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HYDROGENATION OF CARBON MONOXIDE BY RUTHENIUM COMPLEXES WITH IODIDE PROMOTERS: CATALYTIC AND MECHANISTIC INVESTIGATIONS

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Summary

Carbon monoxide and hydrogen are converted into organic products, including methanol, ethylene glycol, and ethanol, by halide-promoted ruthenium catalysts in organic solvents. Iodide salts are exceptionally good promoters for this system. Spectroscopic and reaction studies have shown that two ruthenium complexes, $HRu_3(CO)_{11}^-$ and $Ru(CO)_3I_3^-$, are present during catalysis and essential for optimum activity. Possible roles for the involvement of these complexes in catalysis are considered.

Introduction

The direct conversion of H_2/CO mixtures (synthesis gas) to organic products is recognized as an important goal in catalytic research. Processes based on such reactions could provide our future supplies of liquid fuel and industrial chemicals, relying on coal or renewable raw materials as sources of synthesis gas. Organometallic chemistry contributes to this research in such areas as the search for or design of new homogeneous catalysts for synthesis gas conversion, and in the elucidation of catalytic mechanisms involved in H_2/CO chemistry. Mechanistic information is invaluable in the search for new catalyst systems; likewise, information gained from studies on novel catalytic systems can provide the key to a general mechanistic understanding of related processes. In this paper I would like to describe some catalytic properties of a quite highly active system for CO hydrogenation, and then present some results of experiments carried out to aid in our understanding of the organometallic chemistry involved in the catalytic process.

The hydrogenation of CO by homogeneous catalysts has been known for some time. Gresham showed more than thirty years ago that cobalt complexes could convert H_2/CO to alcohols and polyols under rather severe conditions (ca. 3000 atm, 250°C) [1]. More recently, cobalt-catalyzed CO hydrogenation has been studied under milder conditions by Rathke and Feder [2] and by Fahey [3]. Soluble rhodium

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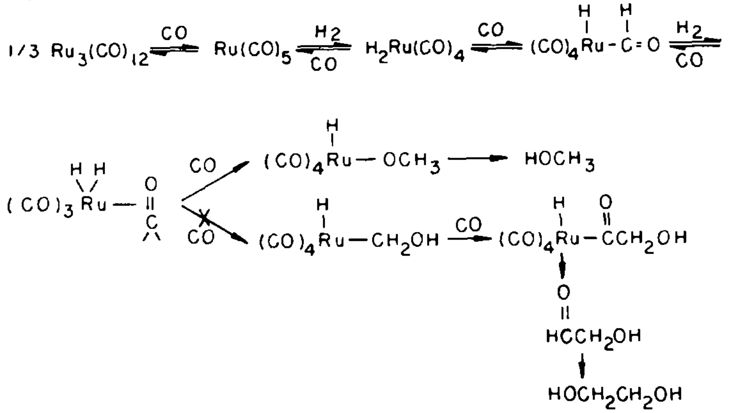
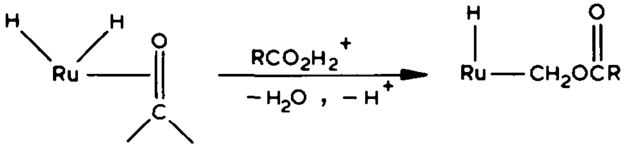
complexes were also discovered to catalyze direct synthesis gas conversion [4,5] and the activity of these catalysts has been found to be significantly greater, in general, than that of the cobalt catalysts [3]. In the hope that complexes of other metals could be even more reactive, we began a search for new catalyst systems, and our attention was drawn toward ruthenium. Not only is this metal adjacent to rhodium in the periodic table, but it is highly active for heterogeneous CO hydrogenation [6]. Indeed, we found that $Ru_3(CO)_{12}$ was a catalyst precursor for a system which reduced CO to methanol with quite high selectivity. (The major complex present under catalytic conditions was found to be $Ru(CO)_5$.) Bradley [7] and King et al. [8] have published their studies of this reaction as well. Although the cobalt and rhodium catalysts previously mentioned produce ethylene glycol and other two- and three-carbon products as well as methanol, this ruthenium system was notable for the absence of these higher products. Based on mechanistic and model studies to be reported in more detail elsewhere, we proposed that the selectivity to the one-carbon product in this mononuclear catalyst system was the result of forming with high specificity a catalytic intermediate which could not be converted to a two-carbon chain, a metal methoxide intermediate. Since the carbon monoxide molecule being reduced is originally carbon-bound, it was thought that a coordinated formaldehyde ligand might be an intermediate on the pathway to the oxygen-bound methoxide ligand, as shown in Scheme 1. (Similar mechanisms have been presented by Feder and Rathke [2] and by Fahey [3].)

SCHEME 1



We found an interesting modification of this system which allowed the production of two-carbon products, ethylene glycol esters, as well as methyl esters, by simply carrying out the reaction in a carboxylic acid solvent [9–11]. (Similar reactions have been reported by Knifton [12], but most of those reactions are complicated by the presence of ionic promoters.) Most characteristics of the glycol-producing reaction (dependences on H_2 and CO pressure and catalyst concentration, for example) were the same as for the methanol-forming process, so it appeared that the catalysts for the two processes were essentially the same. One explanation for the crucial role of the carboxylic acid in promoting formation of the two-carbon product may be that an activated form of the acid, such as a protonated carboxylic acid molecule, could acylate the bound formaldehyde, thus forming an acyloxymethyl ligand (eq. 1). This reaction would prevent the formaldehyde from being converted into a methoxide ligand and would transform it into a metal–carbon bonded intermediate which could grow to a two-carbon product by CO insertion [13]. Floriani and coworkers have recently demonstrated just such an acylation process with a formaldehyde complex of vanadium, a much more oxophilic metal which in other reactions favors metal–oxygen bond formation [14].



(1)

Although this ruthenium catalytic system was mechanistically interesting, its activity for CO hydrogenation was considerably lower than that of the rhodium system. Furthermore, its selectivity to the more valuable two-carbon products was also much lower. We were therefore interested in modifying the system to increase its selectivity to the glycol product, especially by means which would avoid the use of the reactive and corrosive carboxylic acid solvent. (Free alcohol products are also more desirable than the carboxylate esters, which must be hydrolyzed in a separate step.) It seemed apparent that the key to selectivity lay in the reactivity of a metal formaldehyde complex, such as in Scheme 1. We reasoned that making the metal atom more nucleophilic might increase its propensity to form a metal–carbon bond in its subsequent reactions, thus producing an intermediate which could be converted to a two-carbon product. It appeared that the desired effect might be obtained by adding anionic ligands to the system, which could impart a negative charge to a possible intermediate containing coordinated formaldehyde. It also did not escape us that Lewis acids might be beneficial since they could bind to the oxygen atom of the coordinated formaldehyde molecule and perhaps assist in attack of the transition metal on the formaldehyde carbon atom. Experiments were therefore carried out in non-reactive, but polar solvents with ruthenium complexes and salts containing alkali metal cations, which could be expected to exhibit some Lewis acidity. These mixtures were indeed found to exhibit unusual selectivity characteristics. An unexpected result was that these catalyst systems also possessed greatly enhanced activity for H_2/CO conversion in some cases. Our initial studies of these reactions have been reported in a communication [15]. Work on a closely related system has been reported by Knifton [16].

Results and discussion

1. Effects of salts as promoters

Addition of a number of salts to solutions containing $Ru_3(CO)_{12}$ or $Ru(CO)_5$ significantly increases the activity of the catalyst for CO reduction. For example, potassium salts of acetate, phosphate, fluoride, and chloride anions were observed to increase the activity by a factor of 3 or 4 under a standard set of conditions [15]; bromide and iodide salts were even more effective. All of these salts were found to cause the production of at least small quantities of ethylene glycol, but chloride, bromide, and iodide salts gave the best selectivity to this two-carbon product. Since iodide salts provided the highest activity, most of our attention was directed toward this halide.

TABLE 1

CATALYTIC REACTIONS CONTAINING DIFFERENT IODIDE SALTS[a]

Salt	CH_3OH (mmol h^{-1})	$(CH_2OH)_2$ (mmol h^{-1})
LiI	146	24.8
NaI	119	26.3
KI	152	23.3
CsI	120	21.0
PPNI[b]	143	26.3

[a] Conditions: 75 ml sulfolane solvent, 18 mmol salt, 3 mmol Ru (charged as $Ru_3(CO)_{12}$), $H_2/CO = 1$, 86.1 MPa, 230°C. [b] PPN = bis(triphenylphosphine)iminium.

The possibility existed that the promoter cation was involved in the catalytic reaction as a Lewis acid, so a number of experiments were carried out with iodide salts containing different cations. A typical series of such experiments is shown in Table 1. No trend in activity or selectivity is apparent. Even the large, delocalized PPN^+ cation behaves similarly to the alkali metal cations. These results suggest that the cation has little, if any, involvement in the catalytic process under these conditions, and that Lewis acid effects are not important in determining the activity or selectivity of this system.

2. *Activity of the catalyst*

Many factors influence the catalytic activity of this system, and these will be described in some detail in sections to follow. Many of the reactions reported here were carried out under a pressure of 86.1 MPa (850 atm) of 1/1 H_2/CO at 230°C. At these conditions, the combined rate to the two major products, methanol and ethylene glycol, is found to fall generally within the range of $1.5–4.0 \times 10^{-2}$ s^{-1} (turnovers based on metal atoms). The actual rate is largely determined by the solvent and level of iodide promoter. For comparison, the activities (at the same conditions) of the two most active systems previously known to homogeneously reduce CO were estimated by interpolation of results reported by Fahey [3] at this temperature and a range of pressures. The rate obtained for the cobalt system is 0.5×10^{-2} s^{-1}, and that for the rhodium system is 1.0×10^{-2} s^{-1}. Without the halide promotor, the ruthenium catalyst exhibits rates of less than 0.5×10^{-2} s^{-1} under these conditions.

3. *Products*

As stated above, the major products of this system are methanol and ethylene glycol. The three-carbon polyol glycerol can also be detected in the product mixture. A number of other products are also observed, most of which are probably secondary products; the relative abundances of these products increase as reactions are allowed to proceed for longer periods of time. Ethanol, for example, can build up to substantial levels in this system, as shown in Fig. 1. It appears to be derived from initially-formed methanol via homologation [17]. Acetaldehyde can sometimes be detected in product solutions, and glycol acetals of acetaldehyde, glycolaldehyde,

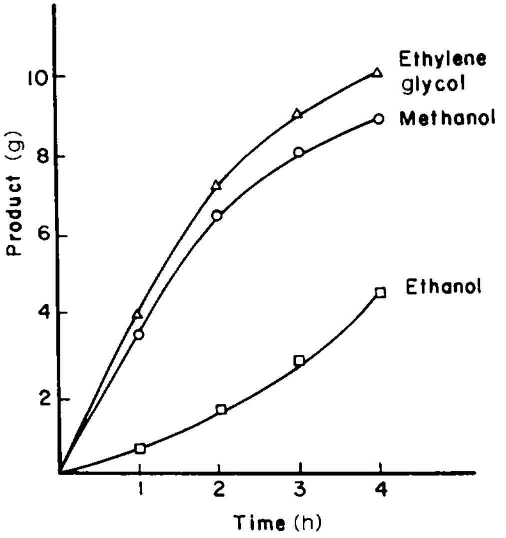


Fig. 1. Plot of product distribution vs. time. Conditions: 75 ml *N*-methylpyrrolidone, 30 mmol Ru, 120 mmol KI, 86.1 MPa H_2/CO, 200°C.

and formaldehyde can also be observed. Small amounts of ethers are sometimes observed as well. Analyses of the vent gas usually show low levels of methane. Some of these typical products and their approximate fraction by weight of the total organic products are listed in Table 2. Factors influencing the distribution of these products will be described below, as will possible mechanistic implications of this product array.

4. *Solvents*

Properties of the solvent for a homogeneous catalytic reaction can be critically important to its success, as is the case for many other reactions involving organometallic complexes. In this catalytic system it seemed apparent that there were several constraints on the choice of solvent. First, it needed to be a material resistant to hydrogenation and thermolysis, to withstand the reaction conditions. Second, the solvent had to be sufficiently polar to dissolve an ionic promoter and ionic organometallic complexes which would presumably be formed. Several solvents

TABLE 2

TYPICAL PRODUCTS FROM CO HYDROGENATION BY IODIDE-PROMOTED Ru CATALYSTS

Product	Weight Percent
Methanol	30–80
Ethylene glycol	5–60
Ethanol	2–30
Glycerol	0.2–3
2-Methyl-1,3-dioxolane	0.2–4
2-Hydroxymethyl-1,3-dioxolane	0.2–3

TABLE 3

CATALYTIC HYDROGENATION OF CO IN DIFFERENT SOLVENTS[a]

Solvent	CH_3OH (mmol h^{-1})	$(CH_2OH)_2$ (mmol h^{-1})
Sulf[b]	270	44
NMP[c]	398	48
Pr_3PO[d]	435	50
18-C-6[e]	380	45
TG[f]	75	5.2
n-BuOH[g]	16	tr.
H_2O	23	tr.

[a] Conditions: 75 ml solvent, 6 mmol Ru, 18 mmol KI, $H_2/CO = 1$, 86.1 MPa, 230°C. [b] Sulfolane. [c] *N*-Methylpyrrolidone. [d] Tri-n-propylphosphine oxide. [e] 18-crown-6. [f] Tetraglyme. [g] n-Butanol.

meeting these requirements had proven effective in the Lewis base-promoted rhodium system [18], including sulfolane, 18-crown-6, *N*-methylpyrrolidone, and tri-n-propylphosphine oxide. These materials are also excellent solvents for this ruthenium system, and some typical results are given in Table 3.

Other potential solvents gave considerably inferior results. Tetraglyme, for example, was a much less effective solvent than 18-crown-6. This may be attributable to the considerably lower solubility of KI in the open-chain polyether. Hydroxylic solvents also cause unexpectedly low activity in this system. As an example, water is capable of dissolving KI and ionic ruthenium complexes, but nevertheless yields only very low rates of CO reduction. This may be the result of a chemical reaction involving the hydroxyl group which retards the productive catalytic pathways, and this subject will be addressed later. Possibly related is the fact that a substantial portion of the water, when used as solvent, is converted to CO_2 and H_2 via the water-gas shift reaction.

5. Promoter concentration

As increasing amounts of an iodide salt, such as KI, are added to this catalytic system the catalytic activity for both methanol and glycol products continues to rise [15], apparently up to the solubility limit of the iodide salt in the system under catalytic conditions. (This phenomenon does not appear to be a general salt effect or cation effect; addition to this system of another salt, KCl, brings about only small increases in rates which might be predicted based on its lower individual promoter activity.) The rate dependences on iodide concentration are slightly different for the methanol-producing reaction (0.6 order in $[I^-]$) and the glycol-forming process (0.45 order in $[I^-]$). As incrementally lower iodide concentrations are employed, a point is reached below which the rate to glycol falls off more sharply than expected from this dependence. The break occurs at an I^-/Ru ratio of about 0.5, which may correspond to the stable catalyst composition during catalysis. Iodide added above this level apparently promotes the reaction as free iodide, but iodide concentrations below this point would not be sufficient to convert all of the $Ru_3(CO)_{12}$ (or $Ru(CO)_5$) to the stable form of the catalyst. As previously described, this Ru/I^-

ratio closely corresponds to that required (0.43) for the reaction of eq. 2 [15]. There

$$\tfrac{7}{3}Ru_3(CO)_{12} + 3\,I^- + H_2 \rightarrow 2\,HRu_3(CO)_{11}^- + Ru(CO)_3I_3^- + 3\,CO \qquad (2)$$

is other evidence as well that the products of eq. 2 are the stable form of the system under catalytic conditions, as will be described below.

6. Catalyst concentration

An interesting effect was noted in this system as the concentrations of the iodide promoter and the Ru component were varied while being held at a constant ratio. (In a sense, this corresponds to using differing amounts of solvent for the reaction, although the solution volume was actually held constant for experimental reasons.) Figure 2 shows the results of some of these reactions, plotted as turnover frequencies (mol product per mol of metal per unit time) vs. metal concentration. For a process first-order in catalyst, this plot would show lines of zero slope. It is evident that increased catalyst concentrations lead to increased normalized activity for glycol formation, while the corresponding methanol activity either remains constant or declines, depending on the solvent. (Log-log plots of glycol rates vs. catalyst concentration show an overall dependence on catalyst of about 1.3 order.) The consequence is that higher concentrations of catalyst form the glycol product with substantially higher selectivites.

These results may suggest that processes intermolecular in the catalyst components are important in the glycol-producing reaction, but are perhaps not as much involved in the methanol-forming reaction(s). The differences in methanol activity and its concentration dependence in the two solvents shown may also suggest that several different routes to methanol are operating, although the glycol-forming reaction appears to be much less sensitive to such solvent effects. The mechanism for

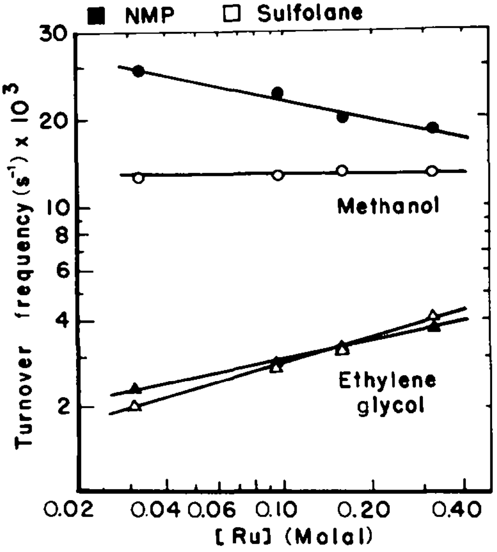


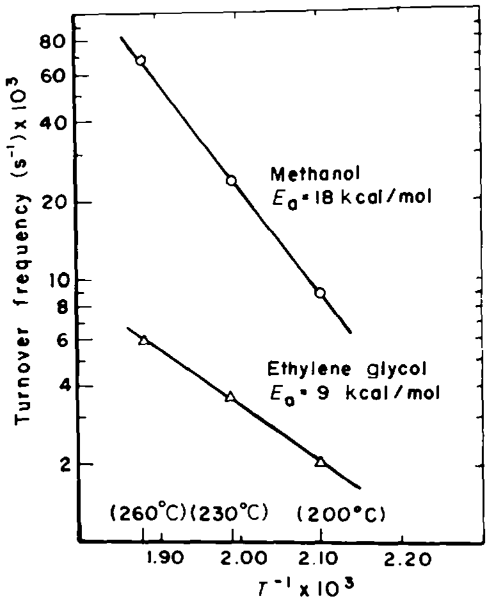
Fig. 2. Plot of turnover frequencies to methanol and ethylene glycol as a function of catalyst concentration. Conditions: *N*-methylpyrrolidone or sulfolane solvent (75 ml), [KI] = 6 [Ru], 86.1 MPa H_2/CO, 230°C.

glycol formation may therefore be quite unrelated to those involved in methanol production by this system. When mechanistic considerations are addressed later, the major emphasis will therefore be placed to the glycol-forming process.

7. *Temperature and pressure*

Two of the most effective means of altering the rates in this catalytic system involve changing the reaction temperature and pressure. As seen in Fig. 3, the formation of methanol increases more rapidly than that of glycol as the temperature is raised. Expressed in activation energies, the methanol-forming process is about twice as sensitive to changes in temperature as the glycol-producing reaction. This difference in behavior means, in a practical sense, that selectivity to the two-carbon product can be greatly enhanced by operating at low temperatures, but this is achieved at the expense of some activity to this product.

Although rates are increased by raising the reaction temperature, the increase in productivity which can be gained by this method is limited. At some point, a temperature is reached beyond which catalytic activity does not increase, or drops.



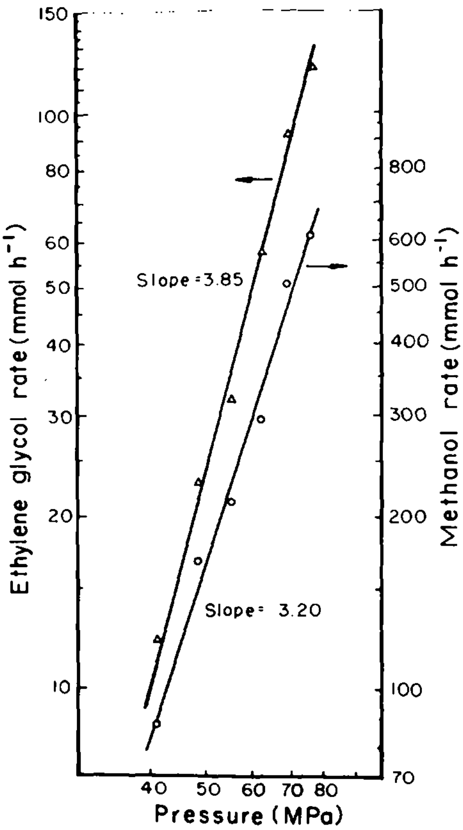


Fig. 3. Plot of log (turnover frequency) vs. $1/T$. Conditions: 75 ml 18-crown-6, 15 mmol Ru, 60 mmol KI, 86.1 MPa H_2/CO.

Fig. 4. Log-log plots of rates to ethylene glycol and methanol vs. pressure. Conditions: 75 ml *N*-methylpyrrolidone, 15 mmol Ru, 45 mmol NaI, 230°C.

TABLE 4

EFFECT OF TOTAL PRESSURE ON CO HYDROGENATION [a]

$p(H_2)$ (MPa)	$p(CO)$ (MPa)	$p(N_2)$ (MPa)	CH_3OH (mmol h^{-1})	$(CH_2OH)_2$ (mmol h^{-1})
43	43	–	426	44
43	43	86	961	137

[a] Conditions: 75 ml 18-crown-6, 6 mmol Ru, 18 mmol KI, 230°C.

This complex temperature dependence may be observed at temperatures from 230–270°C and above, depending on the reaction pressure, and does not appear to involve irreversible changes in the catalyst system. However, at sufficiently high temperature, changes take place which are essentially irreversible, and involve carbide cluster formation as will be described below.

The reaction pressure has a profound effect on the rate of CO hydrogenation by this system. As shown in Fig. 4, the dependence of the glycol-forming reaction on $p(H_2/CO)$ is approximately fourth-order, while that for the methanol-forming process is somewhat greater than third-order. Previous work on cobalt- and ruthenium-catalyzed CO hydrogenation has shown overall pressure dependences of first order or slightly above [2,3,9], but the Lewis base-promoted rhodium system has been reported to exhibit a higher pressure dependence, in the vicinity of third- to fourth-order [3].

Much of the rate enhancement achieved in this system by increasing the pressure is the result of increased concentrations of CO and H_2 in the catalyst system. However, some of this effect may be attributed to a negative volume of activation for the CO hydrogenation processes. This was demonstrated by carrying out two similar reactions, each with the same catalyst charge and under the same partial pressures of H_2 and CO. One of these reactions was performed under a higher total pressure achieved with inert N_2 gas. The results (shown in Table 4) suggest a substantial volume of activation effect. Therefore, the pressure dependences observed upon changing H_2 and CO pressures cannot strictly be taken as indicating kinetic orders in these reagents.

8. Complexes present in catalyst solutions

Reaction of $Ru_3(CO)_{12}$ with iodide salts under H_2 or H_2/CO yields two ruthenium complexes, $Ru(CO)_3I_3^-$ and $HRu_3(CO)_{11}^-$, according to eq. 2. These complexes are also observed by IR spectroscopy in reaction solution after catalysis. Additionally, $HRu_3(CO)_{11}^-$ has been detected in catalyst solutions by ^1H NMR, and the $Ru(CO)_3I_3^-$ complex has been observed by ^{99}Ru NMR [19].

Stoichiometry studies described above suggest that a catalyst composition corresponding to the products of eq. 2 is present under catalytic conditions, and infrared spectroscopy of solutions at reaction conditions (Fig. 5) indicate that the same two complexes are essentially the only observable species present during catalysis. Even the characteristic bridging carbonyl absorption of the $HRu_3(CO)_{11}^-$ complex is observed; thus there is strong evidence that the cluster is stable under high pressures of CO and H_2. Its possible involvement in catalysis will be discussed below.

When catalytic reactions are carried out at sufficiently high temperatures (usually 260–290°C, depending on the pressure and catalyst concentration), catalytic activity greatly declines and a different ruthenium complex is observed after catalysis. This

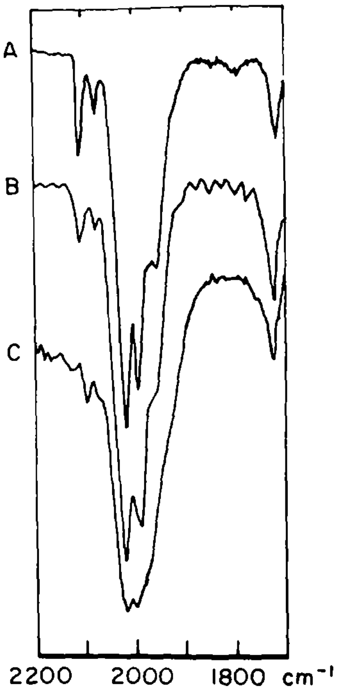


Fig. 5. Infrared spectra of (A) synthetic mixture of PPN[$HRu_3(CO)_{11}$] and PPN[$Ru(CO)_3I_3$] (2/1 molar ratio), (B) catalytic mixture obtained from $Ru_3(CO)_{12}$ and KI in sulfolane, after catalysis, and (C) same catalytic mixture during catalysis at 55.1 MPa H_2/CO, 230°C.

TABLE 5

REACTIONS OF Ru COMPLEXES WITH H_2/CO [a]

No.	Complex	mmol	Total Ru (mmol)	NaI (mmol)	CH_3OH (mmol h^{-1})	$(CH_2OH)_2$ (mmol h^{-1})
1	$Ru_3(CO)_{12}$	2	6	18	171	35
2	$(PPN)_2[Ru_6C(CO)_{16}]$	1	6	18	89	8
3	$(PPN)_2[Ru_6C(CO)_{16}]$ PPN[$Ru(CO)_3I_3$]	0.86 0.86	6	18	12	trace
4	PPN[$Ru(CO)_3I_3$]	6	6	0	0	0
5	PPN[$Ru(CO)_3I_3$]	6	6	18	0	0
6	PPN[$HRu_3(CO)_{11}$]	2	6	0	33	trace
7	PPN[$HRu_3(CO)_{11}$]	2	6	18	123	8
8	PPN[$HRu_3(CO)_{11}$] PPN[$Ru(CO)_3I_3$]	1.72 0.86	6	18	188	34
9	PPN[$HRu_3(CO)_{11}$] PPN[$Ru(CO)_3I_3$]	1.72 0.86	6	0	80	15

[a] Conditions: 75 ml sulfolane solvent, 86.1 MPa, H_2/CO = 1, 230°C.

product has been identified as $Ru_6C(CO)_{16}^{2-}$, a carbide cluster which has previously been synthesized by alternate methods [20,21]. It initially appeared possible that this cluster could be involved in the production of such products as ethanol and methane by this system, since they could be derived from the central carbon atom in the cluster. However, several experiments showed that this is an unlikely possibility, since this cluster is quite unreactive under normal catalytic conditions. Rates of CO hydrogenation are low when this complex is used as a catalyst precursor, as shown in Table 5. There was not a notable increase in either methane or ethanol selectivities in these reactions.

Since most active catalyst solutions contained both $Ru(CO)_3I_3^-$ and $HRu_3(CO)_{11}^-$, it was necessary to test the catalytic activity of these complexes individually. Results are given in Table 5. It can be seen that $Ru(CO)_3I_3^-$ has no activity for CO hydrogenation, either in the absence (no. 4) or presence (no. 5) of NaI. This complex is observed unchanged after the reactions. The $HRu_3(CO)_{11}^-$ complex has some activity alone (no. 6), which is substantially enhanced by addition of NaI to the solution (no. 7). However, the activity of this individual complex still remains significantly below that observed for a mixture of $Ru(CO)_3I_3^-$ and $HRu_3(CO)_{11}^-$, either prepared synthetically (no. 8) or derived in situ from $Ru_3(CO)_{12}$ (no. 1). As expected from the study of I^-/Ru stoichiometry described above, a mixture of these complexes even in the absence of added iodide has substantial activity (no. 9).

It was expected that more information about the involvement of these two complexes in catalysis might be gained from studies in which the concentration of one complex was held constant, while that of the second was varied. Results of these reactions were somewhat surprising, as seen in Fig. 6. It was found that small amounts of one complex added to a fixed concentration of the second cause increased glycol activity, but a maximum in activity is obtained at or near the 2/1 molar ratio of $HRu_3(CO)_{11}^-$ to $Ru(CO)_3I_3^-$. (Coincidentally, this is the ratio in which these complexes are formed from $Ru_3(CO)_{12}$ by eq. 2). Although not shown, the activity of the system for methanol follows the same pattern. This complicated behavior probably indicates that each of these two complexes, or a species in equilibrium with it, interacts with an important intermediate in the catalytic process, leading to its non-productive decomposition. This interaction can be considered to be an inhibition process, and can have a higher order in the complex than the

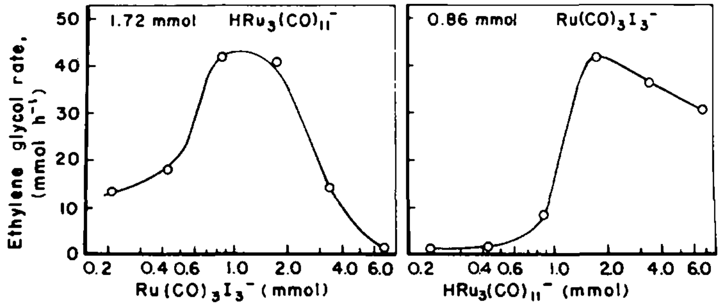


Fig. 6. Plots of rates to ethylene glycol at different ratios of $PPN[HRu_3(CO)_{11}]$ and $PPN[Ru(CO)_3I_3]$. Conditions: 75 ml sulfolane, 36 mmol NaI, 86.1 MPa H_2/CO, 230°C.

productive pathways. Nevertheless, the results suggest that a 2/1 ratio of these complexes is somehow significant in the catalytic process. A possible explanation for the importance of this ratio will be presented in the section on the mechanism of this process.

Since a 2/1 ratio of these two complexes in catalytic solutions provides optimum activity, added reagents which alter this ratio cause diminished activity. These reagents may be oxidizing agents, including acids, or reducing agents, including bases. Likewise, mixtures containing an excess of $HRu_3(CO)_{11}^-$ or $Ru(CO)_3I_3^-$ can be adjusted to a more active ratio by the addition of acid (oxidizing agent) or base (reducing agent). The importance of the average oxidation state in determining the CO reduction activity of this system has been described elsewhere in more detail [22].

9. Mechanism

The chemistry of product formation by this system must be very complex, as evidenced by the fractional orders in iodide promoter concentration, changing selectivity with catalyst concentration, and substantial pressure dependences. Unlike the cobalt system for CO reduction, which is postulated to have a common catalytic intermediate leading to both methanol and ethylene glycol products [3], there is no indication of such behavior by this system. It appears probable that methanol is produced by several separate pathways, and the mechanism(s) of its formation may be more difficult to determine. This discussion of mechanism will therefore be directed toward the glycol-forming process, which may also produce some of the methanol formed by this system.

Interpretation of kinetic measurements obtained from catalytic processes requires knowledge of the stable form of the catalyst under reaction conditions. The kinetic data then provide information on transformations involving the catalyst up to and including the rate-determining step. (In previous studies of CO hydrogenation, data are consistent with the rate-determining step occurring at or near the formation of a formaldehyde-containing intermediate [2,3,9,10].) Evidence from several directions shows that the predominant species present in this system under catalytic conditions are $HRu_3(CO)_{11}^-$ and $Ru(CO)_3I_3^-$, usually in a 2/1 ratio. Since both complexes are necessary for highest activity, it appears probable that they, or complexes in equilibrium with them, interact in some manner related to catalysis. One possible form of this interaction could be related to the reverse of eq. 2, thus producing a ruthenium(0) complex from the stable catalyst components. Since iodide is a promoter in the catalytic system, it could be involved in such a process, and a possible representation of this reaction is given in eq. 3.

$$\tfrac{2}{7}HRu_3(CO)_{11}^- + \tfrac{1}{7}Ru(CO)_3I_3^- + \tfrac{4}{7}I^- + \tfrac{3}{7}CO \rightleftharpoons \tfrac{1}{7}H_2 + Ru(CO)_4I^- \xrightarrow{H_2/CO} \text{Product} \tag{3}$$

A catalytic process based on this conversion has some appeal, because it could be expected to show an iodide dependence close to that observed (0.45 order). It is also plausible from the standpoint that a complex which could be identified as $Ru(CO)_4I^-$ has never been observed in this system; this intermediate could therefore be expected to be quite unstable and reactive, perhaps in a catalytically significant way. Nevertheless, it is difficult to see why a catalytic system based on eq. 3 would exhibit a catalyst concentration dependence greater than unity and a large pressure dependence. Although this pathway or modifications of it cannot be rigorously excluded, they appear unlikely to be significant in glycol formation. (However, such a reaction could be involved in production of some of the methanol product.)

Another way in which $HRu_3(CO)_{11}^-$ and $Ru(CO)_3I_3^-$ could interact is by an intermolecular hydride transfer process. The $HRu_3(CO)_{11}^-$ complex has been shown by Shore and coworkers to act as a hydride donor [23], and the $Ru(CO)_3I_3^-$ (being a ruthenium(II) complex) may be expected to be capable of stabilizing the additional negative charge. It is also probable that under high CO pressure $Ru(CO)_3I_3^-$ is in equilibrium with neutral $Ru(CO)_4I_2$ (eq. 4), a complex expected to be much more

$$Ru(CO)_3I_3^- + CO \rightleftharpoons Ru(CO)_4I_2 + I^- \qquad (4)$$

susceptible to hydride attack. However, a catalytic scheme based on this direct interaction of $HRu_3(CO)_{11}^-$ with $Ru(CO)_3I_3^-$ would be expected to show a higher catalyst concentration dependence than is observed, and such a reaction involving $Ru(CO)_4I_2$ should show inverse iodide dependence.

The large pressure dependence of this system suggested the possibility of cluster fragmentation as an integral part of the catalytic process. Reaction of $HRu_3(CO)_{11}^-$ under CO pressure is expected to produce the more reactive mononuclear hydride $HRu(CO)_4^-$ [24] (eq. 5). Although this declusterification has not been directly

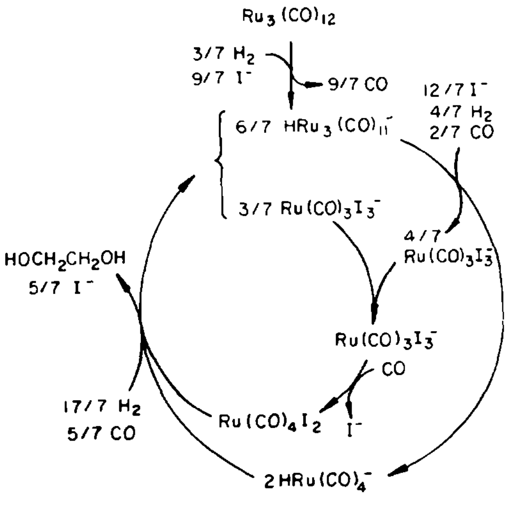
$$HRu_3(CO)_{11}^- + 3\ CO \rightleftharpoons HRu(CO)_4^- + 2\ Ru(CO)_5 \qquad (5)$$

observed (the equilibrium apparently lies far toward the cluster), the iron analog is known to fragment under CO pressure [25]. Any $Ru(CO)_5$ produced by cluster fragmentation will rapidly react with H_2 and I^- as in eq. 2 to produce more $HRu_3(CO)_{11}^-$ and $Ru(CO)_3I_3^-$. The net conversion of $HRu_3(CO)_{11}^-$ can then be represented by eq. 6. It can be seen that this reaction would contribute positive

$$HRu_3(CO)_{11}^- + \tfrac{2}{3}H_2 + \tfrac{1}{3}CO + 2\ I^- \rightarrow \tfrac{7}{3}HRu(CO)_4^- + \tfrac{2}{3}Ru(CO)_3I_3^- \qquad (6)$$

pressure and iodide concentration dependences to the catalytic process.

SCHEME 2



As suggested above, conversion of $Ru(CO)_3I_3^-$ to $Ru(CO)_4I_2$ by eq. 4 will produce a complex which should be more susceptible to nucleophilic attack. (This reaction will also provide additional pressure dependence to the catalytic process.) The interaction of $HRu(CO)_4^-$ with $Ru(CO)_4I_2$ could therefore be involved in the catalytic process, and a cycle based on this chemistry is presented in Scheme 2.

Transformation of $Ru_3(CO)_{12}$ catalyst precursor to the stable mixture of $HRu_3(CO)_{11}^-$ and $Ru(CO)_3I_3^-$ by eq. 2 provides entrance to the cycle. The $HRu_3(CO)_{11}^-$ is partially converted to additional $Ru(CO)_3I_3^-$ and to $HRu(CO)_4^-$ by the reaction of eq. 6, a process having a high dependence on iodide concentration. Nevertheless, this dependence is lowered for the overall process by the conversion of $Ru(CO)_3I_3^-$ to $Ru(CO)_4I_2$, a step with inverse iodide dependence. The interaction of $HRu(CO)_4^-$ with $Ru(CO)_4I_2$, or a step immediately following, could be the rate-determining step in the catalytic process. This would provide concentration dependences roughly in agreement with those observed, particularly if additional H_2 and/or CO is involved in this step, as might be expected. The predicted dependence on iodide concentration would be less than first-order (observed 0.45), and that on total pressure substantially above second-order and perhaps greater than third-order (observed 3.8). The dependence on total catalyst concentration might be predicted from this scheme to be in the vicinity of second-order, but this simple scheme does not include the inhibition pathways of higher order in catalyst components which are indicated by the stoichiometry studies described above. The dependence on catalyst concentration actually expected should then be somewhat less than second-order (observed 1.3).

If the hypothesis presented in Scheme 2 is valid, then neither $Ru(CO)_3I_3^-$ nor $HRu_3(CO)_{11}^-$ alone (in the absence of promoter) should possess catalytic activity for glycol formation, which is observed to be the case. Even in the presence of added iodide, $Ru(CO)_3I_3^-$ is inactive as would be predicted. Scheme 2 may be used to explain the observation that $HRu_3(CO)_{11}^-$ produces glycol (at a low rate) when iodide is present (Table 5, no. 7), since this complex may be fragmented to both $HRu(CO)_4^-$ and $Ru(CO)_3I_3^-$. This scheme also suggests a reason for the relatively poor performance of hydroxylic compounds as solvents for this system. It is known that $HRu(CO)_4^-$ is reactive toward water and alcohols [24], producing H_2 and $HRu_3(CO)_{11}^-$. Thus one of the important catalytic intermediates in this system could be destroyed by such a reaction before it can carry out productive catalysis.

10. Model studies

According to Scheme 2, the rate-determining process takes place quite early in the product-forming sequence. Kinetic data will therefore be of limited value in outlining the pathway to the organic products. Nevertheless, investigations of the chemistry of $PPN[HRu(CO)_4]$ and $Ru(CO)_4I_2$ are beginning to cast some light on at least the early stages of CO reduction (PPN = bis(triphenylphosphine)iminium). These complexes are found to react rapidly at room temperature (1 atm N_2), but no organic products can be detected; the product mixture contains $Ru(CO)_3I_3^-$ and $HRu_3(CO)_{11}^-$ as well as other unidentified complexes. There was no evidence of a metal formyl complex, although such a complex might be expected to be formed initially. The reaction between $Ru(CO)_4I_2$ and $PPN[DRu(CO)_4]$ is quite rapid even at −60°C. The reaction was followed by ^2H NMR at this temperature, but no signals assignable to a metal formyl complex were detected. An apparent formyl complex was immediately generated from $Ru(CO)_4I_2$ by reaction with $LiDB(C_2H_5)_3$ at −60°C, but it decomposed very rapidly. This result indicates that it may be impossible to observe such a formyl product from the reaction of $HRu(CO)_4^-$ because of the rapid rate of its decomposition.

Reactions were then carried out between PPN[$HRu(CO)_4$] and a suitable model for $Ru(CO)_4I_2$, the rhenium complex $[(C_5H_5)Re(CO)_2(NO)]PF_6$, which is known to produce a relatively stable formyl complex upon reduction with boron hydrides [26–28]. Although the rhenium complex is cationic, comparison of its ν(CO) values (2105, 2049 cm^{-1}) [29] with those of $Ru(CO)_4I_2$ (2161m, 2107vs, 2096s, 2066s cm^{-1}) [30] suggests that the carbonyl ligands in the two complexes should be similar in their susceptibility to attack by nucleophiles. The rhenium complex is found to react rapidly with $HRu(CO)_4^-$ at room temperature [31], and the characteristic formyl proton resonance of $(C_5H_5)Re(CO)(NO)(CHO)$ [26–28] is observed in the product mixture. Similar results were found when the deuterated analog was observed by ^2H NMR. The other major products of the reaction are $(C_5H_5)Re(CO)(NO)H$ and $HRu_3(CO)_{11}^-$; the yield of the formyl product is generally 20–30 percent. A reaction of the stoichiometry given in eq. 7 is suggested by these results.

$$3HRu(CO)_4^- + 2(C_5H_5)Re(CO)_2(NO)^+ \rightarrow HRu_3(CO)_{11}^- + (C_5H_5)Re(CO)(NO)(CHO) + CO \qquad (7)$$

The reaction of eq. 7 is the first production of a metal formyl complex known to us which involves intermolecular hydride transfer from a metal hydride which is presumed to be regenerable from H_2 under catalytic conditions. This reaction provides a plausible model for the interaction of $HRu(CO)_4^-$ with $Ru(CO)_4I_2$ during catalysis, and suggests a possible role for the second equivalent of $HRu(CO)_4^-$ which the kinetics indicate to be involved in the process. Since the $Ru(CO)_4$ fragment which would remain after hydride transfer apparently reacts with $HRu(CO)_4^-$ to be converted, eventually, to $HRu_3(CO)_{11}^-$, it appears possible that the second $HRu(CO)_4^-$ ion may be involved in the catalytic system in a similar trapping role (eq. 8). The details of this process can perhaps be investigated in the model reaction of eq. 7.

$$2\,HRu(CO)_4^- + Ru(CO)_4I_2 \rightarrow HRu_2(CO)_8^- + Ru(CO)_3I_2(CHO)^- \qquad (8)$$

Since the hydride transfer process appears to be rapid at room temperature, it may not be the rate-limiting step in the catalytic process. It is possible that a subsequent step involving further reaction of the formyl complex with H_2 or CO could be a slower process. It is interesting to consider the possibility that reaction of the formyl complex in eq. 8 with CO or H_2 could cause reductive elimination of ICHO, formyl iodide, which could act as a formyl transfer reagent or be reduced to ICH_2OH, iodomethanol. However, the observed products (Section 3) are typical of other CO hydrogenation systems, and are those expected of a reaction proceeding through aldehyde intermediates. As described above, the glycol acetals of formaldehyde, glycolaldehyde, and acetaldehyde are observed as minor products in this system; organic iodides have not been detected as products. Nevertheless, the possibility remains that elimination processes involving an iodide ligand may be involved, and such reactions are under further investigation in this catalytic process and related systems.

Conclusions

It is evident that ionic iodide promoters have a profound effect on the activity, selectivity and probable mechanism of CO reduction by ruthenium catalysts. These promoters cause formation within the system of an oxidized complex, $Ru(CO)_3I_3^-$, and a reduced species, $HRu_3(CO)_{11}^-$. Further reactions under catalytic conditions may transform these species into even more reactive electrophilic and nucleophilic complexes, respectively. This separation of active centers induced by iodide ion (as well as H_2/CO) is perhaps responsible for the relatively high activity of the system. Such charge separation is expected to be difficult to achieve in a single mononuclear complex, or even in a metal cluster with delocalized charge.

If Scheme 2 is valid, the importance of a metal cluster in this system (apart from its role as the precursor of a more reactive mononuclear species) may be questioned. There are, however, at least two ways in which a metal cluster may be involved in the catalytic process. First, it is possible that a cluster could participate in product formation by reaction, for example, with a reactive intermediate such as formyl iodide. A metal cluster could thus be influential in determining the product selectivity of the system. Second, metal–metal bond formation could be an important component of the hydride transfer process, as shown in eq. 8. Formation of a strong metal–metal bond in this reaction would provide an important thermodynamic driving force in the formyl generation step.

The general outline depicted by Scheme 2 appears to be consistent with all of our observations made on this complex catalytic system. Although it is possible that other pathways could be written which would also fit the experimental data, the plausibility of the scheme has been demonstrated by the reactions of $HRu(CO)_4^-$ with electrophilic carbonyl complexes. Details of product-forming processes occurring under catalytic conditions may never be known with certainty because of the difficulty of their direct observation. It is in this regard that organometallic chemistry can be very useful as a tool in investigating the reactivities of possible intermediates and models for such complexes.

Experimental

The complexes $PPN[HRu_3(CO)_{11}]$ [32], $PPN[Ru(CO)_3I_3]$ [33], $Ru(CO)_4I_2$ [30], $PPN[HRu(CO)_4]$ [24], $(PPN)_2[Ru_6C(CO)_{16}]$ [20], and $[C_5H_5)Re(CO)_2(NO)]PF_6$ [29] were prepared using literature procedures or modifications thereof. $Ru_3(CO)_{12}$ was obtained from Strem Chemicals, Inc. Sulfolane (Phillips) and *N*-methylpyrrolidone (Burdick and Jackson) were obtained commercially. Tri-n-propylphosphine oxide was prepared by American Cyanamid, Inc. 18-Crown-6 was prepared at Union Carbide under the supervision of Dr. Fedor Poppelsdorf.

High-pressure infrared spectra were recorded by Dr. Jack Jamerson on a Digilab FTS-10 spectrometer, using a high-pressure infrared cell described elsewhere [34]. Catalytic experiments were carried out in an Autoclave Engineers stainless steel autoclave of 125 ml nominal volume, stirred by a magnetically coupled turbine. The catalyst mixture was charged to the reactor, and the system was purged and pressurized with approximately 2 MPa of CO. The autoclave was then heated to the desired reaction temperature before admitting pre-mixed H_2/CO at the specified pressure. As gas was consumed by reaction, incremental amounts were added to maintain the pressure within about ±3.4 MPa of the specified pressure. Reactions were normally allowed to proceed until a standard amount of H_2/CO had been consumed; thus amounts of products formed in most reactions are similar even though reaction times may be different. The reactor was then cooled immediately with circulating cold water. Product amounts were determined by vapor-phase chromatography using internal standard methods. Reported rates are calculated based on product amounts and reaction times.

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