

HOMOGENEOUS CATALYSIS OF THE WATER GAS SHIFT REACTION BY IRIIDIUM CARBONYL IN ALKALINE SOLUTION *

DAVID M. VANDENBERG, TOSHISHIGE M. SUZUKI ** and PETER C. FORD*

Department of Chemistry, University of California, Santa Barbara, California 93106 (U.S.A)

(Received February 22nd, 1984)

Summary

The water gas shift reaction, $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}_2$, catalyzed homogeneously by a system based on tetrairidiumdodecacarbonyl ($\text{Ir}_4(\text{CO})_{12}$) in alkaline 2-ethoxyethanol/water solution was examined at moderate temperatures (90–130 °C) and pressures (P_{CO} 0.5–2.0 atm). The catalytic reaction showed an approximate first-order dependence on base concentration and on the concentration of iridium. The catalytic cycle was shown to have a zero order dependence on the partial pressure of CO. An apparent activation energy of 10.7 kcal mol⁻¹ was obtained from a linear Arrhenius plot based on hydrogen production over the temperature range 90–130 °C. The predominant pathway of the reaction can be explained by a mechanism in which activation of CO by nucleophilic attack of hydroxide on the metal hydride species $\text{HIr}_4(\text{CO})_{11}^-$ produces the dihydride species, $\text{H}_2\text{Ir}_4(\text{CO})_{10}^{2-}$ in the rate-limiting step. Subsequent reaction of this anion with H_2O gives H_2 plus $\text{HIr}_4(\text{CO})_{11}^-$ again. The complex $\text{Ir}_8(\text{CO})_{20}^{2-}$ is shown to be a catalytically poor component of the solution. The system has also been shown to be active toward the decomposition of formate. This pathway however, is concluded to make an insignificant contribution to the catalysis rate under water gas shift reaction conditions.

Introduction

There has been considerable recent attention directed toward homogeneous catalysis of the water gas shift reaction (WGSR, eq. 1) [1–5].



This interest has been stimulated in part by the knowledge that WGSR is a key step in schemes for the liquifaction or gasification of coal and by the proposition that

* Submitted in honor of Prof. Sei Otsuka.

** On leave (1980) from the Government Industrial Research Institute, Tohoku Nigatake, Haranomachi, Sendai 983, Japan.

effective low temperature catalysts may prove more energy efficient. Also of interest are the possible applications of CO/H₂O mixtures in the hydrogenation, hydroformylation and hydrohydroxymethylation of organic substrates [4], reactions related to CO activation in WGSR catalysis systems.

In recent years several homogeneous systems have been reported which can catalyze the WGSR under relatively mild conditions (temperature and pressure) [1]. A wide range of metal carbonyls including both mononuclear and cluster complexes have proved to be precursors to WGSR catalysts in basic media [4], and the ability to form such catalysts appears to be a quite general reactivity property of metal carbonyls under such conditions. In this context, we reported several years ago that alkaline solutions of iridium carbonyl served as WGSR catalysts [5]. Described here are more detailed studies of this system.

Experimental section

Reagents. Tetrairidiumdodecacarbonyl (Ir₄(CO)₁₂) was prepared according to a method described in the literature [6] or used as obtained from Strem Chemicals. Other tetrairidium clusters, [NEt₄][HIr₄(CO)₁₁], [PPN]₂[H₂Ir₄(CO)₁₀], and [PPN][Ir₄(CO)₁₁(COOCH₃)] were synthesized according to their literature preparations [7–9]. 2-Ethoxyethanol was distilled from anhydrous stannous or cuprous chloride followed by distillation from magnesium turnings. Methanol and isopropanol were distilled from calcium hydride and tetrahydrofuran (THF) from sodium benzophenone ketyl. A 94%/6% carbon monoxide/methane mixture, prepurified grade (Linde) was used for the carbon monoxide source. All other materials were of reagent grade. All air-sensitive manipulations were done using standard Schlenk apparatus.

Catalytic runs. A standard catalysis run solution was prepared from Ir₄(CO)₁₂ and anhydrous K₂CO₃ or KHCO₃ suspended in an aqueous 2-ethoxyethanol solution (1/4, v/v, H₂O)/EtOEtOH contained in a 100 or 200 ml round flask. This flask included a teflon stopcock and a ground glass joint for attachment to vacuum line equipped with a manometer and relevant gas inlets. The suspension was degassed by freeze-pump-thaw cycles, after which time the system was charged with the CO/CH₄ mixture such that P_{CO} equaled 0.9 atm at 100 °C. The vessel was then immersed and stirred in a thermostated oil bath. Gas samples were periodically removed with Analytical Pressure Lok syringes (Precision Sampling Corporation) and were analyzed by high resolution gas chromatography. The reaction stoichiometries were analyzed with methane serving as an internal standard. Turnover frequency (*TF*) was defined as the number of mol of H₂ produced/gram atomic weight of iridium/day. (Note that *TF* calculations based on mol of Ir₄(CO)₁₂ added would give values a factor of four larger).

Kinetic runs. Activation energies were based on initial rates of hydrogen production measured over the temperature range 90–130 °C with other conditions kept constant. In a 200 ml round bottom glass flask, Ir₄(CO)₁₂ (22 mg, 2 × 10⁻⁵ mol), K₂CO₃ (138 mg, 1 × 10⁻³ mol), H₂O (1 ml) and 2-ethoxyethanol (4 ml) were introduced and the system was degassed. The flask was then charged with a CO/CH₄ mixture such that P_{CO} equaled 0.9 atm at the reaction temperature. The flask was suspended and stirred in the heated oil bath and gas samples were extracted periodically. Since the solution pH changed during the course of the

reaction (*vide infra*), catalytic solutions were newly prepared for each run. The kinetic dependences on base and iridium concentrations were performed similarly but at a single temperature, 100°C.

Instruments. Gas sample analyses were performed on a Hewlett-Packard 5830A programmable gas chromatograph with Carbosieve B 80–100 mesh columns, the carrier gas was a 8%/92% hydrogen/helium mixture obtained from Linde. Calibration curves for H₂, CO, CO₂, and CH₄ were prepared periodically for gas samples ranging 0.1 to 2.0 ml of gas. The calibration curves were linear for CO, CO₂ and CH₄ but not for H₂. The pH's of solutions were determined using a Radiometer model PHM84 pH meter after diluting the largely organic solvent twofold with water. Infrared spectra were recorded on a Perkin-Elmer 683 IR spectrometer. IR spectra of aqueous catalyst solutions were obtained using Irtran-2 plates. Spectra of catalytic solutions at 100°C under CO were recorded in a cell similar to that described by King [10]. Proton NMR were obtained on a Nicolet NCT300 spectrometer operating in the FT mode.

Isolation of [PPN]₂[Ir₈(CO)₂₀]. This was prepared by a method analogous to one previously reported [7] by Angoletta et al. A solution prepared from Ir₄(CO)₁₂ (150 mg), K₂CO₃ (600 mg), 2-ethoxyethanol (8 ml) and water (2 ml) was heated at 100°C for 4 h under nitrogen. The solvent from the dark brown solution was removed by vacuum and the remaining solid was stirred with THF then filtered to remove the insoluble carbonates. Bis(triphenylphosphine)iminium chloride (PPN), (0.3 g) in ethanol and 3 ml cold water were then added to the THF filtrate solution to effect precipitation of the iridium carbonyl anions. The product was washed with ethanol and water, then vacuum dried. Filtering the product in methanol followed by addition of water to the filtrate gave, after collection, a light brown air-sensitive powder (14% yield overall). Anal. Found: C, 33.64; H, 2.38; N, 0.89. [PPN]₂[Ir₈(CO)₂₀], C₉₂H₆₀O₂₀N₂P₄Ir₈ calcd.: C, 34.8; H, 1.90; N, 0.88%.

Results

Activity studies

The WGSR catalysis in the present study was typically carried out in a 100 ml glass bulb using K₂CO₃ as the base and 2-ethoxyethanol-water (4/1 volume ratio) as the solvent. Although the catalysis precursor Ir₄(CO)₁₂ is sparingly soluble in the aqueous organic solvent, it reacted readily with base to give a light yellow solution at room temperature under a CO blanket. Upon heating at 100°C under the CO atmosphere, this solution turned to a yellow-brown color within several hours but continued to appear homogeneous at this temperature when examined visually under a strong light. Under these conditions, the system catalyzed the WGSR as evidenced by the consumption of CO and the concurrent production of H₂ and CO₂.

Figure 1 shows a typical catalysis run using K₂CO₃ as the initial base plotted in terms of turnover frequency ($TF = \text{mol of H}_2 \text{ produced/gram atomic weight of iridium/day}$) as a function of time. In this experiment the solution was degassed and recharged to the same initial P_{CO} (0.9 atm at 100°C) after each sampling of the gas mixture above the solution. Notably, the catalytic activity was found to be higher in the early stages, but rapidly decreased to a significantly lower value over the longer run. Furthermore, there was a continued, although gradual, decrease in TF over a period of days. These changes in activity paralleled changes in the solution pH. A

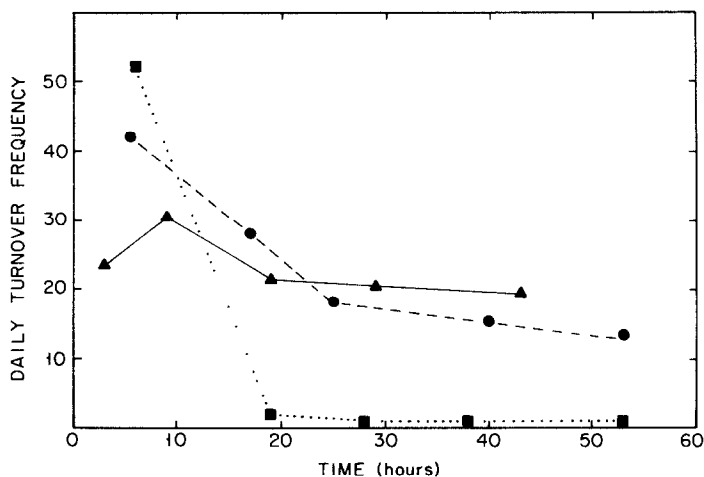


Fig. 1. H₂ WGSR activities vs. time, prepared from Ir₄(CO)₁₂ (0.020 mmol) in 5 ml aqueous 2-ethoxyethanol (20% water by volume) with various bases at same normality ● 0.2 M K₂CO₃; ▲ 0.4 M KHCO₃; ■ 0.4 M KOH. Runs done at 100 °C under 0.9 atm CO (system was flushed and recharged after each reading). The turnover frequency represents the moles of H₂ produced/gram atomic weight of Ir/day. Lines drawn for illustrative purposes.

0.2 M K₂CO₃ solution of this salt gave an initial pH reading of 11.5, however, the pH drops rapidly to a near constant value of about 8.2 during the course of the reaction as a carbonate-bicarbonate buffer system was established upon the production of CO₂ (eq. 2).



The buffering of the system was also reflected in the reaction stoichiometry in the early stages of the reaction. Hydrogen to CO₂ ratios were initially high, reflecting consumption of CO₂ by the base in solution. In this context, it is notable that catalysis solutions prepared using 0.4 M KHCO₃ as the initial base (the same number of base equivalents as 0.2 M K₂CO₃) gave long term activities comparable to but slightly higher than those of mature solutions prepared from K₂CO₃ as the initial base (Fig. 1). We have concluded that this difference was due to the base dependence of the formation of the catalytically inactive species Ir₈(CO)₂₀²⁻ (vide infra). For the solutions where KHCO₃ was used as the initial base, carbon dioxide production was initially very high due to the reverse of eq. 2 and hydrogen formation activities (Fig. 1) showed an initial rise before falling off somewhat from maximum values. The rise in H₂ TF was presumably due to an increase in pH as the carbonate-bicarbonate equilibrium is shifted to the left as excess CO₂ is evolved. Catalysis solutions prepared using KOH as the initial base (0.4 N) gave high early TF values (Fig. 1), however, the activity decayed to near zero within a few hours. The loss in activity was accompanied by the formation of dark precipitates from these solutions. Lastly, initial rates of H₂ production from catalyst solutions prepared with different initial concentrations of K₂CO₃ ranging from 0.2 to 1.0 M showed a comparable five fold range in TF (7–25 mol H₂/g-atom Ir/day) paralleling the base concentrations. The activities of the mature solutions were also higher for the more concentrated bases, but the differences were not nearly as great.

The conclusions one can draw from these data are that initial rates of H_2 production from fresh solutions show a first order dependence (within experimental uncertainty) on the amount of K_2CO_3 added, possibly because initial hydroxide concentrations parallel initial carbonate concentrations. However, the drop in activity as the reaction progresses was much less than the drop in the $[OH^-]$ indicated by the pH change of three units. Thus, the residual catalytic activity may reflect general base catalysis by the various buffer species present and/or the contribution of a mechanism involving the decomposition of formate (vide infra). The dependence on $[K_2CO_3]$ would be consistent with either interpretation, since higher base concentrations also lead to greater concentrations of formate formed by the direct hydrolysis of free CO (eq. 3).



The WGSR activity of a mature alkaline iridium carbonyl catalyst prepared in the standard manner was shown to be independent of P_{CO} in the following manner. The activity was first checked at P_{CO} 0.9 atm and found to give a H_2 *TF* value of 15. Then the P_{CO} was raised to 1.9 atm and the turnover frequency was found to be unchanged. However, a different situation was found when catalysis runs were prepared with different starting pressures of CO and these pressures were maintained throughout the run. Those with a higher P_{CO} definitely displayed higher *TF* values. The apparent contradiction in behavior can be explained in terms of a side reaction not directly related to the catalysis cycle. Under conditions of high pH (the initial pH of the K_2CO_3 solutions) and low P_{CO} , the inactive higher order iridium species $Ir_8(CO)_{20}^{2-}$ (vide infra) is formed irreversibly, thus giving the system a lower concentration of active species and a lower *TF*.

Catalysis of the reaction was shown to have a first-order dependence on the total concentration of iridium in the range 0.009–0.033 g-atom Ir/L. This is illustrated in Fig. 2 where the total H_2 production is plotted as a function of time for various initial concentrations of $Ir_4(CO)_{12}$. At lower [Ir] values, a doubling in iridium concentration results in an approximate doubling in the total H_2 produced. The values plotted for the highest [Ir] (0.064 g-atom Ir/L) show a lesser activity than would be expected for a first-order dependence on [Ir], however, in this case there apparently was irreversible generation of a larger concentration of the catalytically inactive species $Ir_8(CO)_{20}^{2-}$, which is favored at low P_{CO} (vide infra). The higher WGSR rates at this [Ir] led to depletion of P_{CO} sufficient to enhance formation of the octanuclear cluster.

Catalysis by the iridium carbonyl system was shown to be temperature sensitive. An apparent activation energy (E_a) of 10.7 ± 0.2 kcal mol $^{-1}$ was calculated from linear Arrhenius plots of initial H_2 production rates measured over the temperature range 90–130 °C under otherwise standard conditions.

Iridium species in solution

IR spectra. Heating of the $Ir_4(CO)_{12}$ catalyst precursor in aqueous alkaline 2-ethoxyethanol under CO initially gave a yellow solution which progressively acquired a brown appearance as the catalysis proceeded. Infrared spectra under catalytic conditions [10] (100 °C, 0.9 atm CO) were found to be identical to those obtained for samples removed from the reaction vessel and measured at room temperature. The highest resolution spectra however, were obtained by samples

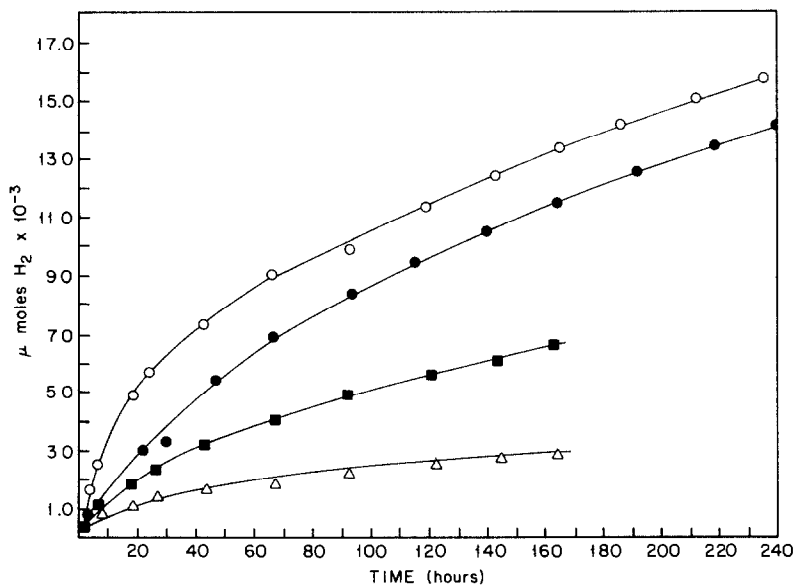


Fig. 2. Total H_2 produced vs. time at varying initial iridium carbonyl concentrations. Δ 0.009, \blacksquare 0.018, \bullet 0.032, \circ 0.064 g-atom Ir/L. Lines drawn for illustrative purposes.

prepared by vacuum removal of the aqueous organic solvent, followed by dissolving in THF then filtering under nitrogen to remove the insoluble carbonates. A spectrum obtained in this way from an active catalyst solution which had been operating for 24 h is shown in Fig. 3a.

The relative intensities of the $\nu(\text{CO})$ bands of the catalyst system proved to be sensitive to the operating P_{CO} . If P_{CO} were allowed to drop significantly via the WGSR, the solution became darker brown in color and the WGSR activity dropped

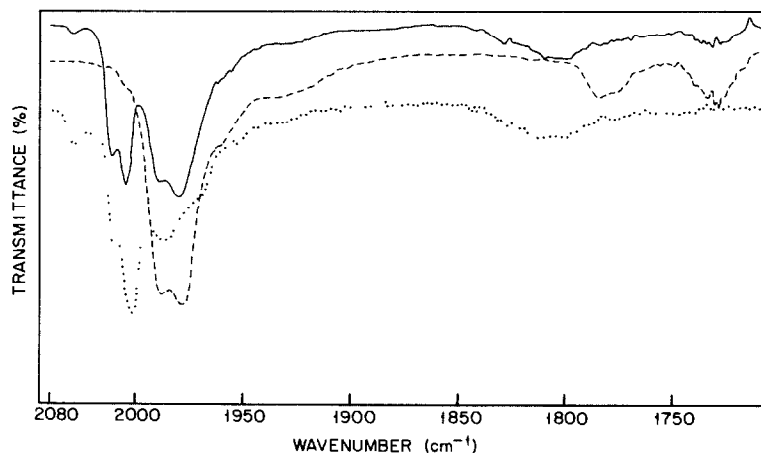


Fig. 3. IR spectra (carbonyl region) of species in iridium carbonyl catalyzed WGSR, (a) ——— Spectrum of active catalyst after 24 h reaction time, followed by vacuum removal of solvent and filtration with THF, (b) - - - Spectrum of catalyst after 10 h under low P_{CO} , followed by vacuum removal of solvent and filtration with THF; (c) ····· Spectrum of $[\text{NEt}_4][\text{HIr}_4(\text{CO})_{11}]$ in THF.

significantly to $TF = 1$. The decreased WGS activity did not recover even after recharging the bulb with CO to 0.9 atm. The IR spectrum of such solutions (Fig. 3b) showed that the activity changes were concurrent with the disappearance of the $\nu(\text{CO})$ bands at 2068, 2030, 2018 and 1805 cm^{-1} corresponding to the yellow metal hydride species $\text{HIr}_4(\text{CO})_{11}^-$. The IR spectrum of an authentic sample of $[\text{NEt}_4][\text{HIr}_4(\text{CO})_{11}]$ prepared from $\text{Ir}_4(\text{CO})_{12}$ and K_2CO_3 in methanol [7,11] is shown in Fig. 3c. Notably, the WGS activity of a catalyst solution prepared using $[\text{NEt}_4][\text{HIr}_4(\text{CO})_{11}]$ as the catalyst precursor showed activities comparable to those for a solution beginning with $\text{Ir}_4(\text{CO})_{12}$ (Table 1). The disappearance of $\text{HIr}_4(\text{CO})_{11}^-$ from the catalysis solution under conditions of low P_{CO} proved irreversible. The IR spectra showed that prolonged heating under 0.9 atm of CO does not regenerate the hydride once converted to the brown material. Thus, the IR spectral studies suggest that the catalyst solutions contain only two iridium carbonyl species in measureable concentrations. This was also demonstrated by chromatography of the iridium species obtained by evaporating the solvent from a catalyst solution, dissolving in THF and eluting from oxygen-free silica gel with THF/ CH_3OH (95%/5%) as eluant. Two bands were eluted, a yellow band corresponding to $\text{HIr}_4(\text{CO})_{11}^-$ and a brown band corresponding to $\text{Ir}_8(\text{CO})_{20}^{2-}$ as confirmed by IR.

¹H NMR spectra. A standard catalytic mixture was prepared then allowed to mature for 4 h to give a yellow, catalytically active solution. The solvent was pumped off and the remaining solid was dissolved in THF then filtered to give a yellow solution containing predominantly $\text{HIr}_4(\text{CO})_{11}^-$ as shown by the IR spectrum. Vacuum removal of the THF followed by redissolving the resulting yellow oil in CD_3CN under a CO atmosphere, gave a sample which showed a signal at $\delta -15.4$ ppm in the proton NMR. This frequency is identical to that obtained for an authentic sample of $\text{HIr}_4(\text{CO})_{11}^-$ as prepared by the literature procedure [7]. Notably, protonation of the hydride with trifluoroacetic acid under a CO atmosphere yields $\text{Ir}_4(\text{CO})_{12}$, presumably through reductive elimination of dihydrogen from the known species, $\text{H}_2\text{Ir}_4(\text{CO})_{11}$ [8].

A NMR sample prepared from a catalysis solution as above but from a bulb in which the progress of the reaction had led to complete depletion of CO showed no hydride signals to $\delta -30$ ppm.

Isolation and characterization of $\text{Ir}_8(\text{CO})_{22}^{2-}$. The identity of the brown complex in the catalytic solution was suggested to be $\text{Ir}_8(\text{CO})_{20}^{2-}$ given observations by

TABLE 1
WGS ACTIVITIES USING DIFFERENT CATALYST PRECURSORS^a

Initial complex	H ₂ activity ^d	H ₂ activity ^e
$\text{Ir}_4(\text{CO})_{12}$ ^b	40	15
$\text{Ir}_4(\text{CO})_{12}$ ^c	1	1
$[\text{NEt}_4][\text{HIr}_4(\text{CO})_{11}]$	42	15
$[\text{NEt}_4]_2[\text{Ir}_8(\text{CO})_{20}]$	2	1
$[\text{PPN}]_2[\text{H}_2\text{Ir}_4(\text{CO})_{10}]$	35	12

^a Identical standard conditions used except where noted. Activities represent average for a number of daily runs; uncertainty $\pm 15\%$. ^b P_{CO} maintained between 0.7 and 0.9 atm. ^c P_{CO} allowed to go to zero, then recharged to 0.9 atm. ^d H₂ activity = (mol of H₂ produced/gram atomic weight Ir/day) Activity for first 8 h period. ^e Activity for mature solution (after 48 h).

Malatesta [7] and co-workers while studying reactions of $\text{Ir}_4(\text{CO})_{12}$ with bases. These workers suggested that $\text{HIr}_4(\text{CO})_{11}^-$ gives the insoluble brown cluster anion $\text{Ir}_8(\text{CO})_{20}^{2-}$ by the reaction



under a nitrogen atmosphere in the presence of base.

The presence of $\text{Ir}_8(\text{CO})_{20}^{2-}$ in the catalysis system was indicated by precipitation of its PPN^+ salt from a solution derived from a catalysis bulb matured under nitrogen (Experimental section). The analysis was consistent with the formulation $[\text{PPN}]_2[\text{Ir}_8(\text{CO})_{20}]$, and the infrared spectrum was the same as that of an authentic sample prepared as described by Malatesta et al. [7] In addition, the IR spectrum (1990s, 1983s, 1781w and 1753w cm^{-1}) of the NEt_4^+ salt is in good agreement with the in situ spectrum of a catalyst solution allowed to react at 100 °C after the CO atmosphere had become depleted (Fig. 3b). Proton NMR of the isolated carbonyl (CD_3CN) confirms the lack of a hydride signal to $\delta -30$ ppm.

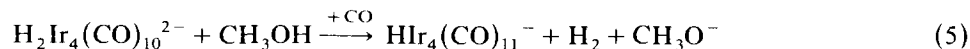
The WGS activity measured using $[\text{NEt}_4]_2[\text{Ir}_8(\text{CO})_{20}]$ showed it to be a poor catalyst ($TF = 1$). This activity is similar to that for a system using $\text{Ir}_4(\text{CO})_{12}$ as the catalyst precursor (Table 1) but run for several hours under low P_{CO} before recharging with CO.

As previously noted, the rate of formation of $\text{Ir}_8(\text{CO})_{20}^{2-}$ was found to be a function of the solution basicity. This would explain the higher long term activity for mature solutions using the milder base KHCO_3 (Fig. 1). Catalyst runs using KOH as the initial base led to the irreversible generation of $\text{Ir}_8(\text{CO})_{20}^{2-}$ during the early, high pH stage, thus gave low activities for mature buffered solutions. Similarly, some irreversible formation of $\text{Ir}_8(\text{CO})_{20}^{2-}$ is apparent in the early stages of runs initiated with K_2CO_3 as base. Notably, the synthesis of the octanuclear cluster as described by Malatesta [7] used KOH under a nitrogen atmosphere.

Reactivity of iridium hydride species

The presence of $\text{HIr}_4(\text{CO})_{11}^-$ in the catalysis system and the base dependence of the catalysis suggests that base attack on this cluster anion may be involved in the reaction. To test this hypothesis, a sample of $[\text{NEt}_4][\text{HIr}_4(\text{CO})_{11}]$ was allowed to react under CO with two equivalents of NaOCH_3 in wet THF. Within minutes the initial yellow color of the hydride was replaced by an orange-colored solution. The IR spectrum of this solution showed the iridium species to be present as the dihydride species $\text{H}_2\text{Ir}_4(\text{CO})_{10}^{2-}$ when the spectrum was compared with that of an authentic sample of the dihydride prepared from the methoxycarbonyl complex $[\text{PPN}][\text{Ir}_4(\text{CO})_{11}(\text{COOMe})]$ as suggested by Garlaschelli et al. [8].

The ease of formation of $\text{H}_2\text{Ir}_4(\text{CO})_{10}^{2-}$ from the monohydride species under basic conditions suggests that the dihydride is also involved in the WGS cycle (see Discussion). The basicity of the dihydride cluster was demonstrated as follows. When $[\text{PPN}]_2[\text{H}_2\text{Ir}_4(\text{CO})_{10}]$ was simply dissolved in neat methanol under CO, it rapidly converted to $\text{HIr}_4(\text{CO})_{11}^-$ and dihydrogen as followed by IR and gas chromatography respectively (eq. 5).



With an added strong acid such as $\text{CF}_3\text{CO}_2\text{H}$, the dihydride was converted to

$\text{Ir}_4(\text{CO})_{12}$ under CO via the subsequent protonation of $\text{HIr}_4(\text{CO})_{11}^-$ and loss of H_2 .

Using $[\text{PPN}]_2[\text{H}_2\text{Ir}_4(\text{CO})_{10}]$ as a WGS catalyst precursor showed it to have very similar activity (Table 1) to catalysts beginning with $\text{Ir}_4(\text{CO})_{12}$ or $[\text{NEt}_4][\text{HIr}_4(\text{CO})_{11}]$. The IR spectrum of the resulting solution after about 24 h operation showed that almost all of the dihydride had been converted to $\text{HIr}_4(\text{CO})_{11}^-$ and $\text{Ir}_8(\text{CO})_{20}^{2-}$ as is found in a standard catalysis solution.

Formate decomposition studies

A notable feature of the present alkaline iridium carbonyl WGS catalyst is that this system also catalyzes the decomposition of formate (eq. 6).



For example, when a sample of sodium formate (2.0 mmol) was added to a mature catalyst system prepared under the standard conditions then reheated under a nitrogen atmosphere, quantitative decomposition to CO_2 and H_2 was observed over a period of 36 h. The initial turnover number for H_2 production was measured at 11, higher than the WGS activity ($TF = 6$) observed under 0.9 atm of CO for this solution immediately prior to formate addition. In contrast, active WGS catalysts prepared from $\text{Ru}_3(\text{CO})_{12}$ in similar alkaline solution, were not active for the decomposition of formate [4a]. Given that formate ion is formed in the uncatalyzed direct reaction between hydroxide and CO (eq. 3), the activity of the iridium catalyst toward formate decomposition leads to the suggestion that the catalytic cycle may proceed through a metalloformate intermediate as has been suggested by King [4e] and by Sleiger [4f] for the Group VIB metal carbonyl catalysis of the WGS.

Although the iridium carbonyl system does decompose formate ion under a nitrogen atmosphere, the contribution of formate decomposition to the overall catalytic activity is apparently small. This is indicated by three experiments. First, when sodium formate (2 mmol) was added either to a mature active catalyst or to

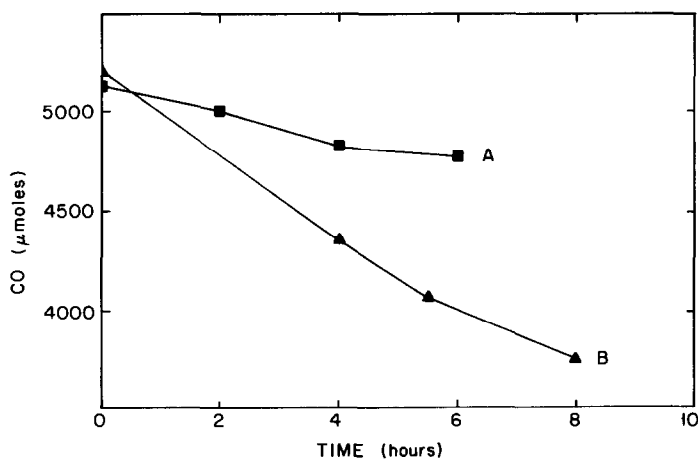


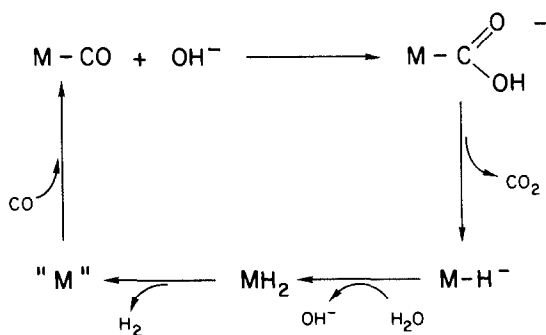
Fig. 4. Consumption of carbon monoxide by alkaline aqueous 2-ethoxyethanol solutions (20% water by volume). A: $[\text{K}_2\text{CO}_3]$ 0.20 M, no added catalyst, B: $[\text{K}_2\text{CO}_3]$ 0.20 M, $[\text{Ir}_4(\text{CO})_{12}]$ 8.0×10^{-3} M. Reactions carried out at 100°C in a 200 ml flask. The ordinate represents the total CO present in the reaction vessel as determined by comparing GC samples to the methane internal standard (corrected for small sampling effects). Lines drawn for illustrative purposes.

one freshly prepared in the standard fashion, then allowed to react under CO (P_{CO} 0.9 atm), there were no changes in the rates of CO₂ or H₂ production from those measured in the absence of added formate. In the second experiment, NaHCO₂ (2.0 mmol) was added to a catalyst solution which had been first allowed to react under N₂ to give predominantly Ir₈(CO)₂₀²⁻ (as identified by IR). Under 0.9 atm CO at 100 °C there was no increase in the inherently low activity ($TF = 1$) of these octanuclear cluster solutions. Finally, the consumption of CO was carefully monitored by GC techniques for freshly prepared aqueous 2-ethoxyethanol solutions containing the standard initial concentration of K₂CO₃ (0.2 M) but not including the iridium carbonyl catalyst. At 100 °C, CO consumption was much slower than for an analogous solution containing iridium carbonyl (Fig. 4). These results lead to the conclusion that the uncatalyzed hydrolysis of CO to formate (eq. 4) is considerably slower than the consumption of CO by iridium catalyzed reactions. Notably, no hydrogen was produced in the absence of iridium carbonyl.

Discussion

The catalysis of the water gas shift reaction has been shown to be a general property of metal carbonyl complexes in alkaline solution. One mechanism prominently proposed [1,4a,b] for CO activation involves nucleophilic attack of hydroxide on coordinated carbonyl to form a hydroxycarbonyl intermediate which decarboxylates to give a metal hydride species (Scheme 1). The first-order dependence of the

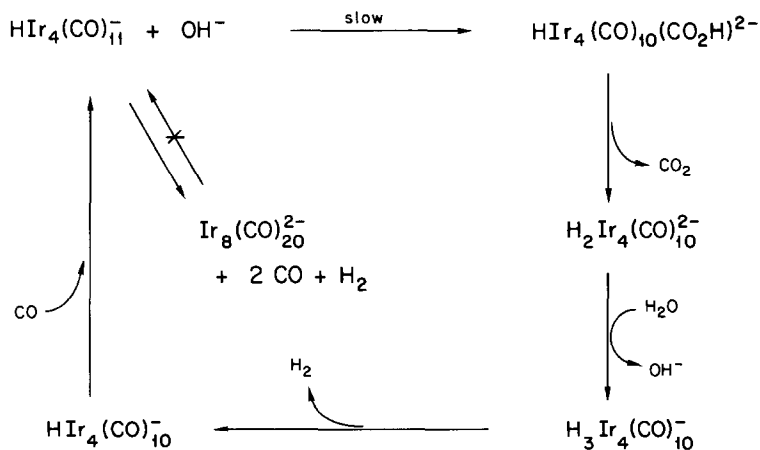
SCHEME 1



initial rates of H₂ formation on the concentration of K₂CO₃ is suggestive that such a mechanism is operable here and that the rate limiting step is the base activation of CO. However, the only active form for the iridium catalyst detectable is the hydride anion HIr₄(CO)₁₁⁻. Thus, it is probable that this, or a species in equilibrium with this cluster, is the iridium complex involved in the rate limiting step of the catalysis cycle. We therefore propose the cycle shown in Scheme 2, which is an elaboration on Scheme 1, for the catalysis of the WGS by iridium carbonyl.

The Ir₄(CO)₁₂ starting complex does not appear in the cycle and is proposed to be a precursor of the key species. (Reaction of Ir₄(CO)₁₂ in alkaline media leads to the facile formation of HIr₄(CO)₁₁⁻). The rate limiting step is considered to be the reaction of HIr₄(CO)₁₁⁻ with base to give the dihydride dianion H₂Ir₄(CO)₁₀²⁻, presumably via the formation of a hydroxycarbonyl intermediate. The stoichiometric

SCHEME 2



formation of the dianion from $[\text{NEt}_4][\text{HIr}_4(\text{CO})_{11}]$ was demonstrated by the rapid reaction with NaOCH_3 in wet THF.

The reactivity of the dihydride species is consistent with its proposed role in Scheme 2. The facile conversion of the dihydride to the monohydride with evolution of H_2 using only methanol to protonate the cluster (eq. 7) supports the proposed steps for the completion of the catalytic cycle. The independence of the catalysis rate on P_{CO} is consistent with CO coordination to the (presumably reactive) intermediate proposed in these steps, $\text{HIr}_4(\text{CO})_{10}^-$. The WGS activity using $[\text{PPN}]_2\text{-}[\text{H}_2\text{Ir}_4(\text{CO})_{10}]$ as a catalyst precursor and its ready conversion to $\text{HIr}_4(\text{CO})_{11}^-$ and $\text{Ir}_8(\text{CO})_{20}^{2-}$ under these alkaline conditions again justifies the role of this species in the proposed cycle.

The formation of the higher order cluster $\text{Ir}_8(\text{CO})_{20}^{2-}$ serves as an irreversible, low catalysis activity sink for the iridium species of these alkaline solutions. Formation of this species is favored by conditions of low P_{CO} and of high alkalinity. The slow degradation of catalytic activity even of mature solutions may reflect the eventual accumulation of the iridium in this irreversible sink.

An alternative mechanism in which decomposition of formate ion is involved we conclude to make little or no contribution to the overall activity under WGS conditions. The fact that added formate ion is not decomposed by the iridium catalyst at significant rates under CO suggests that, in a competition for an open coordination site, CO is greatly preferred over formate. This would be consistent with the anionic nature of the iridium species in solution. In contrast, the formate decomposition mechanism proposed by King [4e] for the Group VI metal carbonyl catalyzed WGS involves coordination of formate to a coordinatively unsaturated but neutral intermediate, $\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). Darensbourg [12] has suggested that such a reactive intermediate should probably be scavenged equally well by HCO_2^- and CO.

In summary, activity measurements and spectroscopic studies are consistent with the homogeneous catalysis of the WGS by iridium carbonyl clusters. The mechanism for CO activation involves rate-limiting nucleophilic attack by hydroxide on $\text{HIr}_4(\text{CO})_{11}^-$ followed by decarboxylation giving $\text{H}_2\text{Ir}_4(\text{CO})_{10}^{2-}$. Protonation of the

latter ion followed by dihydrogen elimination and addition of CO completes the cycle. The formation of a complex of low catalytic activity, $\text{Ir}_8(\text{CO})_{20}^{2-}$, also occurs under the catalysis conditions. The catalytic decomposition of formate to CO_2 and H_2 is of minor importance under WGS conditions.

Acknowledgements

This research was supported by a contract DEAT0376ER70262 with the U.S. Department of Energy, Office of Basic Energy Sciences. Dr. T.M. Suzuki was supported by a fellowship from the government of Japan during his study leave at UCSB.

References and notes

- 1 P.C. Ford, *Acct Chem. Res.*, 14 (1981) 31 and references therein.
- 2 (a) T. Yoshida, T. Okano, Y. Ueda and S. Otsuka, *J. Am. Chem. Soc.*, 103 (1981) 3411, (b) P.C. Ford, (Ed.), *Catalytic Activation of Carbon Monoxide*, ACS Symposium Series, Vol. 152, American Chemical Society, Washington DC, 1981, chapters 5,6,7,8 and 21.
- 3 (a) R. Eisenberg and D.E. Hendriksen, *Adv. Catalysis*, 28 (1979) 79; (b) H. Kang, C.H. Mauldin, T. Cole, W. Sleiger, K. Cann and R. Pettit, *J. Am. Chem. Soc.*, 99 (1977) 8323; (c) R.M. Laine, *J. Am. Chem. Soc.*, 100 (1978) 6451; (d) C.H. Cheng, L. Kwirtzkes and R. Eisenberg, *J. Organomet. Chem.*, 190 (1980) C21.
- 4 (a) C. Ungermann, V. Landis, S.A. Moya, H. Cohen, H. Walker, R.G. Pearson, R.G. Rinker and P.C. Ford, *J. Am. Chem. Soc.*, 101 (1979) 5922; (b) R. Pettit, K. Cann, T. Cole and C.H. Mauldin, *Adv. Chem. Ser.*, 173 (1979) C21; (c) R.B. King, C.C. Frazier, R.M. Haines and A.D. King, *J. Am. Chem. Soc.*, 100 (1978) 2925; (d) T. Yoshida, Y. Ueda and S. Otsuka, *J. Am. Chem. Soc.*, 100 (1978) 3941; (e) A.D. King, R.B. King and D.B. Yang, *J. Am. Chem. Soc.*, 103 (1981) 2699, (f) W.A. Sleiger, R.S. Sapienza, R. Rayford and L. Lam, *Organometallics*, 1 (1982) 1728
- 5 (a) P.C. Ford, R.G. Rinker, C. Ungermann, R.M. Laine, V. Landis and S.A. Moya, *J. Am. Chem. Soc.*, 100 (1978) 4595; (b) P.C. Ford, R.G. Ringer, R.M. Laine, C. Ungermann, V. Landis and S.A. Moya, *ACS Adv. Chem. Ser.*, 173 (1979) 81.
- 6 F.A. Cotton, (Ed.), *Inorganic Syntheses*, Vol. 13, 1972, p. 95.
- 7 M. Angoletta, L. Malatesta and G. Caglio, *J. Organomet. Chem.*, 94 (1975) 99
- 8 G. Ciani, M. Manassero, V.G. Albona, F. Canziani, G. Giordano, S. Martinengo and P. Chini, *J. Organomet. Chem.*, 150 (1978) C17.
- 9 L. Garlaschelli, S. Martinengo, P. Chini, F. Canziani, and R. Bau, *J. Organomet. Chem.*, 213 (1981) 379.
- 10 A.D. King, R.B. King, M.Z. Iqbal and C.C. Frazier, *J. Am. Chem. Soc.*, 100 (1978) 1687.
- 11 Notably, the hydride anion may also be synthesized using 2-ethoxyethanol rather than methanol. A weak IR band at 1655 cm^{-1} before hydrolysis of the solution in the synthesis indicates the presence of an "ethoxyethoxycarbonyl" species analogous to the methoxycarbonyl species observed by Garlaschelli et al. [9]. These workers concluded that alkoxide attack on coordinated carbonyl in $\text{Ir}_4(\text{CO})_{12}$ is the first step in the formation of the hydride under basic alcoholic conditions
- 12 D. Darensbourg and A. Rokicki, *Organometallics*, 1 (1982) 1685.