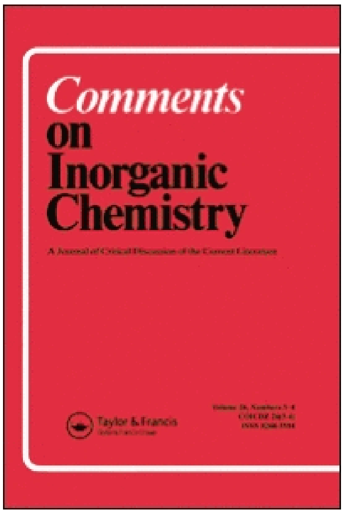

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Oxidation of Carbon Monoxide by Metal Ions and Homogeneous Catalysis of the Water Gas Shift Reaction and Related Processes

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Oxidation of Carbon Monoxide by Metal Ions and Homogeneous Catalysis of the Water Gas Shift Reaction and Related Processes

A variety of metal ions and complexes oxidize CO in aqueous solution through mechanisms that differ in detail but have in common the involvement of an intermediate hydroxycarbonyl complex (MCOOH). Such oxidation reactions can also be incorporated into various catalytic cycles including the homogeneously catalyzed water gas shift reaction.

Introduction

Early examples of the homogeneous oxidation of CO in aqueous solution are provided by the results of studies reported in 1961 on the oxidation of CO by mercury(II) and silver(I) according to Eq. 1 and 2, respectively.[1,2]

$$CO + 2Hg^{2+} + H_2O \rightarrow CO_2 + Hg_2^{2+} + 2H^+ \qquad (1)$$

$$CO + 2Ag(NH_3)_2^+ + 2H_2O \rightarrow CO_3^{2-} + 2Ag + 4NH_4^+ \qquad (2)$$

Subsequently, many other metal ions and complexes, including those listed in Table I, have been reported to be effective oxidants for CO in aqueous solutions under relatively mild conditions.[3-7] In addition, certain complexes of metals in low oxidation states, for example cobalt(I), have been shown to be effective catalysts for the oxidation of CO by, otherwise inert, oxidants such as $Fe(CN)_6^{3-}$.[8]

This subject has continued to attract considerable interest which recently has been directed particularly at the following themes.

1) Mechanistic aspects of CO oxidation including characterization of the intermediate hydroxycarbonyl complexes.

2) The possibility of accomplishing the reverse reaction, i.e., reduction of CO_2 to CO.

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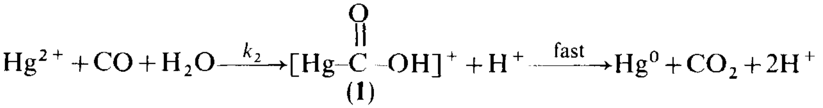
TABLE I
Metal ion oxidants for CO in aqueous solution

—	Ni(II)	Cu(II)	—
Rh(III)	Pd(II)	Ag(I)	—
—	Pt(II)	-	Hg(II)

3) The coupling of CO oxidation with the reduction of water, resulting in homogeneous catalysis of water gas shift reaction with the formation of H_2 or *in situ* utilization of the latter for hydrogenation or reduction reactions. The present Comment addresses all three of these themes.

Mechanistic Aspects of CO Oxidation

The mechanism originally proposed by Harkness and Halpern[1] for the oxidation of CO by Hg^{2+} [see Eq. (1)] is depicted by Eq. (3) and (4).

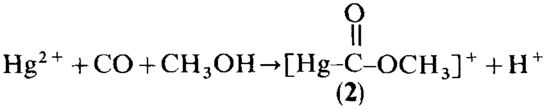


$$\mathrm{Hg^{2+} + CO + H_2O \xrightarrow{k_2} \underset{(\mathbf{1})}{[Hg{-}\overset{\overset{O}{\|}}{C}{-}OH]^+} + H^+ \xrightarrow{fast} Hg^0 + CO_2 + 2H^+} \quad (3)$$

$$\mathrm{Hg^0 + Hg^{2+} \xrightarrow{fast} Hg_2^{2+}} \quad (4)$$

$$\mathrm{2Hg^{2+} + CO + H_2O \rightarrow CO_2 + Hg_2^{2+} + 2H^+} \quad (1)$$

This mechanism is consistent with the observed rate law, $-d[\mathrm{CO}]/dt = k_2[\mathrm{Hg}^{2+}][\mathrm{CO}]$, corresponding to the activation parameters $\Delta H_2^\ddagger = 14.6$ kcal mol^{-1} and $\Delta S_2^\ddagger = -13$ cal deg^{-1} mol^{-1}. Support for the proposed intermediate $[\mathrm{HgCOOH}]^+$ (**1**), which was not detected and for which there was no precedent, was provided by the interception and characterization of the stable analog $[\mathrm{HgCOOCH_3}]^+$ (**2**) which was formed when mercury(II) salts were reacted with CO in methanol solution [see Eq. (5)].[9]



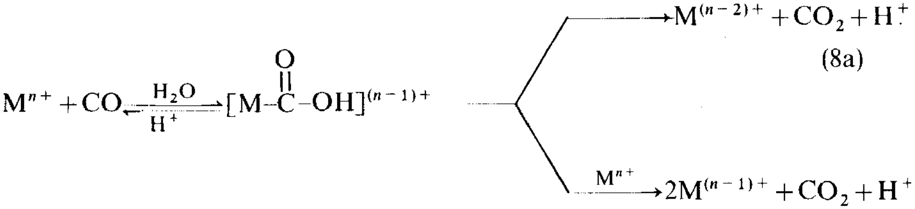
$$\mathrm{Hg^{2+} + CO + CH_3OH \rightarrow \underset{(\mathbf{2})}{[Hg{-}\overset{\overset{O}{\|}}{C}{-}OCH_3]^+} + H^+} \quad (5)$$

It seems likely that $[HgCOOH]^+$ is formed by nucleophilic attack of water on a transient mercury(II)–carbonyl complex [Eq. (6)], analogous to the mercury(II)–olefin intermediate that has been postulated in the closely related olefin oxymercuration reaction [Eq. (7)], but evidence for such intermediates is still lacking.[10]

$$Hg^{2+} + CO \rightleftharpoons [Hg(CO)]^{2+} \xrightarrow{H_2O} [HgCOOH]^+ + H^+ \qquad (6)$$

$$Hg^{2+} + CH_2{=}CH_2 \rightleftharpoons [Hg(CH_2{=}CH_2)]^{2+} \xrightarrow{H_2O} [HgCH_2CH_2OH]^+ + H^+ \qquad (7)$$

Features of the mechanism of oxidation of CO by Hg^{2+}, notably the intermediacy of a hydroxycarbonyl complex, extend to virtually all the other reactions involving the oxidation of CO by metal ions that have been investigated. A general mechanistic scheme for such reactions is depicted by Eq. (8).



$$M^{n+} + CO \underset{H^+}{\overset{H_2O}{\rightleftharpoons}} [M\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OH]^{(n-1)+} \begin{cases} \longrightarrow M^{(n-2)+} + CO_2 + H^+ & (8a) \\ \xrightarrow{M^{n+}} 2M^{(n-1)+} + CO_2 + H^+ & (8b) \end{cases}$$

The following variants of this mechanistic scheme are noteworthy:

1) Whereas the $[MCOOH]^{(n-1)+}$ intermediate can decompose directly to stable products, according to Eq. (8a), when M^{n+} is a two-electron oxidant [e.g., Hg(II) or Co(III)], a second equivalent of M^{n+} is required to effect the transformation of $[MCOOH]^{(n-1)+}$ to stable products when M^{n+} is a one-electron oxidant. This situation, depicted by Eq. (8b), is realized for the oxidation of CO by $Ag(NH_3)_2^+$ [Eq. (2)] which obeys the limiting rate law $-d[CO]/dt = k[CO][Ag(NH_3)^+]^2[OH^-]^2$.[2]

2) When the second step of the sequence encompassed by Eq. (8) is fast compared to the reverse of the first step, the reaction obeys a pH-independent rate law, i.e., $-d[CO]/dt = k[CO][M^{n+}]$. In the other limit, when the first step corresponds to a reversible pre-equilibrium, the rate law exhibits a first-order dependence on OH^- (or inverse dependence on H^+). The former situation is encountered for Hg(II), and the latter for most other metal ions, e.g., Ag(I), Ni(II), and Cu(II), whose reactivities toward CO increase markedly with increasing pH.[2-5]

3) Pathways similar to those described above for the oxidation of free CO also extend to the oxidation of coordinated CO. Thus, certain metal–carbonyl complexes are decomposed by reaction with OH^-, or H_2O, with the formation of CO_2 (or CO_3^{2-}) and a reduced metal–carbonyl. An early example of such a reaction is depicted by Eq. (9).[11,12]

$$[\mathrm{Fe(CO)_5}] \xrightarrow{\mathrm{OH^-}} \underset{(3)}{[\mathrm{Fe(CO)_4(COOH)}]^-} \xrightarrow{\mathrm{2OH^-}} \underbrace{[\mathrm{Fe(CO)_4}]^{2-} + \mathrm{H_2O}}_{\displaystyle \downarrow\!\uparrow \atop \displaystyle [\mathrm{HFe(CO)_4}]^- + \mathrm{OH^-}} + \mathrm{CO_3^{2-}} \tag{9}$$

4) The oxidation of CO may result in the formation of a hydrido–metal complex rather than in a metal complex of lower oxidation state as in the examples of Eq. (9) and (10).[13]

$$\textit{trans}\text{-}[\mathrm{Pt^{II}Cl(CO)(PEt_3)_2}]^+ + \mathrm{H_2O} \rightarrow \underset{(4)}{\textit{trans}\text{-}[\mathrm{PtCl(COOH)(PEt_3)_2}]} + \mathrm{H^+}$$

$$\rightarrow \textit{trans}\text{-}[\mathrm{Pt^{II}HCl(PEt_3)_2}] + \mathrm{CO_2} + \mathrm{H^+} \tag{10}$$

Catalytic Oxidation of CO

It seems likely, as depicted in Eq. (6), that formation of the key [MCOOH] intermediate in the oxidation of CO results from external nucleophilic attack of H_2O (or OH^-) on a coordinated CO ligand. To the extent that such prior coordination of CO is an important component of the oxidation pathway, the scope for such oxidations would appear to be constrained by the limited tendency of CO to coordinate to metal ions in high oxidation states [e.g., Co(III)]. A possible approach to get around this limitation and thereby extend the scope for metal ion oxidation of CO would be to start with a stable metal–carbonyl complex in a low (i.e., non-oxidizing) oxidation state and to oxidize the *preformed* complex to a higher oxidation state (which normally would not complex CO).

This approach was successfully applied to effect the oxidation of CO in the mixed ligand cobalt(I) complex, $[\mathrm{Co^I(CN)_2(PEt_3)_2(CO)}]^-$ (abbreviated to $[\mathrm{L}_n\mathrm{Co^I(CO)}]^-$), using $[\mathrm{Fe(CN)_6}]^{3-}$ (abbreviated to Y^{3-}) as oxidant.[8] $[\mathrm{L}_n\mathrm{Co^I(CO)}]^-$ was found to undergo two successive one-electron oxidations in aqueous solution to form the CN-bridged binuclear cobalt(III) complex $[\mathrm{YL}_n\mathrm{Co^{III}(CO)}]^{3-}$. The fate of the latter was determined by the pH of the solution in accord with the scheme of Eq. (11) where the paths corresponding to Eq. (11a), (11b), and (11c) were dominant in the pH ranges, <4.5, 4.5–11.5, and >11.5, respectively. The values of the rate constants k_{11b} and k_{11c} were determined to be 1.0×10^{-3} sec^{-1} and 3.4 sec^{-1}, respectively (at 25°).[8]

$$\begin{tikzcd}[column sep=small]
{[L_nCo^{I}(CO)]^-} \arrow[r, shift left, "Y^{3-}"] & {[L_nCo^{II}(CO)]} \arrow[l, shift left, "Y^{4-}"] \arrow[r, "Y^{3-}"] & {[YL_nCo^{III}(CO)]^{3-}} \arrow[r, "H_2O"] \arrow[d, shift right, "OH^-"'] & {[YL_nCo^{III}(H_2O)]^{3-} + CO} & \text{(11a)} \\
 & & {[YL_nCo(COOH)]^{4}} \arrow[u, shift right] \arrow[r, "k_{11b}"] \arrow[d, shift right, "OH^-"'] & {[YL_nCo^{I}]^{5-} + CO_2 + H^+} & \text{(11b)} \\
 & & {[YL_nCo^{I}(CO_2)]^{5-}} \arrow[u, shift right, "H_2O"'] \arrow[r, "k_{11c}"] & {[YL_nCo^{I}]^{5-} + CO_2} & \text{(11c)}
\end{tikzcd}$$

In the presence of excess $[Fe(CN)_6]^{3-}$, the cobalt(I) produced in reactions (11b) or (11c) is irreversibly oxidized to cobalt(III) [Eq. (12)] resulting in the overall stoichiometry of Eq. (13), according to which $[L_nCo^{I}(CO)]^-$ acts as a four-electron reducing agent.

$$[YL_nCo^{I}]^{5-} + 2Y^{3-} + H_2O \rightarrow [YL_nCo^{III}(H_2O)]^{3-} + 2Y^{4-} \qquad (12)$$

$$[L_nCo^{I}(CO)]^- + 4Y^{3-} + 2OH^- \rightarrow [YL_nCo^{III}(H_2O)]^{3-} + 3Y^{4-} + CO_2\left(\underset{H_2O}{\overset{2OH^-}{\rightleftharpoons}} CO_3^{2-}\right) \qquad (13)$$

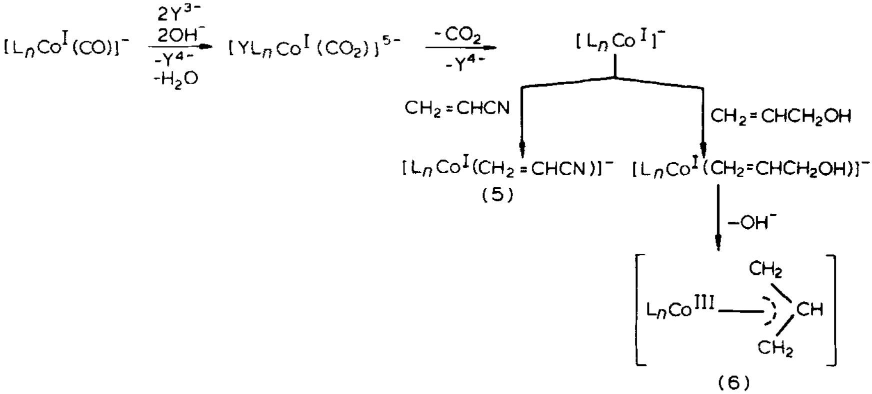
The following features of the system are of some interest:[8]

1) Under the conditions of occurrence of reaction (13), the effective reducing power of CO [as well as of cobalt(I)] in the original $[L_nCo^{I}(CO)]^-$ complex is utilized to supply electrons for the reduction of $[Fe(CN)_6]^{3-}$. As discussed later, this has important implications for the potential utilization of CO/H_2O as a reducing agent.

2) The apparent reversibility of the sequence of steps corresponding to Eq. (14), and the relatively slow decomposition rate ($k_{11c} = 3.4$ sec^{-1}) of the intermediate CO_2 complex $[YL_nCo^{I}(CO_2)]^{5-}$, identifies a pathway (which operates in this system) for the reduction of coordinated CO_2 to CO. Since CO_2 has been demonstrated to coordinate to other cobalt(I) complexes,[14] this behavior suggests a possible approach to the homogeneous catalytic reduction of CO_2, an objective of considerable current interest.

$$[YL_nCo^{III}(CO)]^{3-} \overset{OH^-}{\rightleftharpoons} [YL_nCo^{III}(COOH)]^{4-} \underset{H_2O}{\overset{OH^-}{\rightleftharpoons}} [YL_nCo^{I}(CO_2)]^{5-} \qquad (14)$$

3) Because of the effectiveness of CO_2 as a leaving group, redox pathways such as those of reaction (11) may result in the formation of 'coordinatively unsaturated' species, e.g., $[YL_nCo^I]^{5-}$ (or$[L_nCo^I]^-$ which presumably is formed readily from the latter by loss of Y^{4-}), with high affinities for a variety of ligands, notably those such as olefins which are effective in stabilizing low oxidation states. This opens up the possibility of synthetic approaches involving the 'oxidative substitution' of CO by other ligands to generate complexes that are not readily synthesized by other methods, such as (**5**) and (**6**) in the examples of Eq. (15).



(15)

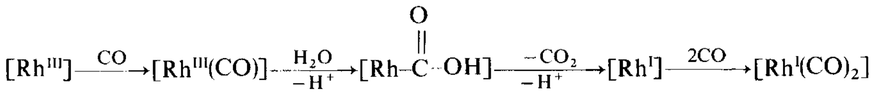
4) When the oxidation corresponding to Eq. (11b) and (11c) is conducted in the presence of an excess of CO, the coordinatively unsaturated $(L_nCo^I]^-$ product is readily trapped by coordination with CO to reform the initial $[L_nCo^I(CO)]^-$ complex. This results in establishment of a catalytic cycle for the oxidation of CO depicted schematically by Eq. (16). When $[Fe(CN)_6]^{3-}$ is the oxidant the catalytic reaction corresponds to Eq. (17).

$$\begin{tikzcd}
{[Co^I(CO)]} \arrow[r, "-2e^-"] & {[Co^{III}(CO)]} \arrow[d, "2OH^-\ (-H_2O)"] \\
{[Co^I]} \arrow[u, "{[CO]}"'] & {[Co^I(CO_2)]} \arrow[l, "-CO_2"']
\end{tikzcd} \tag{16}$$

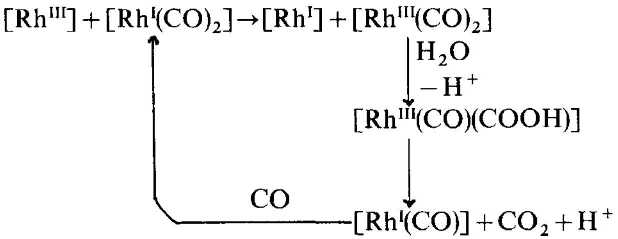
$$CO + 2OH^- + 2[Fe(CN)_6]^{3-} \xrightarrow{[L_nCo^I(CO)]^-} CO_2 + 2[Fe(CN)_6]^{4-} + H_2O \tag{17}$$

Catalysis of the oxidation of CO also has been observed in the case of certain metal ion oxidants [e.g., Cu(II) and Rh(III)] whose reduction products [i.e., Cu(I) and Rh(I), respectively] form stable CO complexes.[5,7] In such cases, reduction by CO may be autocatalytic as in the reduction of rhodium(III) chloride by CO [Eq. (18)] where both uncatalyzed and autocatalytic pathways are observed [Eq. (19) and (20), corresponding to the rate laws k' $[Rh^{III}][CO]$ and k'' $[Rh^{III}][Rh^{I}(CO)_2]$, respectively].[7]

$$[Rh^{III}] + 3CO + H_2O \rightarrow [Rh^{I}(CO)_2] + CO_2 + 2H^+ \tag{18}$$



$$[Rh^{III}] \xrightarrow{CO} [Rh^{III}(CO)] \xrightarrow[-H^+]{H_2O} [Rh-\overset{\overset{\displaystyle O}{\|}}{C}-OH] \xrightarrow[-H^+]{-CO_2} [Rh^{I}] \xrightarrow{2CO} [Rh^{I}(CO)_2] \tag{19}$$

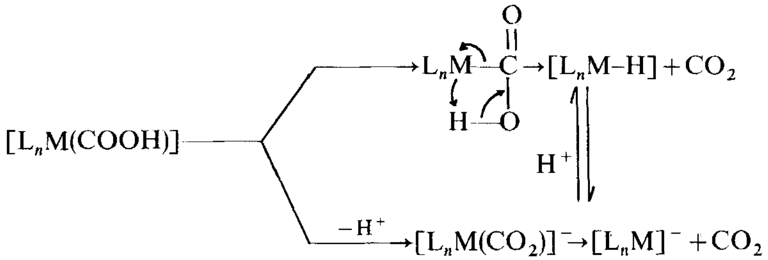


(20)

Hydroxycarbonyl–Metal Complexes

The postulated involvement of hydroxycarbonyl complexes (also designated metallocarboxylic acids), such as (**1**), (**3**), (**4**), as intermediates in the oxidation of free or coordinated CO, and in the isotopic oxygen exchange of metal–carbonyls with water,[15] has rested largely on indirect evidence [including analogies with the corresponding stable alkoxycarbonyl complexes such as (**2**)].[1,16] Only recently have several examples of such complexes actually been intercepted and characterized. These include the complex *trans*-$[PtCl(COOH)(PEt_3)_2]$, which has been isolated, characterized by IR and NMR (^1H, ^{31}P, and ^{13}C) spectroscopy, and shown to be an intermediate in the reaction of water with *trans*-$[PtCl(CO)(PEt_3)_2]^+$ to form *trans*-$[PtHCl(PEt_3)_2]$.[17] Other hydroxycarbonyl complexes that have been isolated and characterized are $[IrCl_2(CO)(COOH)(PMe_2Ph)_2]$,[18] $[(C_5H_5)Re(CO)(NO)(COOH)]$,[19] and $[(C_5H_5)Fe(CO)(PPh_3)(COOH)]$.[20] In general, such hydroxycarbonyl complexes decompose on warming or on reaction with water, with loss of CO_2, to form the corresponding hydrides. An unresolved mechanistic question is whether the decomposition, especially in the presence of water, involves the direct transfer of hydrogen to the metal (β

elimination of CO_2) according to Eq. (21a) or deprotonation to yield an intermediate CO_2 complex (or metallocarboxylate) according to Eq. (21b). Both processes seem inherently plausible and it is possible that both occur in appropriate circumstances. The detailed mechanistic aspects of this important and interesting reaction remain to be elucidated.



$$[L_nM(COOH)] \rightarrow L_nM{-}C(=O){-}OH \rightarrow [L_nM{-}H] + CO_2 \qquad (21a)$$

$$[L_nM(COOH)] \xrightarrow{-H^+} [L_nM(CO_2)]^- \rightarrow [L_nM]^- + CO_2 \qquad (21b)$$

Homogeneous Catalysis of the Water Gas Shift Reaction

An obvious mechanistic scheme for the homogeneous catalysis of the water gas shift reaction [Eq. (22)] involves the coupling of the two separate reactions corresponding to the oxidation of CO to CO_2 by a metal complex [Eq. (23)] and the reduction of H_2O (or H^+) to H_2 by the reduced form of the metal complex [Eq. (24)].

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (22)$$

$$[L_nM] + CO + H_2O \rightarrow CO_2 + [L_nM]^{2-} + 2H^+(\rightleftarrows [L_nMH]^- + H^+ \rightleftarrows [L_nMH_2]) \qquad (23)$$

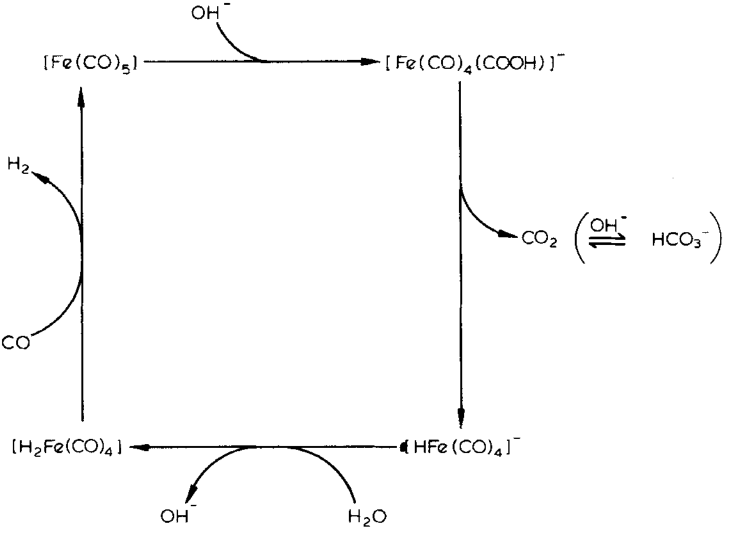
$$[L_nM]^{2-} + 2H^+(\rightleftarrows [L_nMH]^- + H^+ \rightleftarrows [L_nMH_2]) \rightarrow [L_nM] + H_2 \qquad (24)$$

Both these processes have ample precedent, the oxidation of CO in the many examples cited in this account [e.g., Eq. (3)], and the interconversion of H_2 and H^+ in the many reported examples of the homogeneous reactions between H_2 and metal ions in aqueous solution, e.g., Eq. (25) and (26).[21]

$$Hg^{2+} + H_2 \rightarrow [(HgH^+ + H^+(?))] \rightarrow Hg^0 + 2H^+ \qquad (25)$$

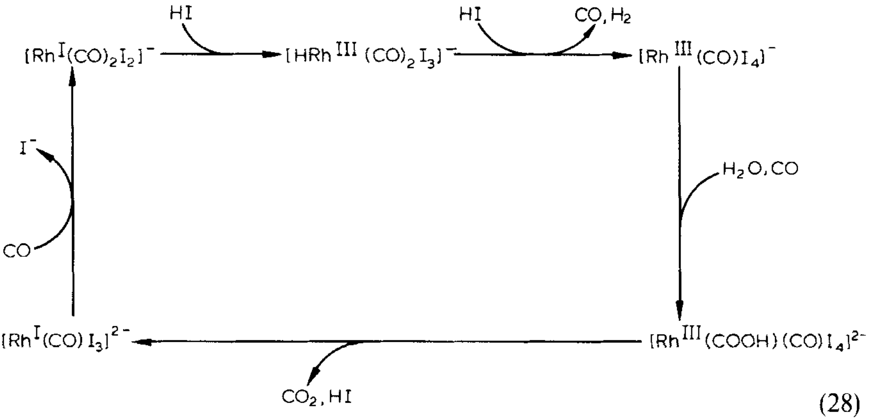
$$Cu^{2+} + H_2 \rightleftarrows CuH^+ + H^+ \xrightarrow{Cu^{2+}} 2Cu^+ + 2H^+ \qquad (26)$$

Combination of reaction (3) and the reversal of reaction (25) corresponds to reaction (22), i.e., a catalytic cycle for the water gas shift reaction. However, the equilibrium of reaction (25) lies sufficiently far to the right that its reversal to complete the catalytic cycle is highly unfavorable. Achievement of an effective catalytic cycle thus requires the selection of a system in which the reactions corresponding to Eq. (23) and (24) are so coupled that neither equilibrium lies too far on either side. This has been achieved using $[Fe(CO)_5]$ [*cf.* Eq. (9)] for which, by appropriate adjustment of the pH and CO pressure, the catalytic cycle depicted by Eq. (27) can be achieved.[12,22-24]



(27)

Since alkaline conditions are required to sustain this catalytic cycle the $[Fe(CO)_5]$-catalyzed water gas shift reaction is accompanied by consumption of base, which is used to convert some of the CO_2 produced to HCO_3^- and CO_3^{2-}. In other cases, homogeneous catalysis of the water gas shift reaction has been achieved under acidic conditions, notably with rhodium–carbonyl iodide complexes as catalysts,[25-27] for which the mechanistic scheme depicted by Eq. (28) has been proposed.[26] Homogeneous catalysis of the water gas shift reaction by this catalyst was first reported[28] as a side reaction in the Monsanto process for the carbonylation of methanol to acetic acid which employs the same catalyst system.[29-31]



(28)

Numerous other metal–carbonyl complexes, including $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, as well as clusters such as $Ru_3(CO)_{12}$, $Fe_3(CO)_{12}$, $Rh_6(CO)_{16}$, $Ir_4(CO)_{12}$, and various mixtures thereof, also have been reported to catalyze the water gas shift reaction.[23,32–37] The mechanistic features of these systems remain to be elucidated but presumably are related to those of the systems discussed earlier.

Use of CO/H_2O to Effect Reduction and Hydrogenation

Although the subject of considerable recent research, the homogeneously catalyzed water gas shift reactions discussed above are in themselves of rather limited interest insofar as most of the chemistry thus far revealed by them is well-precedented and the prospect of significant practical application appears only modest. However, these systems do have an interesting and potentially useful extension, namely the use of the combination of CO and H_2O as a source of electrons for reduction reactions or as a source of hydrogen for hydrogenation reactions according to Eq. (29a) and (29b), respectively.

$$CO + H_2O \longrightarrow \begin{cases} \rightarrow CO_2 + 2H^+ + 2[e^-] & (29a) \\ \rightarrow CO_2 + 2[H] & (29b) \end{cases}$$

In relation to the catalytic cycles for the water gas shift reaction described earlier, this involves intercepting the reduced metal complex or metal hydride [e.g., L_nMH^-, or L_nMH_2 in the schematic reaction (23) or $[HFe(CO)_4]^-$ in reaction (27)] by reaction with an appropriate electron or hydrogen acceptor.

An example of this utilization of CO as a reductant already has been provided, and mechanistically elaborated, in the examples of Eq. (16) and (17), involving the reduction of $[Fe(CN)_6]^{3-}$ by CO.[8] Related chemistry presumably is involved in the $[Fe(CO)_5]$-catalyzed reduction of aromatic nitro compounds to amines [Eq. (30)].[38,39]

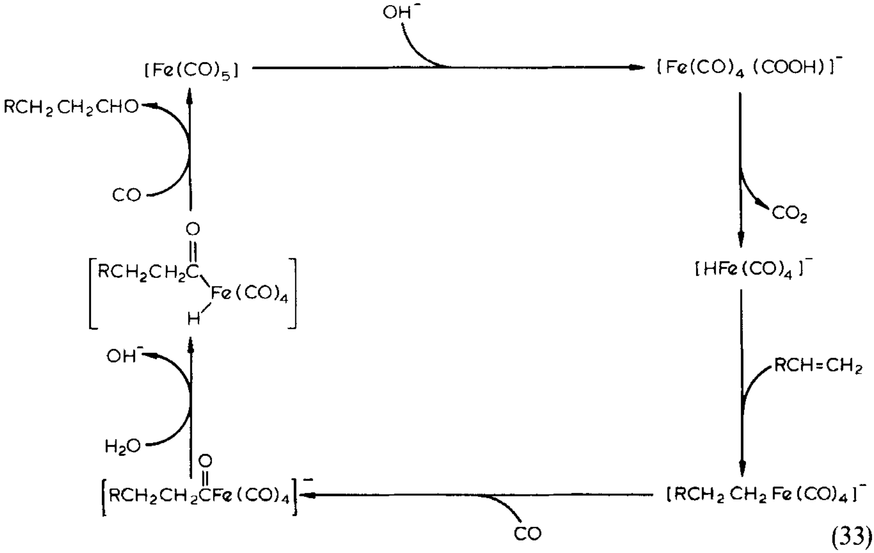
$$RNO_2 + 3CO + H_2O \rightarrow RNH_2 + 3CO_2 \tag{30}$$

The utilization of CO and H_2O as a source of hydrogen is illustrated by the $[Fe(CO)_5]$-catalyzed hydroformylation of olefins depicted by Eq. (31). This process which utilizes CO and H_2O [in place of CO and H_2 in the corresponding $HCo(CO)_4$-catalyzed reaction depicted by Eq. (32)] was first reported by Reppe and Vetter in 1953[40], and more recently reinvestigated and extended to other metal–carbonyl catalysts.[22]

$$\begin{gathered} RCH{=}CH_2 + 2CO + H_2O \xrightarrow{Fe(CO)_5} RCH_2CH_2CHO + CO_2 \\ \left(\xrightarrow[-CO_2]{CO/H_2O} RCH_2CH_2CH_2OH \right) \end{gathered} \tag{31}$$

$$RCH{=}CH_2 + CO + H_2 \xrightarrow{HCo(CO)_4} RCH_2CH_2CHO \left(\xrightarrow{H_2} RCH_2CH_2CH_2OH \right) \tag{32}$$

In the light of the chemistry already discussed and related pertinent chemistry of reaction (32), reaction (31) may be interpreted in terms of the mechanistic scheme depicted by Eq. (33).



(33)

The use of CO/H_2O, in place of H_2, as a source of hydrogen in this and related reactions[38,41,42] is of some interest, not only because of the possible advantages from the standpoint of the availability or cost of CO (relative to H_2), but also because of the mechanistic differences between the two systems and their susceptibility to different types of catalysts [e.g., $Fe(CO)_5$ vs. $HCo(CO)_4$].

Concluding Remarks

It is now 20 years since the homogeneous oxidation of CO by metal ions in aqueous solution was first demonstrated and the involvement of hydroxycarbonyl–metal complexes (MCOOH) as intermediates in such reactions proposed. Subsequent research on this theme has revealed a rich and diverse array of redox and catalytic chemistry associated with a variety of processes coupled to the conversion of CO, by reactions with water, to CO_2. Only recently have the first examples of the postulated intermediate hydroxycarbonyl complexes been prepared and characterized, and studies of their chemistry initiated. Research activity in this field continues at a high level and currently is focused on the achievement of a more thorough understanding of the mechanistic aspects and reactivity patterns of CO oxidation reactions and on the utilization of the combination of CO and H_2O as a source of electrons or hydrogen for reduction and hydrogenation reactions. The scope for the elaboration and extension of such chemistry appears considerable.

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