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Roles of metal carbonyl complexes in the homogeneous hydrogenation of carbon monoxide

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Abstract

Homogeneous catalytic systems for converting carbon monoxide and hydrogen to organic products are of possible commercial interest because of their potential for high product selectivity. Useful products from these reactions are compounds such as ethylene glycol, ethanol and higher alcohols, and acetic acid. Catalysts based on three metals, Co, Rh, and Ru, have been found to have the highest activity for these reactions. Recent developments on homogeneous catalyst systems based on these metals and bimetallic derivatives of these systems are briefly reviewed. The apparent importance of ionic catalytic intermediates is noted, and possible roles for basic promoters are presented.

Introduction

The use of metal carbonyls as catalysts is an active field, and there are many reactions catalyzed by these complexes in solution. The most fundamental of these reactions is the hydrogenation of carbon monoxide, since CO is the basic ligand in metal carbonyl chemistry and hydride is the simplest ligand in coordination chemistry. Nevertheless, many years passed after the discovery by Mond of the first binary metal carbonyl before homogeneous catalysts were discovered to hydrogenate CO. Many heterogeneous catalysts for CO reduction had been discovered and developed in the meantime. This reaction remained strictly within the area of heterogeneous catalysis until the early 1950's when work at DuPont [1] showed that cobalt catalysts, apparently homogeneous, could convert mixtures of CO and H_2 to products including alcohols and glycols. Reported reaction conditions were very severe, in the range of 3000 atm and 290 ° C, perhaps explaining why the reaction was not discovered earlier. Productivities were low, and it appears that mixtures of products were formed. Probably because of these limitations, this chemistry was not further explored until the 1970's when renewed interest in the conversion of CO to chemicals and fuels was sparked by the oil shortages.

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Table 1

Some representative reaction data for experiments with Co, Rh, and Ru catalysts

No.	Catalyst, additives, solvent	Pressure (atm.)	Temperature (°C)	MeOH/EG, (Molar)	TF [a] (h^{-1})	Ref.
1	Rh, cesium benzoate, amine, 18-crown-6	1020	280	0.64	308	3
2	Rh, cesium acetate, amine, 18-crown-6	544	270	0.68	39	3
3	Rh, *N*-methylpyrrolidone (NMP)	2000	300	0.64	3640	26
4	$HCo(CO)_4$, 1,4-dioxane	268	214	–	2.7	4
5	$HCo(CO)_4$, tetraglyme	1361	230	5.2	22	5
6	$Ru_3(CO)_{12}$, ethanol	340	260	–	23	7
7	$Ru_3(CO)_{12}$, KI, NMP	1020	240	8	458	8
8	Ru, *o*-phenylenediamine, tetraglyme	440	250	1.3	61	16
9	Ru, benzimidazole, NMP	500	240	3	304	17
10	$Ru_3(CO)_{12}$, NaI, $YbCl_3$, K_2CO_3, NMP	850	230	–	260	20
11	Rh, *N*-methylimidazole, THF	550	240	0.8	57	22
12	Rh, $P(i\text{-}Pr)_3$, NMP	450	220	1.4	11	23

[a] Turnover frequency, moles organic products/mole catalyst/hour.

At that time, work at Union Carbide [2] led to the discovery that rhodium complexes in solution could more effectively catalyze the reaction between CO and hydrogen, producing ethylene glycol and methanol as the major products. Conditions required were not as severe as those earlier reported for the cobalt catalysts, and further work led to improved catalysts operating under milder conditions (see Table 1, entries 1–3. It is interesting to note the large range of activity for these three experiments with very similar catalyst systems, obtained under different conditions of temperature and pressure. These examples point out the necessity of considering reaction conditions when comparing activities among these CO hydrogenation catalysts.)

This more extensive work established several principles which still largely apply to homogeneous CO hydrogenation catalysts. Firstly, it showed that homogeneous metal carbonyl catalysts can indeed hydrogenate CO. Secondly, the products of these reactions are almost entirely oxygenates, not the paraffins/olefins which are often obtained from heterogeneous catalysts. Thirdly, ethylene glycol and other polyols are significant products; these compounds are not produced by heterogeneous catalysts.

Some questions were also raised by these results. The generality of this reaction was unknown. Could other metal carbonyls also catalyze this conversion under the appropriate conditions? Metal clusters were observed in rhodium catalyst solutions. What was their role and are they essential components of such a catalyst system? Questions also arose concerning the mechanism of the reaction. How might it resemble or differ from mechanisms proposed for heterogeneous catalysts?

The remainder of this discussion will address these questions based on our work and that of others which has been conducted in the last few years. I will only briefly discuss, for background purposes, work which has appeared in a review of this area [3].

Mechanistic studies with cobalt catalysts

Work done at several laboratories [4,5] re-investigated the homogeneous cobalt catalyst and found that this system could be operated under milder conditions

(Table 1, entries 4 and 5). These studies led to several conclusions concerning this particular system. It was evident from spectroscopic studies that the mononuclear cobalt hydride $HCo(CO)_4$ was the major species present during catalysis. Kinetic studies showed that the reaction was unimolecular in cobalt, supporting the involvement of a mononuclear cobalt complex and an intramolecular process. The primary products were methanol, ethylene glycol, and methyl formate. Ethanol was observed as a secondary product, via methanol homologation. A plausible mechanism for the conversion of CO/H_2 to products was outlined, based on observed kinetic responses to different variables. Apparently, the first step involved the intramolecular hydride migration from the cobalt center to a carbonyl ligand to produce a formyl ligand. Further addition of hydrogen to this complex could then generate a formaldehyde-like intermediate.

The further reactions of this intermediate appear to be those of formaldehyde hydrogenation and hydroformylation [3,4,5]. This type of scheme is likely to apply generally to all of the systems studied to the present.

Unpromoted ruthenium catalysts

In the search for new catalysts for the homogeneous hydrogenation of CO, it was found [6,7] that a simple metal carbonyl, ruthenium carbonyl, could also hydrogenate CO (Table 1, entry 6). Many properties of this catalyst were similar to those of the cobalt catalyst. A mononuclear metal carbonyl complex, $Ru(CO)_5$, was observed in catalytic solutions. Kinetic evidence indicated that a mononuclear catalyst, $H_2Ru(CO)_4$, was probably involved. No paraffins or olefins were formed; the primary products were methanol and methyl formate. All of the experimental evidence supports a simple intramolecular mechanism for CO hydrogenation, similar to that proposed for cobalt catalysts.

One difference was observed between the cobalt and ruthenium catalysts; the Ru system gave essentially no ethylene glycol. This is probably because of the preferred direction of insertion of a formaldehyde-like intermediate into the metal–hydride bond, leading to an intermediate which can undergo hydrogenation but no hydroformylation.

Halide-promoted ruthenium catalysts

Further study led us to the development of an improved ruthenium-based catalyst for CO hydrogenation, which will be the described later. Searches for other homogeneous catalysts for CO hydrogenation have been only partially successful; some reactions have been found for complexes of iridium and rhenium, but the activity of these systems is very much lower than the activity found for cobalt, rhodium, and ruthenium catalysts. It is work on catalysts of these three metals which has led to our present understanding of the catalytic process, and which will be the topic of this discussion.

Our encouraging results with ruthenium catalysts, much less expensive than rhodium, led to the discovery that an ionic halide promoter had very significant beneficial effects on the catalyst system (Table 1, entry 7). In fact, these promoters appeared to change the behavior of the system entirely [8].

These results encouraged us to investigate further the chemistry of the catalytic species, with the expectation that further improving our understanding of the chemistry could aid in improving the catalyst system. We first examined the interaction of iodide salts with $Ru_3(CO)_{12}$. A reaction occurs at room temperature, which goes somewhat faster in refluxing THF, yielding a ruthenium iodide cluster, $[Ru_3(CO)_9I]^-$, which has recently been characterized by an X-ray crystal structure determination [9].

Although this reaction is quite interesting, it is chemistry which apparently occurs very early in the catalytic process. Other complexes become more important under actual catalytic conditions. We have found that the $[Ru_3(CO)_9I]^-$ cluster reacts rapidly with H_2/CO to give two products, $[HRu_3(CO)_{11}]^-$ and $[Ru(CO)_3I_3]^-$, along with some $Ru_3(CO)_{12}$. If $Ru_3(CO)_{12}$ itself is treated with H_2/CO or H_2 alone in the presence of sufficient iodide salt, the two complexes alone can be produced. Indeed spectroscopic studies of actual catalytic solutions after a reaction or during catalysis (by high-pressure infrared spectroscopy) show these two complexes as essentially the only species present. They are obviously quite stable and must be regarded as being catalytically important, if not active themselves.

Some of our studies have been directed toward the question of how these complexes are formed. We have found that $Ru_3(CO)_{12}$ will react rapidly with H_2 in the presence of a base such as Et_3N to form $[HRu_3(CO)_{11}]^-$. In fact, a phosphine oxide ($pK_{BH^+} \cong -0.5$) is a sufficiently strong base to promote this reaction [10]:

$$Ru_3(CO)_{12} + R_3PO + H_2 \rightleftarrows R_3POH[HRu_3(CO)_{11}] + CO \tag{1}$$

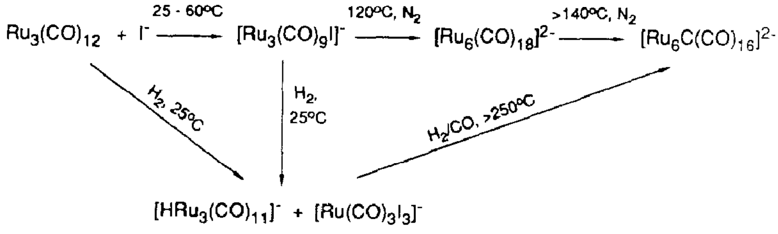
The function of the base must be to stabilize the proton generated by the formation of the hydride cluster and prevent it from reacting with the hydride.

We have also shown that acids react with $Ru_3(CO)_{12}$ in the presence of iodide anions to form $[Ru(CO)_3I_3]^-$:

$$\tfrac{1}{3}Ru_3(CO)_{12} + 2HI + I^- \rightleftarrows [Ru(CO)_3I_3]^- + H_2 + CO \tag{2}$$

Thus the protons formed in the first reaction can apparently react with other ruthenium species in solution to produce the oxidized ruthenium product in the catalytic system.

Further chemistry occurs with the $[Ru_3(CO)_9I]^-$ cluster upon heating more strongly (Scheme 1). It can be transformed by an apparent reduction process to $[Ru_6(CO)_{18}]^{2-}$, and upon further heating, this complex is converted to the carbido cluster. These complexes appear not to be important in the catalytic chemistry,



Scheme 1

unless the conditions become too severe; their formation appears to represent catalyst deactivation.

The two ruthenium complexes observed in solution, $[HRu_3(CO)_{11}]^-$ and $[Ru(CO)_3I_3]^-$, can be prepared in the laboratory, and we have found that neither complex alone has very much catalytic activity for syngas conversion. However, a mixture of the two complexes does have the expected catalytic activity. In fact, in inert solvents the optimum activity was observed with a 2/1 mixture of the two complexes, which is the same ratio in which they are normally formed.

An explanation for the involvement of these compounds which seemed plausible involved the anionic hydride cluster as a hydride source. However, the kinetics did not support such a role for this complex. A more probable role for this hydride cluster is to act as a precursor of an even more reactive metal hydride complex, $[HRu(CO)_4]^-$:

$$[HRu_3(CO)_{11}]^- + 3CO \rightleftarrows [HRu(CO)_4]^- + 2Ru(CO)_5 \quad (3)$$

The $[Ru(CO)_3I_3]^-$ complex could also be involved in an equilibrium under catalytic conditions, leading to a complex even more susceptible to attack by a hydride:

$$[Ru(CO)_3I_3]^- + CO \rightleftarrows Ru(CO)_4I_2 + I^- \quad (4)$$

Reaction of these two complexes in solution could then be envisioned to produce an intermediate Ru formyl complex which could undergo further hydrogenation leading to the observed products. In fact, such a reaction scheme can fit very well with the observed reaction kinetics.

Further support for this pathway was developed in laboratory studies of the reactivity of $[HRu(CO)_4]^-$. This is quite a powerful hydride donor, considering the fact that it is a metal carbonyl hydride. It reacts with methanol at room temperature, decomposing to $[HRu_3(CO)_{11}]^-$ [11]. We found that this hydride does react with $Ru(CO)_4I_2$ at room temperature or below; however, a Ru formyl complex if formed was too unstable to be observed. A model compound, $[CpRe(CO)_2(NO)]^+$, was chosen because its carbonyl ligands should resemble those in $Ru(CO)_4I_2$, based on a correlation of the CO stretching force constants with reactivity toward nucleophiles. This reaction does indeed proceed very well, and the Re formyl complex can be observed in about a 30% yield [12].

These studies have shown that a metal formyl can be generated by intermolecular hydride transfer from a metal hydride apparently regenerable from H_2. Previous mechanisms for CO hydrogenation relied upon intramolecular H atom migration to a carbonyl.

Ruthenium/halide catalysts in phosphine oxide solvents

A modification of this system which gave quite interesting results is obtained by conducting the catalytic reaction in a phosphine oxide solvent [10]. This provides a somewhat basic medium, and the phosphine oxide apparently becomes involved in the reaction. It can do so by acting with hydrogen as a reducing agent, as shown in eq. 1 above. Catalytic solutions obtained from $Ru_3(CO)_{12}$ and KI alone in tri-npropylphosphine oxide solvent show less than the normal amount of $[Ru(CO)_3I_3]^-$, presumably because of the equilibrium:

$$[Ru(CO)_3I_3]^- + 2R_3PO + H_2 \rightleftarrows Ru^0 + 2[R_3POH]I + I^- \tag{5}$$

(Any Ru^0 species formed, such as $Ru_3(CO)_{12}$, could be readily converted to $[HRu_3(CO)_{11}]^-$ by the process of eq. 1.)

Addition of acid (I_2 or HI) adjusts the ratio of $[HRu_3(CO)_{11}]^-$ to $[Ru(CO)_3I_3]^-$ toward the optimum 2/1 ratio and thereby increases the activity of the catalytic system [10]. A second effect observed was that the selectivity toward ethanol also increased very significantly upon the addition of the acid. Apparently the phosphine oxide provides a conjugate acid which is not a sufficiently strong acid to destroy the ruthenium hydrides involved in the catalytic CO hydrogenation, yet is a sufficiently strong acid to become involved in acid-catalyzed conversions involved in methanol homologation to ethanol.

Ruthenium–rhodium catalysts

We have discovered another modification of this catalytic system which is more selective for the production of ethylene glycol [13]. This system was found by the addition of rhodium complexes to the ruthenium system. As increasing amounts of $Rh(CO)_2(acac)$ are added, the selectivity to glycol increases, although the total activity remains essentially unchanged.

Our high-pressure IR studies on this system showed that the same ruthenium complexes are present as in the standard Ru/I^- system. The rhodium is observed in the form of $[Rh(CO)_2I_2]^-$; no rhodium or ruthenium/rhodium clusters were observed.

The behavior of this system could possibly be due to formation of a formaldehyde intermediate by a ruthenium catalyst, followed by further conversion to products by a rhodium catalyst. It could also be explained by an intermolecular hydride transfer process involving both ruthenium and rhodium complexes. The ruthenium hydride can now transfer H^- to either a Ru carbonyl or a Rh carbonyl, generating either a Ru formyl or a Rh formyl. The latter intermediate can proceed to products with a selectivity more characteristic of a Rh catalyst.

This combined Ru/Rh catalytic system appears to have many advantages and could become a practical system if the raw material economics would justify further development.

In the remainder of this discussion, I intend to review some of the more significant and interesting advances in the area of homogeneous CO hydrogenation. Much of the recent work which has been published in this area has come from companies participating in the Japanese C1 chemistry project which was active from 1980 to 1987. This was a joint funding venture of the Agency of Industrial Science & Technology and MITI.

Recent developments

Ruthenium catalysts

The postulated intermediates formaldehyde and glycolaldehyde have been detected in reactions of Ru/halide catalysts [14]. At low temperatures, the rate-determining step is postulated to be the formation of formaldehyde in this system, while at higher temperatures (> 180 °C) formaldehyde exists at a level approaching the equilibrium concentration. It was noted that addition of a rhodium complex to the catalyst system gives an even higher selectivity to glycoaldehyde.

The activity of the Ru-halide system was found to be somewhat enhanced for ethylene glycol formation by addition of a rhenium carbonyl compound [15]. High-pressure infrared studies showed $[HRu_3(CO)_{11}]^-$ and an unidentified rhenium carbonyl complex which is thought to be a rhenium carbonyl halide anion. No ruthenium–rhenium clusters were observed.

The change observed upon addition of the rhenium complex is sufficiently small that it is not possible to determine whether this is a true activity increase or the result of an altered selectivity. It is possible that the synergistic behavior observed is the result of a transfer of hydride from a Ru complex to a Re carbonyl complex.

The use of *o*-phenylenediamine as a promoter for ruthenium catalysts has been described [16]. These results are interesting, since no halide was used, and significant rates and selectivities to ethylene glycol were reported (Table 1, entry 8). The *meta*- and *para*-isomers of phenylenediamine were reported to have no promoter effect.

Later reports have indicated that benzimidazole and related compounds are effective promoters for the ruthenium catalyst. It has become evident from more recent work that *o*-phenylenediamine can be converted under these catalytic conditions into benzimidazole, which may be the catalytically important derivative. Thus, imidazoles, particularly benzimidazole, were reported to be good promoters for ruthenium catalysts [17] (Table 1, entry 9). The imidazole structure is essential to this behavior; other *N*-heterocycles are reportedly not active.

N-Alkyl substituted benzimidazoles are reported to be even better promoters for the Ru catalyst [18]. Studies of this system have indicated that the only ruthenium complex observed after catalysis is the $[HRu_3(CO)_{11}]^-$ cluster. Under catalytic conditions, the complexes $Ru(CO)_5$ and $Ru(CO)_4L$ ($L =$ the benzimidazole) were observed in addition to the cluster.

The equilibrium constant for the reaction below has been studied with various substituted imidazoles at 20 °C in THF:

$$Ru(CO)_5 + \text{Imid} \rightleftarrows Ru(CO)_4(\text{Imid}) + CO \qquad (6)$$

The equilibrium constant for this reaction was found to fall within the range of 0.1–0.4 for the better imidazole promoters; K was less than 0.01 for other amines such as pyridine and *N*-methylmorpholine. The magnitude of this equilibrium constant was observed to correlate with the rate of ethylene glycol formation for various substituted benzimidazoles studied. Therefore it was proposed that the unique promoting effect of imidazoles on ethylene glycol formation is attributable to their high coordination abilities to the Ru carbonyl complex. It is suggested that a species such as $H_2Ru(CO)_3L$ is the active species for ethylene glycol formation, and that this and other neutral species are the most important species in solution.

Another possibility which should be considered involves ionic intermediates and acid-base chemistry. The fact that $[HRu_3(CO)_{11}]^-$ is observed under these reaction conditions must mean that the following equilibrium is operating:

$$H_2 + 3Ru(CO)_5 + \text{Imid} \rightleftarrows [HRu_3(CO)_{11}]^- + [\text{ImidH}]^+ + 4\,CO \qquad (7)$$

$$pK_{BH^+} = 5\text{–}7$$

The hydride cluster is the predominant ruthenium species in solution: $[HRu_3(CO)_{11}]^-/Ru(CO)_5/Ru(CO)_4L \cong 70/19/12$ mol% in a typical run. Thus, nearly 90% of the Ru present is in this cluster. The protonated imidazole is relatively acidic, and could serve as a proton source for various ruthenium complexes in solution, such as $Ru(CO)_4L$. Protonation of such a species could generate a cationic complex which would be readily attacked by a nucleophilic hydride, with possible formation of a formyl intermediate. Such a scheme seems to be consistent with the reported experimental observations, including the correlation of ethylene glycol activity with the coordinating ability of the imidazole.

The imidazole-promoted ruthenium systems are reported to be quite active and selective for the production of ethylene glycol. However, disadvantages appear to be the relative instability of these promoters under the reaction conditions and the difficulty in separating the promoter and its decomposition products from the desired reaction products [19].

We have noted that the use of lanthanide complexes as additives to a Ru/halide system significantly increases the activity of the system, particularly for methanol formation [20]. In some cases, the activity was doubled or tripled by addition of these promoters, although the selectivity for ethylene glycol was greatly diminished (Table 1, entry 10). Further studies have shown that it is possible to alter the selectivity of these systems to allow the enhanced production of ethanol and higher alcohols.

Rhodium catalysts

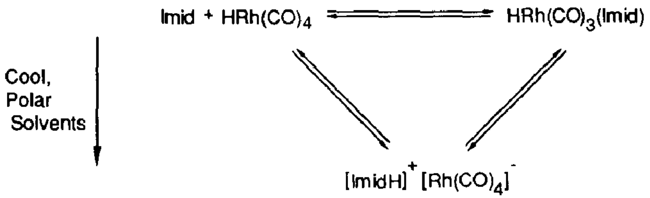
Exposure of $Rh_4(CO)_{12}$ to H_2/CO pressure in *N*-methylpyrrolidone solution gives a colorless solution of $[Rh(CO)_4]^-$, identified by high-pressure infrared spectroscopy (at 200 atm, 25 °C) [21]. Heating this solution to 200 °C causes a second complex to appear at the expense of the $[Rh(CO)_4]^-$; the solution remains colorless and there is no evidence for clusters. This reversible reaction is suggested to be a ligand substitution process leading to a neutral solvent-coordinated Rh hydride species. $PPN[Rh(CO)_4]$ in NMP shows no catalytic activity, but addition of 1-methylimidazolium *p*-toluenesulfonate gives an active catalyst.

These observations suggest that $[R_3NH][Rh(CO)_4]$ is a precursor of a hydride which is catalytically important:

$$[BH]^+[Rh(CO)_4]^- \rightleftarrows [HRh(CO)_3B] + CO \qquad (8)$$

(B = tertiary amine, amide or urea solvent)

It has been reported that the use of large amounts of imidazoles with a rhodium catalyst (100 to 500-fold excess over rhodium) gave active catalysts for CO hydrogenation [22] (Table 1, entry 11). Various other nitrogen bases were reported to provide little activity. In this system, highest activity was seen in nonpolar solvents (toluene, benzene), but low activity was reported in polar solvents (*N*,*N*′-dimethylimidazolidinone, sulfolane). High-pressure infrared studies indicated that three Rh species were present at 200 °C under 300 atm of H_2/CO. These complexes were identified as $[Rh(CO)_4]^-$, $HRh(CO)_4$, and $HRh(CO)_3L$ (L = the imidazole). The identity of the latter complex was supported by changes in its CO frequencies with changing identity of L. A correlation was reported between the activity for ethylene glycol formation and the concentration of $HRh(CO)_3L$ present. Use of a polar



Scheme 2

solvent caused most of the Rh to convert to $[Rh(CO)_4]^-$, and the activity of the system became very low. Likewise, cooling the solution converted the system into the ionic form (Scheme 2).

It is interesting to note that the basicity of the imidazole compounds thus appears to be very closely matched with that of $[Rh(CO)_4]^-$ under the catalytic conditions. Stronger bases, or the presence of polar solvents which can favor the ionic species, lead to the predominant formation of $[Rh(CO)_4]^-$ and a loss in catalytic activity. The coordinating ability of the imidazole compounds is also perhaps significant, and the imidazole-coordinated Rh compound may actually be involved in the catalytic chemistry. However, it is possible that these compounds simply stabilize the Rh and provide a source of the active Rh hydride species.

An active system for the production of ethylene glycol is based on the use of bulky alkylphosphines such as $(i\text{-}Pr)_3P$ [23] (Table 1, entry 12). The phosphine ligands are reported to significantly enhance the activity and stability of the rhodium catalyst. Phosphites, arylphosphines, and alkylphosphines with smaller cone angles decompose to form the inactive $[Rh_9P(CO)_{21}]^{2-}$ cluster, but the bulky phosphines are apparently more resistant to this decomposition. High-pressure infrared studies indicate that $[Rh(CO)_4]^-$ and $HRh(CO)_3L$ (L = phosphine) are present during catalysis. (The protonated phosphine is presumably the counterion present with the tetracarbonylrhodate anion.) The optimum P/Rh ratio for the bulky phosphines was found to be between 0.5 and 2. Other studies indicate that less bulky phosphines can be suitably employed if their concentrations are appropriately chosen [24].

The rhodium system promoted by bulky phosphines has been extensively studied and operated in a continuous pilot plant under the Japanese C1 chemistry program [19].

This recent Rh work thus indicates that compounds of the formula $HRh(CO)_nL_{(4-n)}$ (L = phosphine, imidazole, etc.), and particularly $HRh(CO)_3L$ could be the catalytically significant species present in these systems. Earlier work on hydroformylation of formaldehyde by Chan et al., of Monsanto is interesting to review in light of these studies [25]. The hydroformylation studies showed that phosphine-Rh complexes such as $HRh(CO)_2L_2$ ($L = PPh_3$) can convert formaldehyde to glycolaldehyde at conditions of 270 atm of H_2/CO pressure and 110 °C. A dissociative mechanism appears to be operative, requiring dissociation of L or CO from the Rh to allow coordination of formaldehyde, a weakly coordinating ligand; thus excess phosphine significantly retards the reaction. Addition of an amine such as Et_3N deprotonates $HRh(CO)_2L_2$:

$$HRh(CO)_2L_2 + Et_3N(+H_2/CO) \rightleftarrows [Rh(CO)_4]^- + [Rh(CO)_3L]^- \qquad (9)$$

Addition of the amine causes the rate of formaldehyde hydroformylation to increase significantly, even in the presence of excess phosphine, suggesting the importance of anionic species in catalysis. Since $[Rh(CO)_4]^-$ was shown to be relatively inert, the phosphine-substituted anion is presumed to be the important complex.

The function of the amine is apparently to provide a second, non-dissociative, route for the addition of formaldehyde:

$$[Et_3NH]^+ + [Rh(CO)_3L]^- + H_2CO \rightarrow HOCH_2Rh(CO)_3L + Et_3N \qquad (10)$$

The sodium salt of $[Rh(CO)_3L]^-$ was shown to be a much less active catalyst.

The similarity of the complexes involved in this reaction, the hydroformylation of formaldehyde, and the complexes described above which are involved in the conversion of H_2/CO (perhaps through a formaldehyde intermediate) to ethylene glycol are quite striking. The parallels suggest that much of the catalytic chemistry is quite similar, if not identical.

Conclusions

A common observation which seems to emerge from work on the most active homogeneous catalytic systems for CO hydrogenation is the prevalence of ionic complexes or the potential for forming such species. In many of these systems, the presence of a proton base of the correct basicity can enhance the activity of the various catalysts. When the basicity is closely matched with the acidity of metal hydrides involved, the base provides ready availability of both the metal hydride and the metal carbonyl anion with a readily available proton. Too strong a base will irreversibly deprotonate the carbonyl hydride, thus precluding catalytic hydrogenation activity. The availability of the active proton may be very important in the utilization of formaldehyde, a possible intermediate under the conditions commonly employed. A non-dissociative mechanism for adding formaldehyde to a catalyst species seems particularly important for this reaction, where high CO pressures would compete very effectively with weakly coordinating formaldehyde for any vacant coordination sites.

A second function of an added base may be to control the acid strength of the system, thus determining which metal complexes are present. A more basic system can favor the presence of more highly reduced complexes, while a more acidic system can lead to the production of oxidized complexes.

Although metal carbonyl clusters are observed in some of these catalytic systems, other systems appear to have equally high activity with evidence for only mononuclear catalytic intermediates. Thus, if clusters are actually involved in the catalytic interconversions, their behavior does not seem to be unique.

Although there appear to be some common themes in this catalytic chemistry, particularly with regard to a general route from a formaldehyde-like intermediate to methanol and ethylene glycol, it appears that there are several types of processes possible for the initial activation of CO. It is evident that different catalyst systems have varying characteristics, and only further knowledge of the detailed mechanisms will allow the construction of a more unified picture of these processes.

References

1 W.F. Gresham and C.E. Schweizer, U.S. Patent 2,534,018 (1950); W.F. Gresham, U.S. Patent 2,636,046; W.F. Gresham, U.K. Patent 655,237 (1951).

2 R.L. Pruett and W.E. Walker (Union Carbide Corp.), U.S. Patent 3,833,634 (1974), and many subsequent patents; see ref. 3.
3 B.D. Dombek, Adv. Catal., 32 (1983) 325.
4 H.M. Feder and J.W. Rathke, Ann. N.Y. Acad. Sci., 333 (1980) 45.
5 D.R. Fahey, J. Am. Chem. Soc., 103 (1981) 136.
6 J.S. Bradley, J. Am. Chem. Soc., 101 (1979) 7419.
7 B.D. Dombek, J. Am. Chem. Soc., 102 (1980) 6855.
8 B.D. Dombek, J. Organomet. Chem., 250 (1983) 467.
9 S.-H. Han, G.L. Geoffroy, B.D. Dombek, and A.L. Rheingold, Inorg. Chem., 27 (1988) 4355.
10 B.K. Warren and B.D. Dombek, J. Catal., 79 (1983) 334.
11 H.W. Walker and P.C. Ford, J. Organomet. Chem., 214 (1981) C43.
12 B.D. Dombek and A.M. Harrison, J. Am. Chem. Soc., 105 (1983) 2485.
13 B.D. Dombek, Organometallics, 4 (1985) 1707.
14 M. Ishino, M. Tamura, T. Deguchi, and S. Nakamura, J. Catal., 105 (1987) 478.
15 M. Tanaka, Y. Kiso, and K. Saeki, J. Organomet. Chem., 329 (1987) 99.
16 S. Nakamura, T. Deguchi, T. Takano, and M. Ishino, Japanese Pat. Appl. 1984-73,532.
17 Y. Kiso and K. Saeki, J. Organomet. Chem., 309 (1986) C26.
18 Y. Kiso, K. Saeki, T. Hayashi, M. Tanaka, and Y. Matsunaga, J. Organomet. Chem., 335 (1987) C27.
19 S. Nakamura, Paper I-9, Sixth Intern. Symp. Homogeneous Catalysis, Vancouver, B.C., 1988.
20 B.D. Dombek, U.S. Patent 4,590,216, 1986.
21 E. Watanabe, K. Murayama, Y. Hara, Y. Kobayashi, K. Wada, and T. Onoda, Chem. Commun., (1986) 227.
22 Y. Kiso, M. Tanaka, T. Hayashi, and K. Saeki, J. Organomet. Chem., 322 (1987) C32.
23 M. Tamura, M. Ishino, T. Deguchi, and S. Nakamura, J. Organomet. Chem., 312 (1986) C75.
24 H. Tanaka, Y. Hara, E. Watanabe, K. Wada, and T. Onoda, J. Organomet. Chem., 312 (1986) C71.
25 A.S.C. Chan, W.E. Carroll, and D.E. Willis, J. Mol. Catal., 19 (1983) 377.
26 T. Masuda, K. Murata, T. Kobayashi, and A. Matsuda, Bull. Chem. Soc. Jpn. 59 (1986) 2349.