January, 1988] © 1988 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 61, 325—327 (1988) 325

Cobalt-Catalyzed Hydrohydroxymethylation of Formaldehyde: Effect of $Ru_3(CO)_{12}$ and Phenol

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(Received July 1, 1987)

Synopsis. A catalyst system, containing $Co_2(CO)_8$, $Ru_3(CO)_{12}$, and phenol, was found to be effective for the hydrohydroxymethylation of formaldehyde to give ethylene glycol with the yield of ca.65%, better than those previously reported.

The hydrohydroxymethylation, by which ethylene glycol(EG) is produced directly from formaldehyde, is receiving increasingly wider attention as an attractive route to C_2 compounds.[1] So far, stoichiometric,[2] and catalytic[3] hydroformylation of formaldehyde to glycolaldehyde(GLA) has been achieved by using cobalt and rhodium catalysts with reasonable selectivity. However, these require a successive hydrogenation of GLA to obtain EG. Recently, the hydrohydroxymethylation of CH_2O has been reported with moderate EG yield(ca. 25%) using rhodium-cobalt system.[4]

In the course of our study on a syngas conversion to EG, where cobalt catalyst is employed under high pressure, we have found that the addition of $Ru_3(CO)_{12}$ is effective for enhancing the glycol productivity,[5] in addition to the effectiveness of phenol as solvent.[6] In this study, the effects of addition of $Ru_3(CO)_{12}$ and phenol on the cobalt-catalyzed hydrohydroxymethylation of CH_2O will be described.

Results and Discussion

In the preliminary stage of our study, we examined the behavior of cobalt catalyst under the conditions of 200 atm at 180 °C. The results are given in Table 1. Ethylene glycol was produced in ca. 20% yield after the reaction in dioxane solvent for 7 h, where 37% formaldehyde aqueous solution was used as formaldehyde source (Run 1): Methanol (9%) was obtained as by-product and small amounts of ethanol (1.5%) and methyl cellosolve (18%) were detected. The addition of phosphine (1,2-bis(diphenylphosphino)ethane (dpe), P/Co=0.5(molar ratio)) caused the EG yield to be slightly enhanced (Run 2). Paraformaldehyde was less favorable than CH_2O (aq.) (Run 3), but

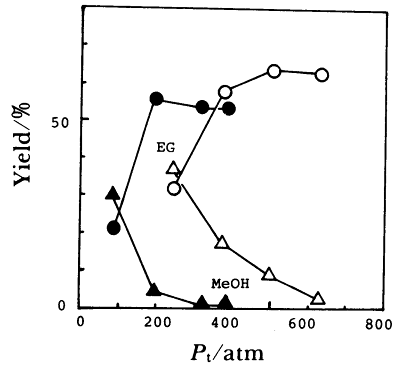


Fig. 1. Effect of total pressure.
○△ $Co_2(CO)_8$ 2.5 mmol, $Ru_3(CO)_{12}$ 0.167 mmol, CH_2O(aq) 40 mmol, PhOH 106 mmol, toluene 12 ml, $H_2/CO=4$, 180 °C, 2 h. ●▲ $Co_2(CO)_8$ 2 mmol, dpe 1.5 mmol, AcOH 50 mmol, CH_2O(aq) 50 mmol, dioxane 50 ml, $H_2/CO=1$, 180 °C, 4.5 h.

Table 1. Effects of Solvents and Organic Acids on the Cobalt-Catalyzed Hydrohydroxymethylation of Formaldehyde[a]

Run No.	Time/h	dpe[b]	Solvent	Acid	EG	Yield/%[c]	MeOH
		mmol		mmol		totalEG	
1	7	—	Dioxane	—	19.4	—	9.0
2	7	1.0	Dioxane	—	22.4	—	6.4
3[d]	7	1.0	Dioxane	—	8.0	—	8.0
4[e]	7	1.0	Dioxane	—	15.0	—	15.4
5	7	1.0	EtOH	—	1.6	57.6[f]	4.6
6	7	1.0	*i*-PrOH	—	9.0	45.0[g]	3.0
7	7	1.5	AcOH	—	11.4	28.2[h]	6.8
8[i]	—	1.0	Dioxane	—	43.2	43.8[j]	6.2
9	4.5	—	Dioxane	AcOH(50)	45.8	49.2[k]	10.0
10	4.5	—	Dioxane	HCOOH(50)	33.8	44.0[l]	4.2
11	4.5	—	Dioxane	PhCOOH(50)	48.4	51.4[m]	5.2
12	4.5	—	Dioxane	PhOH(50)	46.0	—	5.0
13	4.5	1.5	Dioxane	AcOH(50)	44.6	55.8	4.8
14	4.5	1.5	Dioxane	AcOH(75)	35.4	47.0	4.6

a) Conditions: $Co_2(CO)_8$ 2 mmol, solvent 50 ml, CH_2O(aq.) 5 mmol, 180 °C, 200atm($H_2/CO=1$). b) $Ph_2P(CH_2)_2PPh_2$. c) Based on CH_2O initially added(50 mmol). d) Paraformaldehyde(50 mmol). e) Paraformaldehyde(50 mmol)/H_2O(60 mmol). f) EG+$EtOCH_2CH_2OH$. g) EG+*i*-$PrOCH_2CH_2OH$. h) EG+$AcOCH_2CH_2OH$+$AcOCH_2CH_2OAc$. i) Two-stage reaction: 60 °C, 6 h → 190 °C, 2.5 h. j) EG+$HOCH_2CHO$. k) EG+$AcOCH_2CH_2OH$. l) EG+$HCOOCH_2CH_2OH$. m) EG+$PhCOOCH_2CH_2OH$.

the addition of H_2O, in this case, raised the EG yield(Run 4). By use of alcohol solvents, alkyl cellosolves[7] were produced in high yields with a small amount of EG (Runs 5,6). In case of acetic acid solvent, ethylene glycol and its acetate esters were formed in ca. 28% yield, but a partial decomposition of $Co_2(CO)_8$ occurred (Run 7).

When organic acids were used as additives but not solvent, the enhancement of the EG yield was also observed (Table 1, Runs 9—14). The yield decreased by the addition of excess acid (Run 14). Also the yield was influenced by total pressure and temperature: the yield increased with the increases in pressure up to 200 atm (Fig. 1,● and in temperature to 180 °C (Fig. 2,●), whereas methanol formation decreased with the increase in pressure (Fig. 1,▲) and increased with the increase in temperature (Fig. 2,▲).

We have found the Co-Ru system, which is active for syngas conversion to EG;[5] so, effect of ruthenium was examined using cobalt-phenol system, the results of which are given in Table 2. The EG yield as well as MeOH increased with the increase in Ru concentration: EG and MeOH accounts for up to ca. 88% of products (Runs 4,5). Other metal carbonyls such as $Re_2(CO)_{10}$, $Mo(CO)_6$, $Fe(CO)_5$, and $Cr(CO)_6$ were unfavorable.

Figure 2 (○) shows the effect of reaction temperature. The maximum EG yield of ca. 65%, which is the highest value of those previously reported,[1a] was achieved at 180 °C: The yield of MeOH increased with the increase in temperature. As shown in Fig. 1, the pressure effect of Co-Ru-PhOH system was analogous to that of Co-AcOH system: The EG yield increased with the increase in pressure up to 500 atm (○). The effect of H_2 pressure was similar to that of total pressure (Fig. 3) and the EG yield was little affected by CO pressure (Fig. 3,●).

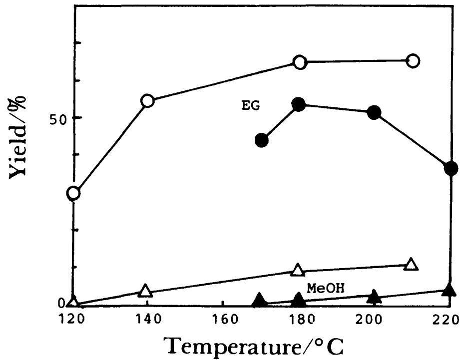


Fig. 2. Effect of temperature.
○△ $Co_2(CO)_8$ 2.5 mmol, $Ru_3(CO)_{12}$ 0.167 mmol, PhOH 106 mmol, CH_2O(aq) 40 mmol, toluene 12 ml, 500 atm(H_2/CO=4), 2 h. ●▲ $Co_2(CO)_8$ 2 mmol, dpe 1.5 mmol, AcOH 50 mmol, CH_2O(aq) 50 mmol, dioxane 50 ml, 390 atm(H_2/CO=1), 4.5 h.

Table 2. Effects of $Ru_3(CO)_{12}$[a)]

Run No.	$Ru_3(CO)_{12}$/mmol	Yield/%[b)] (Sel./%[c)]) EG	MeOH
1	—	26.5(27.4)	1.93(2.0)
2	0.083	41.4(43.5)	12.2(12.8)
3	0.133	46.7(48.7)	14.2(14.8)
4	0.20	55.9(60.8)	25.5(27.7)
5	0.233	56.8(60.4)	26.1(27.8)

a) Conditions: $Co_2(CO)_8$ 2.5 mmol, CH_2O(aq.) 40 mmol, PhOH 106 mmol, Toluene 12 ml, 500 atm(H_2/CO=9), 140 °C, 2 h. b) See footnote (c) of Table 1. c) Selectivity=Product(mol)×100/Converted CH_2O(mol).

In the absence of organic acid and ruthenium, the EG yield was ca. 20% (Table 1, Runs 1,2). The low EG yield might be that the aldol condensation of CH_2O and/or GLA takes place to form higher molecular weight by-products.[3] Glycolaldehyde was produced in ca. 70% yield[2] after the hydroformylation of CH_2O at 60 °C for 6 h: When the resulting solution was further treated at 190 °C for 2.5 h, the EG formed was ca. 43% (Table 1, Run 8), indicating that the condensation as well as hydrogenation of GLA could occur. Therefore, in order to increase the yield of EG formed by one-batch process at 180 °C, it seems to be important that the hydrohydroxymethylation of CH_2O predominates over the condensation at temperature as high as 180 °C.

Considering the schemes of syngas conversion[6—8] and of Rh-catalyzed hydroformylation of CH_2O,[3] this cobalt-catalyzed reaction may be assumed to proceed by the Scheme 1, in which hydroxymethylcobalt complex a,[9] the formation of which might be prompted by phenol,[10,11,12] (steps I—III), is involved as a key intermediate: The complex a thus formed undergoes CO insertion(IV) and subsequent hydrogenation(V) to give GLA, which is reduced to EG(VI) by catalysis of cobalt and/or ruthenium. MeOH could be produced via hydrogenolysis of methoxycobalt complex b(VIII) as well as of the complex a(IX).

An acceleration of MeOH formation as well as EG formation was observed in the presence of Ru (Table 2). So, ruthenium, at least, appears to be responsible for the reduction of GLA and/or CH_2O.[13] The Halcon Group suggested that Ru-phosphine complex could be a catalyst effective for the reduction of GLA to EG.[14] In hydrocarbonylation of MeOH to EtOH, it

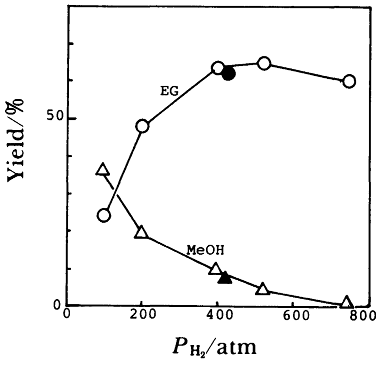
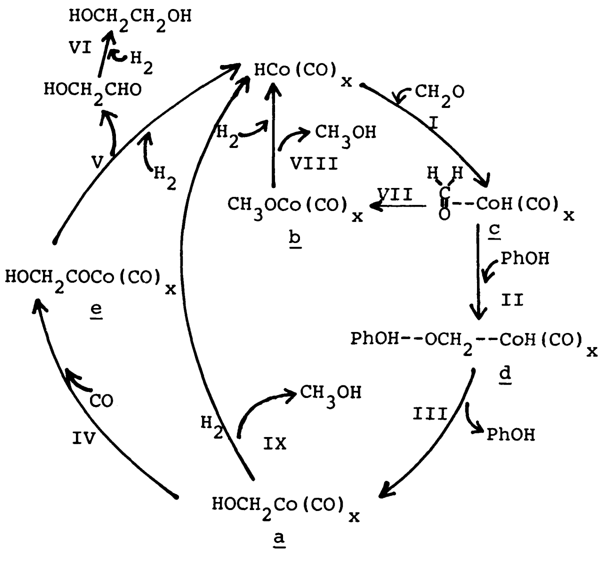


Fig. 3. Effect of hydrogen pressure.
$Co_2(CO)_8$ 2.5 mmol, $Ru_3(CO)_{12}$ 0.167 mmol, PhOH 106 mmol, CH_2O(aq) 40 mmol, toluene 12 ml, Pco=100 at, 180 °C, 2 h. ●▲ Pco=75 atm.



Scheme 1.

has been reported that hydrogenation of CH_3CHO occurs readily by Ru catalysis.[15]

The hydroformylation of CH_2O occurs even at 60 °C (Table 1, Run 8) and also the hydrohydroxymethylation activity is little affected by CO pressure (Fig. 3,●), indicating that CO insertion step(IV) is rapid under the conditions employed. Therefore, it is probable that the EG formation could be accelerated by an increased hydrogen pressure (Fig. 3).

Experimental

Materials. $Ru_3(CO)_{12}$, solvents, and organic acids were obtained commercially and used with no further purification. $Co_2(CO)_8$ was prepared according to an usual procedure. Aqueous 37% formaldehyde solution and paraformaldehyde were commercial products.

Reaction Procedure. A typical experiment can be described as follows: A catalyst solution containing $Co_2(CO)_8$, $Ru_3(CO)_{12}$, PhOH, and $CH_2O(aq)$ in solvent (50 ml) was placed in a stainless steel autoclave (100 ml), which was subsequently charged with syngas ($H_2/CO=4$). When the system was heated to a desired temperature, the total pressure was adjusted to a desired pressure by introducing more syngas mixture. After the reaction, the vessel was cooled to room temperature and the solution was analyzed by GLC.

The two-stage reaction was carried out, first at 60 °C for 6 h to produce glycolaldehyde, then by increasing the temperature to 190 °C for another period of 2.5 h giving EG.

This work is a part of "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.

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