrm{C_1}$ Chemistry Project," a National Research and Development Program of Agency of Industrial Science and Technology, Ministry of International Trade and Industry (M.I.T.I.), Japan. The authors are grateful to members of Ethylene Glycol Research Group of the Project for valuable discussion.

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(Received July 3, 1986)