Reviews

Metal carbonyl catalysis of carbon monoxide and formate reactions

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The water gas shift reaction ($CO + H_2O = CO_2 + H_2$) is catalyzed by aqueous metal carbonyl systems derived from simple mononuclear carbonyls such as $Fe(CO)_5$ and $M(CO)_6$ (M = Cr, Mo, and W) and bases in the 140—200 °C temperature range. The water gas shift reaction in a basic methanol—water solution containing $Fe(CO)_5$ is first order in $[Fe(CO)_5]$, zero order in [CO], and essentially independent of base concentration and appears to involve an associative mechanism with a metallocarboxylate intermediate $[(CO)_4Fe—CO_2H]^-$. The water gas shift reactions using $M(CO)_6$ as catalyst precursors are first order in $[M(CO)_6]$, inverse first order in [CO], and first order in $[HCO_2^-]$ and appear to involve a dissociative mechanism with formatometallate intermediates $[(CO)_5M—OCHO]^-$.

The Reppe hydroformylation of ethylene to produce propionaldehyde and 1-propanol in basic solutions containing $Fe(CO)_5$ occurs at 110—140 °C. This reaction is second order in $[Fe(CO)_5]$, first order in $[C_2H_4]$ up to a saturation pressure >1.5 MPa, and inhibited by [CO]. These experimental results suggest a mechanism where the rate-determining step involves a binuclear iron carbonyl intermediate. The substitution of Et_3N for NaOH as the base facilitates the reduction of propionaldehyde to 1-propanol but results in a slower rate for the overall reaction.

The homogeneous photocatalytic decomposition of the formate ion to H_2 and CO_2 in the presence of $Cr(CO)_6$ appears to be closely related to the water gas shift reaction. The rate of H_2 production from the formate ion exhibits saturation kinetics in the formate ion and is inhibited by added pyridine. The infrared spectra of the catalyst solutions indicate an $LCr(CO)_5$ intermediate. Photolysis of the $Cr(CO)_6$/formate system in aqueous methanol in the presence of an aldehyde RCHO (R = *n*-heptyl, *p*-tolyl, and *p*-anisyl) results in catalytic hydrogenation of the aldehyde to the corresponding alcohol RCH_2OH by the formate ion. Detailed kinetic studies on *p*-tolualdehyde hydrogenation by this method indicates saturation kinetics in formate ion, autoinhibition by the *p*-tolualdehyde, and a threshold effect for $Cr(CO)_6$ at concentrations >0.004 mol L^{-1}. The presence of an aldehyde can interrupt the water gas shift catalytic cycle by interception of an $HCr(CO)_5^-$ intermediate by the aldehyde.

Key words: metal carbonyls, catalysis; carbon monoxide; formate; water gas shift reaction.

An important raw material for modern technology is synthesis gas, the 1:1 CO/H_2 mixture obtained from coal and steam (Scheme 1). Further reactions of synthesis gas can provide methods for the manufacture of hydrocar-

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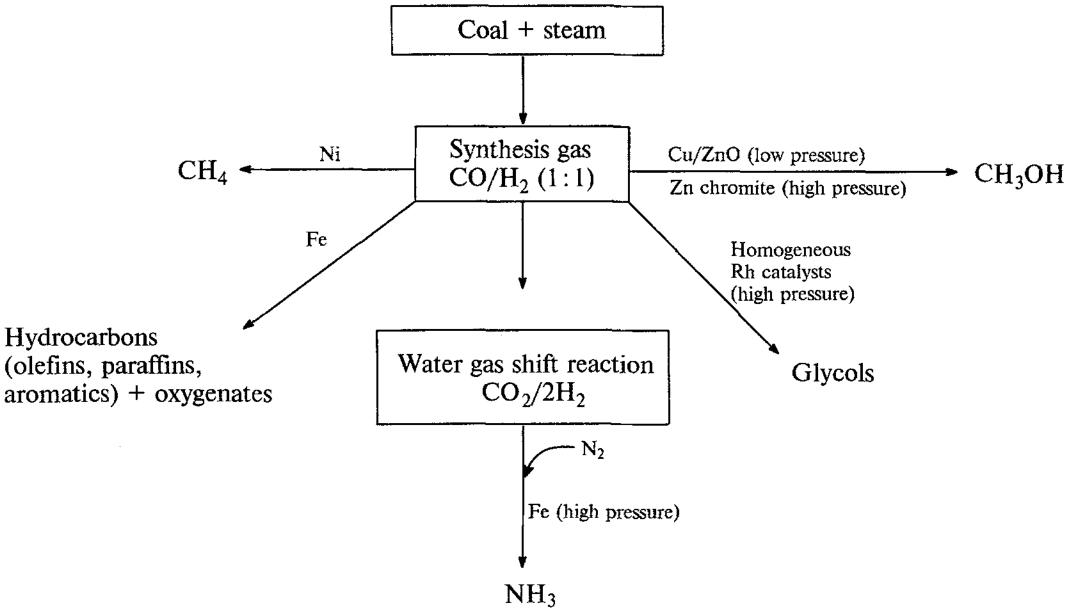
Scheme 1



bons such as methane and gasoline as well as alcohols and glycols. In addition, enrichment in H at the expense of CO of the CO/H_2 mixture obtained from coal and steam by the water gas shift reaction can provide a source of H_2 for other manufacturing processes such as the manufacture of ammonia by the Haber process.

Traditional synthesis gas chemistry frequently uses heterogeneous catalysts. For example, the water gas shift reaction $CO + H_2O \rightleftharpoons H_2 + CO_2$ can be carried out at temperatures >300 °C using heterogeneous catalysts consisting of iron oxides promoted by Cr_2O_3.[1] In more recent years homogeneous transition metal catalysts have been found for many synthesis gas reactions. Since CO is a key synthesis gas component, such homogeneous transition metal catalysis for synthesis gas reactions necessarily involves metal carbonyl chemistry.

The first homogeneous catalyst for the water gas shift reaction was reported in 1977 by Laine, Rinker, and Ford,[2] who found that a catalyst generated from $Ru_3(CO)_{12}$ and a base catalyzed the water gas shift reaction at fairly low temperatures (Eq. (1a)). Subsequently, the late Pettit and his coworkers[3] found that trimethylamine could be substituted for KOH as the base (Eq. (1b)) and that $Rh_6(CO)_{16}$ could be substituted for $Ru_3(CO)_{12}$ (Eq. (1c)).

$$CO + H_2O \xrightarrow{\text{Cat, }\Delta} H_2 + CO_2 \qquad (1a—c)$$

Experimental conditions: a. Cat = $Ru_3(CO)_{12}$/KOH, 100—120 °C, p = 0.1 MPa; b. Cat = $Ru_3(CO)_{12}/Me_3N$/THF, 100 °C, p = 2.4 MPa (8000 catalytic cycles per day); c. Cat = $Rh_6(CO)_{16}/Me_3N$/THF, 150 °C, p = 2.4 MPa (4300 catalytic cycles per day).

Subsequent work showed that non-cluster noble metal compounds could also be used as homogeneous catalysts for the water gas shift reaction and that such reactions did not require basic media. During the period 1977—1978 Eisenberg and coworkers discovered homogeneous water gas shift catalysts based on either the $[Rh(CO)_2Cl]_2$/AcOH/HCl/NaI system[4] or the $K_2PtCl_4/SnCl_4$/AcOH/HCl system;[5] these catalyst systems were active at ~90 °C and p_{CO} = 400 Torr. In 1978 Otsuka and coworkers[6] reported that $(Pr^i_3P)_3Pt$ was an active catalyst for the water gas shift reaction in acetone solution at ~150 °C and p_{CO} = 2.0 MPa.

Our work at the University of Georgia on the water gas shift reaction began with the discovery in 1978 that simple mononuclear metal carbonyls such as $Fe(CO)_5$ and $M(CO)_6$ (M = Cr, Mo, W) were active catalysts for the water gas shift reaction in basic media at ~170 °C.[7] Our subsequent work involved a detailed kinetic and mechanistic study of these reactions[8,9] as well as related reactions such as the Reppe hydroformylation of ethylene to produce propionaldehyde and 1-propanol in basic solutions containing $Fe(CO)_5$ [10] and photocatalytic hydrogen generation[11] and aldehyde hydrogenation[12] using formate in the presence of $Cr(CO)_6$. This short review summarizes the highlights of our results in these areas since 1978. Further details can be obtained by consulting the original papers.[8—12]

Catalysis of the water gas shift reaction using simple mononuclear metal carbonyls

Our studies on the metal carbonyl catalyzed water gas shift reaction were carried out in type 304 stainless steel autoclaves with an internal volume of 700 mL, equipped with a Fisher Flexo-Mix magnetic stirrer with a 1 inch (2.5 cm) Teflon coated magnetic bar. The gas phase was analyzed using a Fisher Model 1200 gas partitioner.* In this system at 140 °C using 200 mL liquid loadings an increment of 0.0068 MPa coincidentally corresponded to approximately 1 mmole of gas.

The water gas shift catalytic activity of systems derived from simple mononuclear metal carbonyls can be illustrated by the following two experiments:

1. A solution of 0.3 mL (0.45 g, 2.23 mmol) of $Fe(CO)_5$, 2.6 g (65 mmol) of NaOH, 190 mL of *n*-butanol, and 10 mL of water at 170—180 °C and p_{CO} = 2.82 MPa led to a hydrogen production rate (measured as turnover number) of 140 mol of H_2/mol of $Fe(CO)_5$ per day.
2. A solution of 0.0442 g (0.126 mmol) of $W(CO)_6$, 20 mL of 10 *M* aqueous KOH, and 100 mL of methanol at 170 °C and p_{CO} = 0.77 MPa led to a turnover number of 920 mol of H_2/mol of $W(CO)_6$ per day. This reaction was carried out to the point at which 66 % of the CO originally introduced had reacted.

Hydrogen production from the iron-carbonyl catalyzed water gas shift reaction was found to be first order in $[Fe(CO)_5]$, zero order in [CO], and essentially independent of base concentration because of the formate buffer system.[8] This suggests the following mechanism:

$$\mathrm{Fe(CO)_5 + OH^- \xrightarrow{k_1} (CO)_4Fe{-}CO_2H}, \tag{2a}$$

$$\mathrm{(CO)_4Fe{-}CO_2H^- \xrightarrow[\text{slow}]{k_2} HFe(CO)_4^- + CO_2}, \tag{2b}$$

$$\mathrm{HFe(CO)_4^- + H_2O \xrightarrow{k_3} H_2Fe(CO)_4 + OH^-}, \tag{2c}$$

$$\mathrm{H_2Fe(CO)_4 \xrightarrow{k_4} Fe(CO)_4 + H_2}, \tag{2d}$$

$$\mathrm{Fe(CO)_4 + CO \xrightarrow{k_5} Fe(CO)_5}. \tag{2e}$$

The following rate equation can be derived using the steady state approximation:

$$\frac{\mathrm{d}[\mathrm{H_2}]}{\mathrm{d}t} = k_1[\mathrm{Fe(CO)_5}][\mathrm{OH^-}] \tag{3}$$

This mechanism (Eqs. (2a—e)) is called an *associative mechanism* since the metal carbonyl precursor $Fe(CO)_5$ enters the catalytic cycle through a second order reaction with OH^- to give the metallocarboxylate intermediate $(CO)_4Fe{-}CO_2H^-$ (see Eq. (2a)).

The kinetics of the tungsten carbonyl catalyzed water gas shift reaction were found to be significantly different from those of the corresponding iron carbonyl catalyzed reaction.[9] Thus hydrogen production from the tungsten carbonyl catalyzed water gas shift reaction was found to be first order in $[W(CO)_6]$, inverse first order in [CO], and first order in base concentration. This corresponds to a first order reaction in $[HCO_2^-]$ since formate can be generated rapidly from a base and CO (Eq. (4a)). These observations suggest the following mechanism:

$$\mathrm{CO + OH^- \xrightarrow{k_6} HCO_2^-}, \tag{4a}$$

$$\mathrm{M(CO)_5 + HCO_2^- \xrightarrow{k_1} HCO_2M(CO)_5^-}, \tag{4b}$$

(M = W)

$$\mathrm{HCO_2M(CO)_5^- \xrightarrow[\text{slow}]{k_2} HM(CO)_5^- + CO_2}, \tag{4c}$$

$$\mathrm{HM(CO)_5^- + H_2O \xrightarrow{k_3} H_2M(CO)_5 + OH^-}, \tag{4d}$$

$$\mathrm{H_2M(CO)_5 \xrightarrow{k_4} H_2 + M(CO)_5}. \tag{4e}$$

The coordinatively unsaturated $M(CO)_5$ fragment required for the above catalytic cycle can (see Eqs. (4a—e)) be generated by dissociation of the $M(CO)_6$ catalyst precursor by the following reaction:

$$\mathrm{M(CO)_6 \overset{\mathit{K}}{\rightleftarrows} M(CO)_5 + CO} \tag{5}$$

The following rate equation can be derived using the steady state approximation:

$$\frac{\mathrm{d}[\mathrm{H_2}]}{\mathrm{d}t} = Kk_1\frac{[\mathrm{M(CO)_6}][\mathrm{HCO_2^-}]}{[\mathrm{CO}]} \tag{6}$$

This mechanism (see Eqs. (4a—e)) is called a *dissociative mechanism* since the metal carbonyl precursor $M(CO)_6$ enters the catalytic cycle through dissociation of one carbonyl group to give the coordinately unsaturated intermediate $M(CO)_5$.

Sulfur-containing impurities are expected to be present in many synthesis gas feedstocks for a water gas shift reactor. For this reason the sulfur tolerance of the water gas shift catalysts were measured using Na_2S as the sulfur source, which generates H_2S by the hydrolysis reactions (Eqs. (7 a,b)).

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* We used a 2 meter, 80 to 100 mesh column field with Columpak PQ in series with a 3.3 meter 13X molecular sieve column attached to a Varian CDS 111 digital integrator. Helium was used as the carrier gas. Argon was used as the internal standard.

Table 1. Sulfur tolerance of the water gas shift reaction catalysts

Metal carbonyl*	Reaction rate in the presence of KOH (v_{KOH})**	Reaction rate in the presence of Na_2S (v_{Na_2S})**	$\frac{v_{Na_2S}}{v_{KOH}}$ (%)
$Cr(CO)_6$ (0.13)	490	60	12
$Mo(CO)_6$ (0.13)	790	130	16
$W(CO)_6$ (0.13)	280	180	64
$Fe(CO)_5$ (2.23)	650	0	0
$Ru_3(CO)_{12}$ (0.021)	870	550	63
$Os_3(CO)_{12}$ (0.021)	210	200	95

* Mmoles used given in parentheses. ** In mol of H_2/mol of metal carbonyl per day; 39 mmol of KOH or 58 mmol of Na_2S.

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^- \quad (7a)$$

$$HS^- + H_2O \rightleftharpoons H_2S + OH^- \quad (7b)$$

The following observations were made (Table 1).

1. With KOH as the base, the 4d transition metal carbonyls (Mo, Ru) exhibit maximum catalytic activity compared with the corresponding 3d and 5d transition metal carbonyls.

2. Among the carbonyl derivatives of each periodic group (Cr, Mo, W and Fe, Ru, Os) inhibition of catalytic activity by sulfur diminishes with increasing atomic number of the central metal atom.

Homogeneous catalysis of the Reppe hydroformylation of ethylene with iron pentacarbonyl

A natural extension of the iron carbonyl catalyzed water gas shift reaction is the Reppe hydroformylation of ethylene to produce propionaldehyde and 1-propanol according to the following reactions:[13]

$$H_2C{=}CH_2 + 2\,CO + H_2O \rightarrow CH_3CH_2CHO + CO_2 \quad (8a)$$

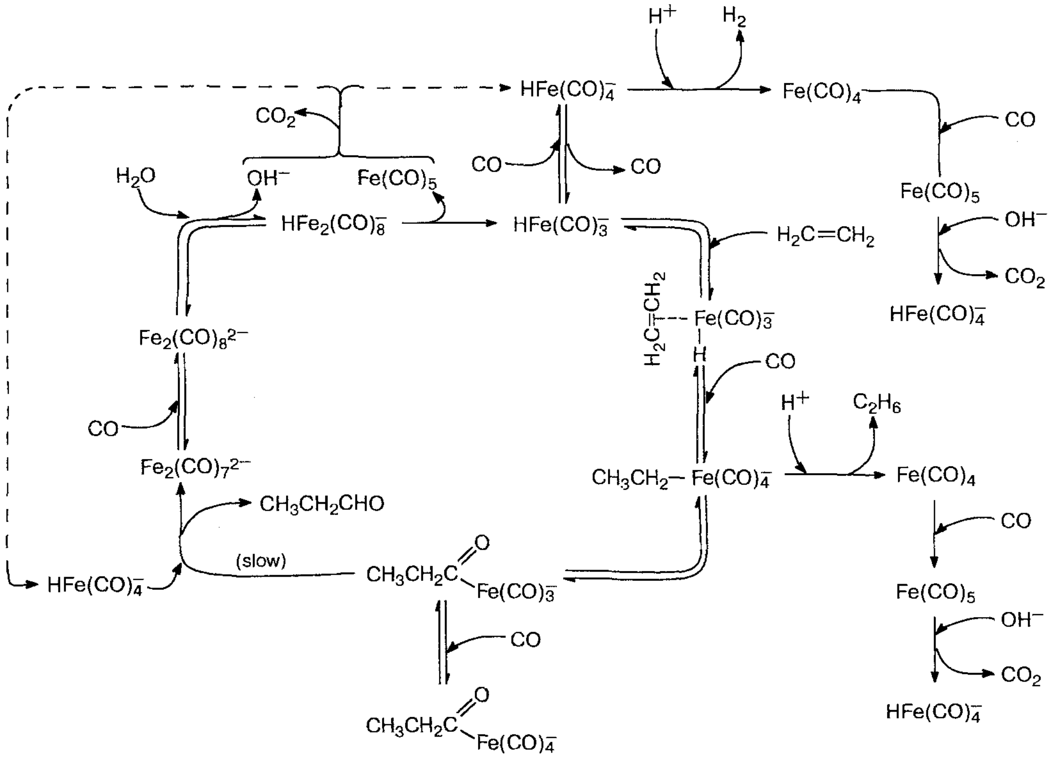
$$CH_3CH_2CHO + CO + H_2O \rightarrow CH_3CH_2CH_2OH + CO_2 \quad (8b)$$

$$H_2C{=}CH_2 + 3\,CO + 2\,H_2O \rightarrow CH_3CH_2CH_2OH + 2\,CO_2 \quad (8c)$$

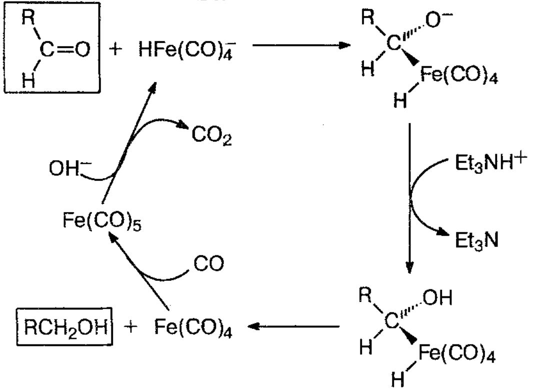
Reaction (8c) can be carried out under essentially the same conditions as the iron carbonyl catalyzed water gas shift reaction but with addition of ethylene to the gas mixture.

The kinetics of the Reppe hydroformylation reaction[10] were studied in the 110—140 °C temperature range using the same methodology as our earlier studies of the water gas shift reaction. Propionaldehyde formed by Eq. (8a) was found to be the principal product when NaOH was used as the base. The rate of the reaction was found to increase with ethylene concentration, to be second order with respect to $[Fe(CO)_5]$, and to be inhibited by [CO]. The infrared spectra indicate that $HFe(CO)_4^-$ and $Fe(CO)_5$ are present in the solution phase under the reaction conditions. The experimental results are consistent with the mechanism summarized

Scheme 2



Scheme 3



in Scheme 2 in which the rate determining step involves the combination of two mononuclear iron carbonyl derivatives to form a binuclear iron carbonyl derivative. In Scheme 2 this rate-determining step is the oxidative addition of $HFe(CO)_4^-$ to $CH_3CH_2COFe(CO)_3^-$ to give the binuclear complex $(CH_3CH_2CO)Fe(CO)_3(H)Fe(CO)_4^{2-}$, which can readily eliminate propionaldehyde to give $Fe_2(CO)_7^{2-}$. The substitution of Et_3N for NaOH facilitates the reduction of propionaldehyde to form 1-propanol but results in a slower rate for the overall reaction. Scheme 3 shows a possible mechanism for the hydrogenation of ketones to alcohols using the $HFe(CO)_4^-/Et_3N$ system. The fact that the ability of Et_3N to facilitate reduction of propionaldehyde to 1-propanol is greater than that of NaOH relates to the ability of its conjugate acid, Et_3NH^+, to function as a proton source.

Formate reactions photocatalyzed by chromium carbonyl

The involvement of the formate ion formed from OH^-/CO by Eq. (4a) in the chromium carbonyl catalyzed water gas shift reaction (see Eqs. (4b) and (4c), M = Cr) suggests that $Cr(CO)_6$ might be an effective catalyst precursor for formate reactions in the presence of light to facilitate its dissociation to the reactive $Cr(CO)_5$ fragment (see Eq. (5)). In this connection in 1981[14] we first observed the photolytic generation of H_2 from formate in the presence of $Cr(CO)_6$. The rate of hydrogen production was found to exhibit saturation kinetics in the formate ion and to be inhibited by added pyridine.[11] The infrared spectra of the catalyst solutions indicated an $LCr(CO)_5$ intermediate. These observations suggest that the mechanism discussed above for the water gas shift reaction with an $M(CO)_6$ catalyst precursor (see Eqs. (4a—e)) also applies to the photolytic generation of H_2 from formate in the presence of $Cr(CO)_6$. The essential features of this mechanism can be reduced to the following two equations:

$$HCO_2^- + Cr(CO)_5 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} HCO_2Cr(CO)_5^- , \tag{9a}$$

$$HCO_2Cr(CO)_5^- + H_2O \xrightarrow{k_3'} Cr(CO)_5 + H_2 + HCO_3^- . \tag{9b}$$

Here Eq. (9b) represents the combined results of the rate determining decarboxylation step (see Eq. (4c)) and the subsequent fast hydrolysis, dehydrogenation, and neutralization reactions (see Eqs. (4d) and (4e)). Since the concentration of water far exceeds that of $HCr(CO)_5^-$ and the H_2 (or HCO_3^-) produced, the decarboxylation reaction (see Eq. (4c)) can be considered to be pseudo-first-order in $[HCO_2Cr(CO)_5^-]$.

The steady state approximation may be applied to Eqs. (9a,b) to yield the following rate expressions for H_2 production:

$$\frac{d[H_2]}{dt} = \frac{k_3'[Cr]_0[HCO_2^-]}{K_M + [HCO_2^-]} , \tag{10}$$

$$[Cr]_0 \approx [Cr(CO)_5] + [HCO_2Cr(CO)_5^-] , \tag{11a}$$

$$k_3' = k_3[H_2O] , \tag{11b}$$

$$K_M = \frac{k_{-2} + k_3'}{k_2} . \tag{11c}$$

Here Eq. (10) has the same functional form as the Michaelis—Menten equation. Therefore, it is convenient to rewrite Eq. (10) in reciprocal form while expressing the rate of H_2 production as the number of catalytic cycles (Eq. (12))

$$\sigma = \frac{1}{[Cr]_0} \cdot \frac{d[H_2]}{dt} \tag{12}$$

to yield:

$$\frac{1}{\sigma} = \frac{1}{k_3'} + \frac{K_M}{k_3'} \cdot \frac{1}{[HCO_2^-]} . \tag{13}$$

Our kinetic data for the simple decomposition of formate ion using 0.14 mmol $Cr(CO)_6$ in 40 mL of 95 % aqueous MeOH plotted in the double reciprocal form (σ^{-1} *vs.* $([HCO_2^-])^{-1}$) were found to describe a straight line having a slope and intercept of $3.6 \cdot 10^{-4}$ mol L^{-1} day and $0.83 \cdot 10^{-3}$ day, respectively. According to Eq. (13) these values correspond to a maximum turnover number of $k_3' = 1.2 \cdot 10^3$ day^{-1} for the decomposition of $HCO_2Cr(CO)_5^-$ and a value of $K_M = 0.43$ mol L^{-1} at 60 °C. The date from a similar experiment with 0.80 mmol of added pyridine were also found to describe a straight line which shared a common intercept with the kinetic data measured in the absence of pyridine. The slope of the line fit to these latter data is $1.9 \cdot 10^{-3}$ mol L^{-1} day. This is the behavior expected for competitive inhibition and therefore suggests that pyridine acts as an inhibitor by competing with the substrate, namely formate ion, for the catalytically active

Cr compound that binds with formate ion in the step in which formate ion is taken into the catalytic cycle. According to the mechanism proposed here, this must occur in Eq. (9a) with pyridine competing with HCO_2^- for solvated $Cr(CO)_5$. Assuming that this mechanism for competitive inhibition by pyridine is correct, Eq. (13) can easily be shown to take the following form in the presence of an inhibitor, L_i.

$$\frac{1}{\sigma} = \frac{1}{k_3'} + \frac{K_M}{k_3'}\left(1 + \frac{[L_i]}{K_{L_i}}\right)\cdot\frac{1}{[HCO_2^-]} \qquad (14)$$

Here $[L_i]$ denotes the molar concentration of the inhibitor ligand and K_{L_i} denotes the dissociation constant that governs the equilibrium

$$L_iCr(CO)_5 \rightleftharpoons Cr(CO)_5 + L_i \; . \qquad (15)$$

In accordance with Eqs. (13) and (14) the ratio of the slopes of the straight lines taken in the presence and absence of pyridine is numerically equal to the term $\left(1 + \frac{[L_i]}{K_{L_i}}\right)$. The concentration of pyridine in these experiments is $[L_i] = 0.80$ mmol/40 mL $= 0.02$ mol L^{-1}. The ratio of the slopes referred to above is $1.9 \cdot 10^{-3}$ mol L^{-1} day/$(3.6 \cdot 10^{-4}$ mol L^{-1} day$) = 5.3$.

This yields a value of $K_{L_i} = 4.7 \cdot 10^{-3}$ mol L^{-1} for the reaction shown in Eq. (15). This is considerably smaller than K_M. This suggests that, to the extent that k_3' can be neglected in comparison to k_{-2} pyridine has a much greater affinity for $Cr(CO)_5$ than the formate ion.

The photocatalytic $HCO_2^-/Cr(CO)_6$ system can also be used to hydrogenate aldehydes to the corresponding alcohols by the following overall reaction:[12]

$$RCHO + HCO_2^- + H_2O \rightarrow RCH_2OH + HCO_3^- . \qquad (16)$$

Thus the aldehydes RCHO (R — *n*-heptyl, *p*-tolyl, and *p*-anisyl) were found to be hydrogenated to the corresponding alcohols RCH_2OH with sodium formate in aqueous methanol when photolyzed in the presence of a catalytic amount of $Cr(CO)_6$. Detailed kinetic studies on the hydrogenation of *p*-tolualdehyde by this method indicates saturation kinetics in the formate ion, autoinhibition by the *p*-tolualdehyde, and a threshold effect for $Cr(CO)_6$ at concentrations greater than 0.004 mol L^{-1}. These data suggest that the presence of an aldehyde can interrupt hydrogen production by the water gas shift catalytic cycle through interception of the $HCr(CO)_5^-$ intermediate by the aldehyde by the following sequence of reactions:

$$HCr(CO)_5^- + RCHO \rightleftharpoons HCr(CO)_4(RCHO)^- + CO \, , \qquad (17a)$$

$$HCr(CO)_4(RCHO)^- \longrightarrow Cr(CO)_4(RCH_2O)^- \, , \qquad (17b)$$

$$Cr(CO)_4(RCH_2O)^- + H_2O \longrightarrow HCr(CO)_4(RCH_2O) + OH^- \, , \qquad (17c)$$

$$HCr(CO)_4(RCH_2O) + CO \longrightarrow RCH_2OH + Cr(CO)_5 \, , \qquad (17d)$$

$$Cr(CO)_5 + HCO_2^- \longrightarrow HCO_2Cr(CO)_5^- \, , \qquad (17e)$$

$$HCO_2Cr(CO)_5^- \longrightarrow HCr(CO)_5^- + CO_2 \, , \qquad (17f)$$

$$OH^- + CO_2 \rightleftharpoons HCO_3^- \; . \qquad (17g)$$

The aromatic aldehyde *p*-tolualdehyde was found to inhibit completely the photoproduction of H_2 by the $NaHCO_2/Cr(CO)_6/MeOH/H_2O$ system whereas the aliphatic aldehyde 1-heptanal was found to inhibit the photoproduction of H_2 only when the partial pressure of hydrogen over the system reaches 0.05 to 0.10 MPa.

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