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High-Pressure Homogeneous Hydrogenation of Carbon Monoxide in Polar and Nonpolar Solvents

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The homogeneous hydrogenation of carbon monoxide was carried out at high pressures. Clusters and complexes of group VIII elements of the periodic table were used as catalysts. A variety of oxygenated compounds such as methyl formate, methyl acetate, ethyl formate, methanol, ethanol, *n*-propyl alcohol, propylene glycols, ethylene glycol, and glycerine were formed in varying degrees. It could be shown that the polarity of the solvent plays an important role. In the nonpolar system toluene/$Co_2(CO)_8$ good conversions and selectivities to methyl formate, methanol, and ethylene glycol could be observed. The mechanism of the cobalt-catalyzed reactions is discussed and noncluster intermediates are proposed for the key steps.

INTRODUCTION

A dwindling supply of crude oil and the worldwide existence of extensive coal reserves have renewed interest in the conversion of coal to liquid products. In particular, the desire to hydrogenate carbon monoxide selectively to organic chemicals has drawn considerable attention to homogeneous analogs of the Fischer–Tropsch synthesis. However, so far, only very few reports dealing with the catalytic conversion of CO to multicarbon-containing compounds have appeared. Thus, Demitras and Muetterties (*1a*) report that the clusters $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$ together with Lewis acids yield various amounts of C_1–C_4 hydrocarbons, and Rathke and Feder (*1b*) describe the catalytic formation of methanol and methyl formate via $HCo(CO)_4$ catalysis. Masters and von Doorn (*1c*) obtained C_1–C_{30}–n-alkanes by using clusters of $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Ir_4(CO)_{12}$. Recently Henrici-Olivé and Olivé (*1d*) observed that benzene could be alkylated with CO/H_2.

Most noteworthy is the work of Union Carbide which describes the formation of ethylene glycol, methanol, glycerine, ethanol, propylene glycol, and erythritol from synthesis gas (*2*).

Reduction of carbon monoxide by hydrogen to alcohols is a highly favorable thermodynamic process, yet rather extreme operating conditions must be used to achieve reasonable rates and selectivities. In 1949 E.I. du Pont de Nemours & Company disclosed two patents in which catalysts containing both manganese and chromium (*3*) and cobalt (*4*) at a pressure above 1000 bars and temperatures of 150 to 400°C convert CO/H_2 to polyhydric alcohols and esters. The selectivity and activity are rather poor. A substantial increase in selectivity toward ethylene glycol was illustrated by Pruett and co-workers at Union Carbide applying rhodium cluster catalysts. They postulate that $Cs_2[Rh_{12}(CO)_{\sim 34}]$ solvates are active intermediates and report selectivities of up to 75% ethylene glycol.

Very little is known about the effect of group VIII metals under comparable conditions. Solvents particularly seem to play an important role in CO insertion and hydrogenation reactions (*5*).

In the present paper we describe high-pressure experiments in which clusters and complexes of group VIII elements were used in polar and nonpolar solvents to hydrogenate carbon monoxide to oxygen-containing compounds.

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EXPERIMENTAL

The reactions were carried out in a 25-ml batch reactor designed and built in our Institute. A 3000-bar compressor of Nova Swiss was used. The system toluene/$Co_2(CO)_8$ was also investigated in a continuous flow unit with CO/H_2 recycle (*6*).

The products were analyzed via GLC-analysis (a 40 m WG 11 capillary column was used). The products were isolated via distillation or preparative glc. Identification was effected by ir and NMR spectroscopy. The CO/H_2 composition, the catalysts, and the reaction conditions are listed in the corresponding tables.

RESULTS AND DISCUSSION

The complexes and clusters used to hydrogenate carbon monoxide homogeneously are listed in Table 1. The reaction conditions and amounts of gaseous and liquid products obtained are exhibited in Table 2. The gaseous products predominantly consisted of C_1–C_4 hydrocarbons. The main attention, however, was focused on the analysis of the liquid phase containing the oxygenated species.

TABLE 1

Catalysts Used for Homogeneous Hydrogenation

$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(acac)_2$
$Fe_3(CO)_{12}$	$Co_4(CO)_{12}$	
$Ru_3(CO)_{12}$	$Rh(CO)_2acac$	$Pd(acac)_2$
	$Rh_4(CO)_{12}$	
$Os_3(CO)_{12}$	$Ir_4(CO)_{12}$	$H_2PtCl_6 \cdot 6H_2O$

Comparison of Activities

As can be seen from Table 2 the amounts of products being formed vary greatly. Obviously, the solvent plays an important role.

For instance, $Fe_3(CO)_{12}$ in *N*-methylpyrrolidone (NMP) shows some activity, but in toluene no products have been obtained. On the contrary, $Rh(CO)_2acac$ exhibits its best activity in NMP, but is a poor catalyst in toluene.

Summarizing the results for NMP the following order of activity has been established

$$Rh > Ru > Ir > Co \sim Pt > Fe > Ni > Pd \sim Os$$

TABLE 2

Reaction Conditions and Results[a]

Catalysts	Solvent	Reaction time (hr)	Conversion (%)	Products (%)	
				Liquid	Gaseous
$Fe_3(CO)_{12}$	Toluene	24	—	—	—
$Fe_3(CO)_{12}$	NMP	12	10	81	19
$Co_2(CO)_8$	Toluene	1	19	100	—
$Co_2(CO)_8$	NMP	1	4	100	—
$Ni(acac)_2$	Toluene	8	2	100	—
$Ni(acac)_2$	NMP	Traces			
$Ru_3(CO)_{12}$	Toluene	2	11	93	7
$Ru_3(CO)_{12}$	NMP	2	25	90	10
$Rh(CO)_2acac$	Toluene	0.3	3	100	—
$Rh(CO)_2acac$	NMP	0.3	25	100	—
$Pd(acac)_2$	Toluene	24	3	100	—
$Pd(acac)_2$	NMP	12	2	100	—
$Os_3(CO)_{12}$	Toluene	24	—	—	—
$Os_3(CO)_{12}$	NMP	24	5	90	10
$Ir_4(CO)_{12}$	Toluene	2	2	98	2
$Ir_4(CO)_{12}$	NMP	2	14	98	2
$H_2PtCl_6 \cdot 6H_2O$	Toluene	2	7	98	2
$H_2PtCl_6 \cdot 6H_2O$	NMP	Traces			

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[a] $CO : H_2 = 1 : 1$; pressure, 2000 bar; temperature, 230°C; catalyst concentration, 50 matom metal/liter; $Fe_3(CO)_{12}$, 100 matom/liter; $Co_2(CO)_8$, 200 matom/liter; reaction vessel, 25 ml.

TABLE 3

Products Identified in the CO Hydrogenation (%)[a]

Catalyst	Solvent	Methyl formate	Methyl acetate	Ethyl formate	Methanol	Ethanol	*n*-Propyl alcohol	Propylene glycol-1,2	Ethyleneglycol monoformate	Ethylene glycol	Propylene glycol-1,3	Glycerine
$Fe_3(CO)_{12}$	NMP	13.7	19.3	—	59.2	0.8	—	—	—	—	—	—
$Co_2(CO)_8$	Toluene	34.7	0.1	—	31.4	0.4	0.1	0.6	2.7	25.1	0.6	2.1
$Co_2(CO)_8$	NMP	6.4	28.9	—	14.4	5.9	—	—	—	—	—	—
$Ni(acac)_2$	Toluene	7.8	18.3	—	5.4	0.3	—	—	—	—	—	—
$Ru_3(CO)_{12}$	Toluene	40.5	2.5	—	18.0	—	—	—	—	0.8	—	—
$Ru_3(CO)_{12}$	NMP	22.2	0.8	—	62.3	1.2	—	—	—	1.2	—	—
$Rh(CO)_2acac$	Toluene	25.6	—	—	46.4	3.7	—	—	—	—	—	—
$Rh(CO)_2acac$	NMP	0.7	—	—	11.6	4.7	0.2	5.4	1.1	44.4	—	3.9
$Pd(acac)_2$	Toluene	19.8	1.0	—	—	—	—	—	—	—	—	—
$Pd(acac)_2$	NMP	34.4	9.0	4.2	13.1	1.6	—	—	—	—	—	—
$Os_3(CO)_{12}$	NMP	4.2	—	—	22.2	—	—	—	—	—	—	—
$Ir_4(CO)_{12}$	Toluene	18.4	2.7	—	45.1	2.1	—	—	—	4.9	—	—
$Ir_4(CO)_{12}$	NMP	2.5	1.7	6.8	81.2	2.6	—	—	—	2.4	—	—
$H_2PtCl_6 \cdot 6H_2O$	Toluene	34.7	7.8	—	5.6	3.1	1.0	—	—	—	—	—

[a] For reaction condition see footnote to Table 2.

In toluene this order of reactivity changes in the following way

$$Co > Ru > Rh > Pt > Ir > Ni > Pd > Fe \sim Os$$

It is interesting to compare the above activities with those of Vannice (*7*) obtained by using heterogeneous catalysts of Group VIII metals on alumina for hydrocarbon formation from CO and H_2

$$Ru > Fe > Ni > Co > Rh > Pd > Pt > Ir$$

Although a number of CO hydrogenation reactions have been reported, the observed influence of solvent has no precedent. It has been proposed by various authors that the rate-controlling step is the hydrogenation of the CO leading to oxygen-containing intermediates. Considering the activity of cobalt in toluene and NMP it can be assumed that $HCo(CO)_4$—formed by the reaction of $Co_2(CO)_8$ with hydrogen—in polar solvents acts as an acid; in nonpolar solvents, however, $HCo(CO)_4$ functions as a reducing agent (*8*).

Comparison of Selectivities

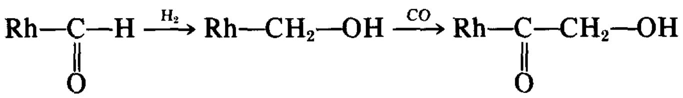
Table 3 lists the compounds isolated via distillation and glc separation. The data show that varying amounts of products have been identified. The system $Co_2(CO)_8$/toluene yielded 98% of identifiable compounds. In other examples—mainly those with poor activity and therefore limited availability of products—only up to 50% have been characterized. However, it should be pointed out that the main interest was directed toward characterizing the oxygen-containing compounds. For instance, the system $Ir_4(CO)_{12}$/toluene gave some *n*-hydrocarbons in the C_1–C_{12} range. Also the $Fe(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ catalysts yielded *n*-alkanes. Using the Pd and Pt catalysts it was very difficult to establish whether the reaction was homogeneous or heterogeneous.

It is interesting to note that besides methanol, ethanol, and *n*-propyl alcohol, polyhydric alcohols such as ethylene glycol, propylene glycols, and glycerine are formed.

The C_1 species methanol and methyl formate appear in different amounts. NMP/$Ir_4(CO)_{12}$ yields about 81% methanol. NMP/$Rh(CO)_2acac$ gives practically no methyl formate; however, toluene/$Rh(CO)_2acac$ and toluene/$Co_2(CO)_8$ form 26 and 35%, respectively.

The C_1 products can be derived from a formyl intermediate (see reaction mechanism).

In polar solvents rhodium is a very active hydrogenation catalyst (9), which in a fast reaction can convert the formyl complex into an alcoholic intermediate which easily can insert an additional CO leading to the C_2 species.



$$\mathrm{Rh{-}\underset{\underset{O}{\|}}{C}{-}H \xrightarrow{H_2} Rh{-}CH_2{-}OH \xrightarrow{CO} Rh{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}OH}$$

In comparison with rhodium, cobalt (in nonpolar solvents) is a poorer hydrogenation catalyst; therefore the C_1 species prevail.

The amount of ethylene glycol and glycerine being formed within the series Co, Rh, Ir confirms the general rule that 3d- and 4d-metal compounds insert CO more easily than 5d-metals.

The formation of ethylene glycol via synthesis gas is interesting from an industrial viewpoint. The rhodium catalyst shows a higher glycol selectivity and activity; the cobalt system, however, is an interesting candidate when compared on the basis of cost and availability.

In order to optimize the selectivity and activity of the cobalt system a number of experiments have been carried out studying the infuence of pressure, temperature, and catalyst concentration.

Influence of Pressure

A series of experiments was carried out varying the pressure from 800 to 2600 bar. Figure 1 shows that the ethylene glycol formation increases with increasing pressure. At 2600 bar about 55% diols are formed. Increasing pressure diminishes the amount of methanol while the build-up of methyl formate passes through a maximum at about 1600 bar. The conversion to oxygenated species approaches appreciable values only above 1000 bar. In other words, the number of CO insertions increases with pressure. Erythritol, originating from four CO molecules, is formed only at pressures above 2000 bars. The impact of such high

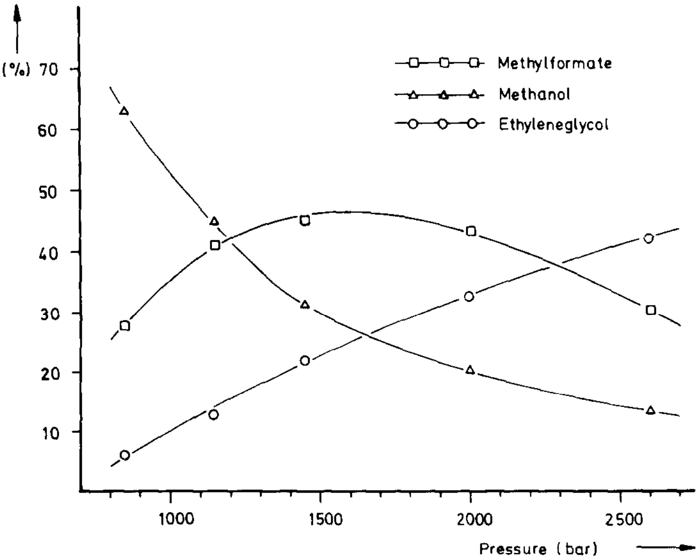


FIG. 1. Pressure dependence of the products formed. Composition: 100 mmol $Co_2(CO)_8$/liter toluene; T = 230°C; t = 0.5–2 hr; CO/H_2 = 1 : 1.

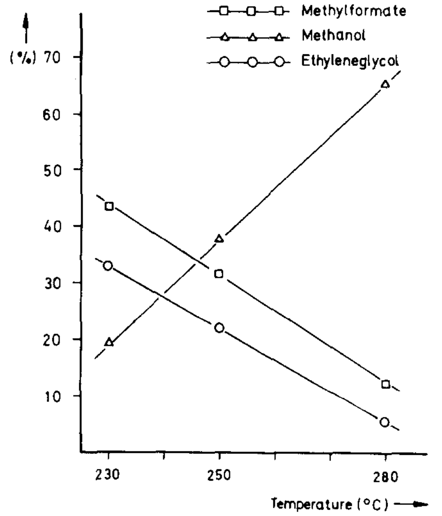


FIG. 2. Temperature dependence of carbon monoxide hydrogenation. Composition: 100 mmol $Co_2(CO)_8$/liter toluene; p = 2000 bar; t = 0.5 hr; at 280°C t = 0.25 hr; $CO/H_2 = 1:1$.

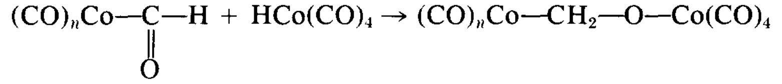
pressures on chemical reactions is not very well understood. Basically the effect of pressure on chemical reactions can be divided into changes of equilibrium yield and changes of reaction rate. At pressures up to 10000 bar the compressibility of gases is greatly enhanced resulting in a diminished volume (*10*). The distances between molecules are minimized and chemical equilibria are directed toward associated species. Bimolecular reactions yielding C–C linkages are highly favored. It is of interest that variations in the $H_2:CO$ ratio from 0.5 to 2 show no difference in the product selectivity.

Influence of Temperature

A minimum temperature of 200°C is needed to start the reaction. Figure 2 illustrates the temperature effect on the formation of glycol, methanol, and methyl formate. Above 280°C methanol is the favored product. The best temperature for glycol formation is about 230°C.

Influence of Catalyst Concentration

Figure 3 illustrates the effect of catalyst concentration. The glycol formation increases upon adding $Co_2(CO)_8$. By analogy with the hydroformylation (*11*) one can speculate that a higher concentration of cobalt leads to an increase of $HCo(CO)_4$ and an acceleration of the following reaction step:



$$(CO)_nCo\text{—}\underset{\underset{\displaystyle O}{\|}}{C}\text{—}H + HCo(CO)_4 \rightarrow (CO)_nCo\text{—}CH_2\text{—}O\text{—}Co(CO)_4$$

Via hydrogenation and CO insertion all products observed can be derived from the bimetallic cobalt intermediate. An increase in hydrogenation activity should decrease the methyl formate and increase the methanol and glycol formation. Indeed, this has been observed as is evident from Fig. 3.

This study provides further support for a postulate that the hydrogenation of a carbon monoxide molecule coordinated to a metal atom is the rate-controlling step (*7, 12*). Using heterogeneous catalysts the hydrogen dissociation and transfer is very rapid. In homogeneous systems high catalyst concentrations and pressures are needed.

Reaction in Two Phases

A major problem with using homogeneous catalysts is the separation of the catalyst from the reaction mixture in a reusable form. This problem can be overcome for systems if it is possible to work in two phases. One phase must contain the catalyst and the other one the reaction products. If no catalyst enters into the produce phase, the products can be "spooned off" thus providing an easy way to separate the homogeneous catalyst from the product (*13*).

Using *n*-pentane or toluene as solvent the glycol which is formed separates at the

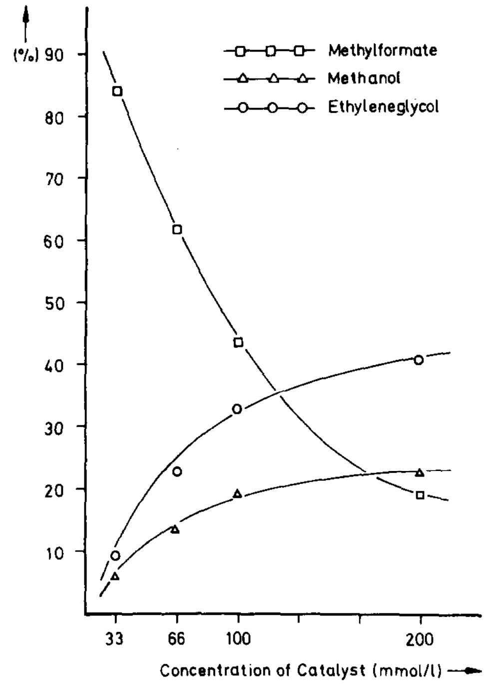


FIG. 3. Product distribution as a function of catalyst concentration. Composition: $Co_2(CO)_8$ in toluene; T = 230°C; p = 2000 bar; t = 0.5 hr; $CO/H_2 = 1:1$.

bottom of the reactor in a nearly catalyst-free phase. The cobalt catalyst stays predominantly in the top layer where it can easily be recycled. In this way up to five recycles were carried out without a loss in activity.

Reaction Mechanism

Figure 4 illustrates the proposed rather speculative reaction mechanism interpreting the major products observed. This mechanism is based on the framework of our current understanding of homogeneous catalytic reactions (*14*). Major features are the invoked intermediates 1, 2, 3, and 4. The formyl complex 1 is a key intermediate. Formyl complexes have been observed and isolated (*15*). Methanol and methyl formate can be derived from 1 by hydrogenation and subsequent reaction with the formed methanol. Reaction of 1 with ethanol gives ethyl formate. To account for the C_2 species a reaction of 1 with $HCo(CO)_4$ is invoked leading to 2, which upon insertion of carbon monoxide gives 3. Glycol and ethanol stem from 3. Via hydrogenation and CO insertion of 3 the intermediate 4 is formed which can account for glycerine. *n*-Propyl alcohol and propylene glycol also can be explained considering hydrogenation and CO insertion of 3.

The proposed mechanism is based on monometallic and bimetallic intermediates, which are in contrast with the cluster mechanism postulated by Pruett (*2*). To prove or disprove the cluster theory the CO hydrogenation was carried out using the following cobalt clusters: $Co_2(CO)_8$, $Co_4(CO)_{12}$, $[Co_6(CO)_{15}]^{2-}$.

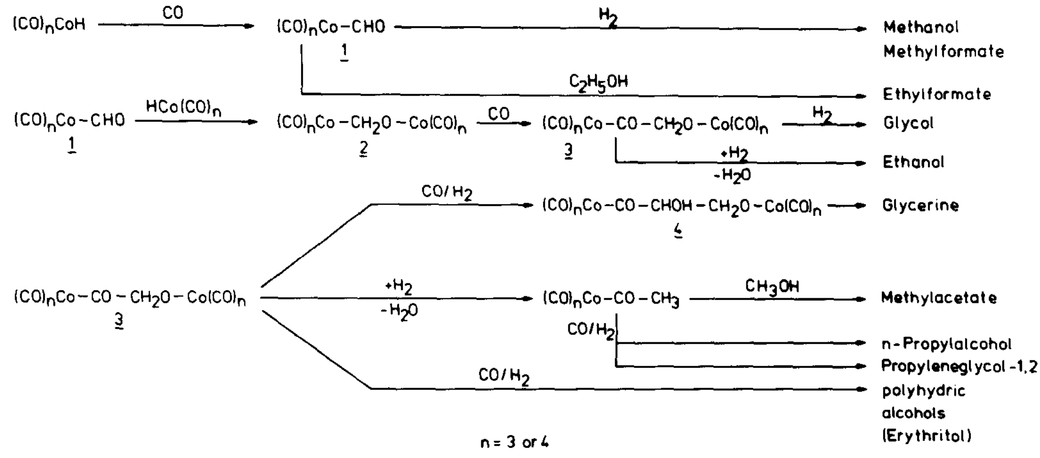


FIG. 4. Proposed reaction mechanism.

Unfortunately, we had no way to follow the reaction by ir spectroscopy at high pressure. However, the reaction mixture was analyzed by ir spectroscopy and liquid phase chromatography. The only compound detectable at the end of the reaction was $HCo(CO)_4$. Therefore, we assume that the cobalt clusters decomposed according to the following equilibria (*16*):

$$[Co_6(CO)_{15}]^{2-} + 9\,CO \rightleftarrows 2\,Co_2(CO)_8 + 2\,[Co(CO)_4]^-$$
$$Co_4(CO)_{12} + 4\,CO \rightleftarrows 2\,Co_2(CO)_8$$
$$4\,Co_2(CO)_8 + 4H_2 \rightleftarrows 8\,HCo(CO)_4$$

We believe that in the cobalt system clusters are of no importance.

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