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Aldehyde Intermediates in the Homogeneous Hydrogenation of Carbon Monoxide by Ruthenium Carbonyl/Halide Catalysts

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Hydrogenation of carbon monoxide by homogeneous catalysts consisting of a ruthenium carbonyl complex and halide salt was studied at relatively mild temperatures. In addition to ethylene glycol and methanol, formaldehyde and glycolaldehyde were found among the reaction products. These aldehydes act as key intermediates in the formation of ethylene glycol or methanol. Through kinetic studies it was concluded that while at relatively low temperatures the rate-determining step is the formation of formaldehyde, at higher temperatures formaldehyde exists in near equilibrium with CO/H_2. It was also found that glycolaldehyde was formed with an even higher selectivity when a rhodium complex was added to this catalyst system. © 1987 Academic Press, Inc.

INTRODUCTION

The direct synthesis of ethylene glycol (EG) through homogeneous catalytic hydrogenation of CO is being actively pursued (*1*). (The catalysts used are mainly Co, Rh, and Ru.) Considering the well-known hydroformylation of formaldehyde (FA) (*2, 3*), FA and glycolaldehyde (GLA) have been regarded as important possible intermediates for this reaction. On the basis of his kinetic investigation of EG synthesis catalyzed by Rh or Co, Fahey (*4*) presumed that FA, which may be present in very minute concentration in equilibrium with CO/H_2, may act as a possible intermediate. Parker *et al.* (*5*) showed that in the Rh-catalyzed CO hydrogenation, the added ^{13}C-labeled FA was converted to methanol and EG. However, the conversion of CO/H_2 to FA is a thermodynamically unfavorable process (*6*), and hence Feder and Rathke (*7*) and also Dombek (*1, 8, 9*) presumed that FA could be present only in a form coordinated to a metal center in the case of Co and Ru. In any event, there has been no report on the detection of either FA or GLA in the reaction mixtures. Only those cases in which the formation of their acetal derivatives could be observed were reported (*4, 9*). It still remains of considerable importance to an understanding of the mechanism of the catalytic process to confirm whether FA and GLA are truly formed and act as intermediates.

We report for the first time the actual detection of FA and GLA in the product solutions. The catalyst employed consisted of a ruthenium carbonyl complex and halide salt, and it was vital that CO hydrogenation was carried out at relatively mild temperatures. The formation and the behavior of these aldehyde intermediates are elucidated. The effect of the addition of Rh to this catalyst system is also discussed.

EXPERIMENTAL

Materials. $Ru_3(CO)_{12}$ and $Rh_4(CO)_{12}$ were purchased from Nippon Engelhard, Ltd. 1-Methyl-2-pyrrolidinone (NMP) and bis-(triphenylphosphine)iminium chloride (PPNCl) were also obtained commercially. Other PPN salts were prepared from PPNCl by anion exchange with the corresponding alkali halides. Deuterated FA (CD_2O) was generated by the dehydrogenation of deuterated methanol (CD_3OD) and

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was prepared in the form of an ethanol solution (25.37 wt% solution).

CO/H$_2$ reaction. Experiments were carried out in 30-ml autoclaves made of Hastelloy C-276 stainless steel. In each experiment, the reactor was charged with catalyst components, promoters (if any), and NMP as solvent. The reactor was pressurized with 22–25 MPa of synthesis gas (CO/H_2 = 1/1), and then heated under shaking. After a specified time, heating and shaking were stopped, and the reactor was then cooled immediately by immersion in running water. After the reactor had been cooled, unreacted synthesis gas was cautiously vented and the product solution was recovered. Liquid products including FA and GLA were analyzed by temperature-programmed (80 to 240°C at 8°C/min) GLC using a 1-m column packed with 10% PEG-20M-TPA on Chromosorb 102 and were identified by GLC/mass spectral analysis. The reaction solutions including the products and the catalyst components were directly injected into a gas chromatograph, without any separation. In the CD_2O tracer experiments, a part of the vent gas was collected and analyzed to determine the amounts of D_2 and HD by GLC using a 2-m molecular sieve 5A column at −196°C. The reaction data for time dependence were obtained by repeated runs (reaction time was varied in each run).

RESULTS AND DISCUSSION

Experiments of CO hydrogenation were carried out under a pressure of 30 MPa (CO/H_2 = 1/1) and at relatively mild temperatures (140–230°C) using $Ru_3(CO)_{12}$ and various halide salts as the promoters and NMP as the solvent. Careful analyses of the reaction mixture by GLC/MS enabled us to identify FA and GLA among the products together with EG and methanol and also to quantify their yields. Similar efforts with Rh and Co catalyst systems failed to detect the formation of FA or GLA.

Table 1 summarizes the typical results of the reactions at 180°C in which bis(triphenylphosphine)iminium halides were added. When a halide was absent or when a fluoride was present, the formation of neither FA nor GLA was observed. The reaction activities were in the order PPNCl > PPNBr > PPNI, but the selectivities of FA and GLA were in the order PPNI > PPNBr > PPNCl.

TABLE 1

CO/H_2 Reaction by Ru/Halide Catalysts[a]

PPNX[b]	Yield (mmol)			
	EG	MeOH	CH_2O	GLA
None	0.000	0.009	0.000	0.000
PPNI	0.016	0.191	0.038	0.111
PPNBr	0.061	0.372	0.064	0.168
PPNCl	0.324	1.455	0.072	0.185
PPNF	0.000	0.040	0.000	0.000

[a] Reaction conditions: $Ru_3(CO)_{12}$ = 0.1 mg-atom, PPNX = 0.6 mmol, NMP = 7.5 ml, H_2/CO = 1/1, 32–30 MPa; 180°C; 3 h.

[b] Bis(triphenylphosphine)iminium halide salts.

We then studied the behavior of the aldehydes under various reaction conditions. CsI was employed as the halide promoter throughout the studies described in the following.

Reaction Time

Figure 1 shows how the products vary with time in the case of the Ru/CsI/NMP system at 160 and 180°C. While FA reached a stationary concentration at an early stage, GLA increased gradually, finally arriving at a stationary concentration. In addition, an induction period was observed for the formation of EG corresponding to the buildup of GLA, indicating that GLA is very likely the precursor of EG.

CD_2O Tracer Experiments

To elucidate the nature of FA as an intermediate, reactions were carried out in which deuterated FA (CD_2O as an ethanol solution) was added. The results are shown in Table 2. The yields of methanol, GLA,

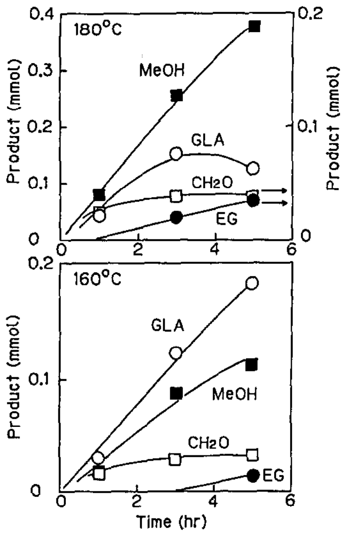

FIG. 1. Influence of reaction time. Reaction conditions: $Ru_3(CO)_{12}$ = 0.1 mg-atom, CsI = 0.6 mmol, NMP = 7.5 ml, H_2/CO = 1/1, 30 MPa.

and EG were increased by the addition of CD_2O. The selectivity of (EG + GLA)/MeOH (180°C) was reasonably close to that in Fig. 1. Among these products, the largest yield was that of methanol, which was subjected to GLC/MS analysis; the formation of CD_2HOH was confirmed, in an amount corresponding to the increase in methanol obtained by addition of CD_2O. These observations indicate that FA of external origin was also incorporated into the reaction as a common intermediate for EG and methanol.

On the other hand, we observed evolution of a considerable amount of HD into the gaseous phase. This can be understood as the consequence of the decomposition of part of the CD_2O and the scrambling with H_2. The deuterium balance in Table 2 tells us that practically all the added FA, except for the part converted to liquid products including methanol and EG, decomposed into CO/D_2:

$$\mathrm{CO} + \mathrm{H_2} \rightleftharpoons \mathrm{CH_2O} \rightarrow \text{products.} \qquad (1)$$

Decomposition of FA into CO/D_2 was 47% at 180°C and 73% at 220°C, indicating that the relative rate for the forward reaction of FA in Eq. (1) is smaller at higher temperatures.

Reaction Temperature

Figure 2 shows the variation of the products with reaction temperature. At temperatures below 160°C, the amounts of FA, methanol, and GLA increased markedly as the temperature increased. This implies that the formation of FA is the rate-deter-

TABLE 2

Addition of CD_2O in CO/H_2 Reaction by the Ru–CsI Catalyst System[a]

Temp. (°C)	CD_2O (mmol)	Product (mmol)				Yield based on CD_2O (%)		
		EG	MeOH	GLA	HD	Liquid[b]	Gas[c]	Total
180	—	tr	0.18	tr	—			
180	10	0.10	3.69	1.43	9.3	50	47	97
220	—	tr	1.39	0.00	—			
220	10	0.18	4.61 (3.23)[d]	0.00	14.6	34	73	107

[a] Reaction conditions: $[Ru_3(CO)_{12}]$ = 10 mg-atom/l, [CsI] = 60 mmol/liter, NMP = 20 ml (180°C) or 15 ml (220°C), H_2/CO = 1/1; 30 MPa, 2 h.

[b] Yield of liquid products.

[c] Yield of HD.

[d] Amount of CD_2HOH analyzed by GLC/MS.

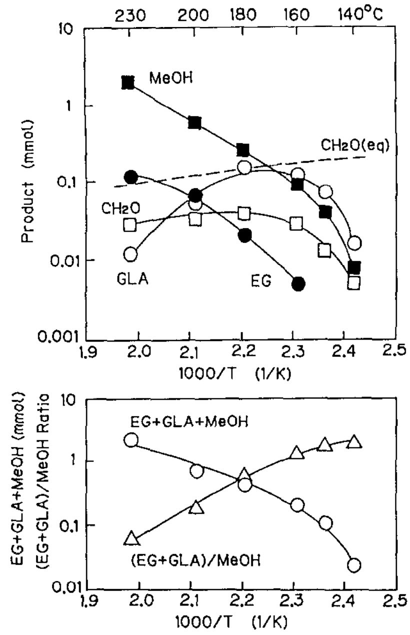

FIG. 2. Temperature dependence of the products formed. Reaction conditions: $Ru_3(CO)_{12}$ = 0.1 mg-atom, CsI = 0.6 mmol, NMP = 7.5 ml, H_2/CO = 1/1, 30 MPa. CH_2O(eq) is the estimated value of the equilibrium concentration of FA.

mining step under these conditions. At temperatures above 180°C, however, the concentration of FA remained nearly constant. As a consequence, the increase in the overall activity for the formation of (EG + GLA + MeOH) became less marked. On the other hand, the yield of GLA reached its maximum at about 160–180°C. Above these temperatures GLA decreased as EG increased. It appears that at lower temperatures the hydrogenation rate of aldehydes is relatively slow, enabling us to observe the buildup of GLA. The observation that the ratio of formation (EG + GLA)/MeOH is greater at lower temperatures may also be attributed to the relative slowness of the hydrogenation rate of FA at these temperatures.

We attempted to estimate thermodynamically the equilibrium concentration of FA according

$$CO\ (g) + H_2\ (g) \overset{K}{\rightleftharpoons} CH_2O\ (g) \quad (2)$$

as a function of temperature (*10*) and plotted it in Fig. 2 (dotted line).

The yield of FA in our experiments at temperatures above 180°C was about one-third of the estimated value, being in order-of-magnitude agreement. Moreover, the change of these two with the reaction temperature coincided reasonably well. All these factors lead us to presume that FA is in near equilibrium with CO/H_2 at temperatures above 180°C. The result in Table 2 showing that the higher the temperature is, the more FA decomposes into CO/H_2 also supports this view.

Based on all these results we conclude that in this catalyst system the reaction proceeds according to

$$\begin{tikzcd} CO/H_2 \arrow[r, shift left] & CH_2O \arrow[l, shift left] \arrow[r] \arrow[dr] & HOCH_2CHO \arrow[r] & EG. \\ & & CH_3OH & \end{tikzcd} \quad (3)$$

According to the results for 180°C in Table 2, more than half of FA formed is converted to either EG or methanol; therefore the formation of FA is certainly the slow step. In contrast, more than half of FA reverts to CO/H_2 at 220°C; thus, the overall reaction rate is determined by the rates of the steps thereafter.

Effect of a Rh Complex

A number of examples have been reported in which addition of Rh complexes to Ru catalyst systems improves the yield of EG (*11–17*). We too looked at the effect of addition of $Rh_4(CO)_{12}$ to the Ru/CsI/NMP catalyst system at mild temperatures. The results are shown in Table 3. Rh in one-third equivalent quantity of Ru has a prominent effect in enhancing the formation of GLA and EG. Thus, this Ru/Rh/CsI/NMP system produced GLA with a selectivity as high as 70 mol%, demonstrating the excellent ability of Rh in inserting CO into FA. On the other hand, hardly any change was observed in the amount of FA detected. This means that the overall rate of formation of FA also must have increased and that Rh takes a part in generating FA. Since

TABLE 3

Addition of Rh Carbonyl to the Ru–CsI Catalyst System[a]

$Ru_3(CO)_{12}$ (mg-atom)	$Rh_4(CO)_{12}$ (mg-atom)	Temp. (°C)	Yield (mmol)			
			EG	MeOH	CH_2O	GLA
0.1	0	180	0.02	0.26	0.04	0.15
0.1	0.033	180	0.10	0.11	0.04	0.61
0	0.033	180	0.00	0.00	0.00	0.00
0.1	0	200	0.06	0.59	0.03	0.05
0.1	0.033	200	0.37	0.62	0.04	0.40
0	0.033	200	0.00	0.00	0.00	0.00

[a] Reaction conditions: CsI = 0.6 mmol, NMP = 7.5 ml, $H_2/CO = 1/1$, 34–32 MPa, 3 h.

Rh alone does not yield FA under these conditions, we presume that there is some kind of synergistic effect between Ru and Rh. A concerted action like that described by

$$\text{CO–[Rh]} \xrightarrow{\text{H–[Ru]}} \text{HCO–[Rh]} \xrightarrow{\text{H–[Ru]}} CH_2O \qquad (4)$$

may be considered as possibility (*17*).

Whether FA exists in a free or coordinated form in the reaction mixture still remains unanswered. Our analytical procedure did not allow us to differentiate free FA from coordinated FA. Since the yield of FA did not exceed the amount of Ru employed, we can only say that FA may or may not be coordinated. GLA, on the other hand, was formed well in excess of Ru or (Ru + Rh) and hence a good portion of it must exist in a free form.

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