Homogeneous Catalysis of the Water Gas Shift Reaction Using Iron Pentacarbonyl

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Abstract: Measurements have been carried out to determine the rate of hydrogen production by the water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) operating at temperatures less than 200 °C with iron pentacarbonyl serving as a catalyst precursor in a basic methanol-water solution. Turnover numbers of 2000 mol H_2/mol $Fe(CO)_5$ per day are achieved at 180 °C with this system. The reaction is shown to be zero order with respect to carbon monoxide. The temperature dependence of this reaction corresponds to an activation energy of 22 kcal/mol. It is shown that a threshold pressure of carbon monoxide exists above which the catalytic reduction of water can be sustained. Below this pressure, the $Fe(CO)_5$ is destroyed in a stoichiometric reduction of water. The overall kinetics of this reaction as well as this threshold phenomenon can be explained according to previously published mechanisms.[4c,1]

Introduction

The water gas shift reaction is used extensively to increase the hydrogen content of water gas (synthesis gas) through the reaction of carbon monoxide with steam to form hydrogen and carbon dioxide according to the reaction

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g) \qquad (1)$$

$$\Delta G°_{298} = -6.82 \text{ kcal}$$

$$\Delta H°_{298} = -9.84 \text{ kcal}$$

$$\Delta S°_{298} = -10.1 \text{ cal/deg}$$

This reaction is carried out over a wide range of pressures and synthesis gas compositions at temperatures in excess of 300 °C using heterogeneous catalysts consisting of iron oxides promoted by Cr_2O_3. The exothermicity of this reaction generally requires that industrial processes for the production of hydrogen be carried out in two or more stages with intermediate cooling.[2] Under operating conditions where steam is present in excess, the above reaction is considered to be first order in carbon monoxide.[3]

This same reaction can proceed at lower temperatures with water being present as a liquid according to the equation

$$CO(g) + H_2O(l) \rightleftharpoons H_2(g) + CO_2(g) \qquad (2)$$

$$\Delta G°_{298} = -4.76 \text{ kcal}$$

$$\Delta H°_{298} = +0.68 \text{ kcal}$$

$$\Delta S°_{298} = +18.3 \text{ cal/deg}$$

Reaction 2 differs from (1) above in that it is slightly endothermic ($\Delta H°$ differing from that of reaction 1 by the heat of vaporization of water) and yet is strongly favored from a free-energy standpoint because of the large positive entropy change associated with this latter reaction.

There are obvious benefits associated with carrying out the shift reaction at lower temperatures, thus eliminating the need to vaporize water. Consequently, several laboratories have examined homogeneous catalyst systems capable of accelerating reaction 2 and several reports concerning this reaction and closely related hydroformylation reactions have been published recently.[4] This paper reports results obtained from a series of studies involving reaction 2 carried out at elevated pressures and temperatures ranging from 110 to 180 °C using a catalyst system based on $Fe(CO)_5$.

Experimental Section

The water gas shift reactions were carried out in small stainless steel (Type 304) autoclaves having an internal volume of 700 mL. These autoclaves were mounted vertically in electrically heated ovens each having a magnetic stirrer (Fisher Flexa-Mix) built into its base. An ordinary 1-in. long Teflon-coated magnetic stirring bar was used to stir the liquid phase within the bomb. Each oven contained a 576-W heater which was controlled by a proportional controller (Love Controls Corp. Model 71) using a thermocouple sensor mounted in a thermocouple well extending into the interior of the bomb. After a short warmup period (~25 min) temperatures within the bomb could be maintained constant to within ±1 °C as determined by an Omega Engineering Inc. Model 250T digital thermocouple read-out meter. The pressure within each bomb was monitored using a Matheson Model 63 test gauge (0-3000 psig), accurate to 0.25% of full scale, which was attached to each bomb through the closure at the top.

A Fisher Model 1200 gas partitioner using a 6.5-ft 80-100 mesh Columnpak PQ column followed by a 11-ft 13X molecular sieve column was used to analyze gas mixtures (CO, CO_2, Ar, H_2) extracted from the bomb. Helium was used as a carrier gas in all determinations. Care was taken to ensure that all hydrogen analyses were performed at concentrations within the linear response region of the sensitivity curve for this gas. Argon was used as an internal standard. A Varian CDS-111 digital integrator was used to integrate the output from the gas partitioner. Two methods were used to compute gas compositions expressed as partial pressures from this data. Both required the prior determination of external sensitivity factors for each gas. The first method required that the pressure of the contents in the bomb be recorded at the time each gas sample was taken. Each pressure was corrected to total pressure of noncondensable gases by subtracting solvent vapor pressure which had been measured previously. The individual partial pressures of the three gases of interest were then computed using the total pressure thus computed and gas mole fractions obtained in the gas analysis according to Dalton's law. The second method used argon as an internal standard. After the initial loading of Ar and CO, a sample analysis was run at room temperature to determine the exact composition of the mixture. The partial pressure of argon computed was then corrected to the high temperature at which the kinetic data were obtained, thus allowing partial pressures of the gases of interest to be computed directly using argon as an internal standard. This latter method has the advantage of not requiring that the total pressure be recorded along with each gas analysis, thus eliminating one source of experimental error. Since all partial pressures are measured relative to that for argon, this latter method does not reflect the small losses of gas due to sampling. In every instance, partial pressures calculated according to the two methods were found to be in excellent agreement. The average experimental error in H_2 partial pressure, derived from repetitive measurements, is ±3 psia; that for the other gases is ±1 psia.

Although glass liners were available, preliminary studies showed that the rate of reaction is totally unaffected by the presence of such a liner. Consequently the reactions reported here were all carried out in unlined autoclaves.

Gas sampling was accomplished by releasing samples of the interior gas mixture into a sample chamber which uses a small balloon to maintain a low positive pressure against a septum. This chamber was purged three times with the gas mixture prior to removing a sample

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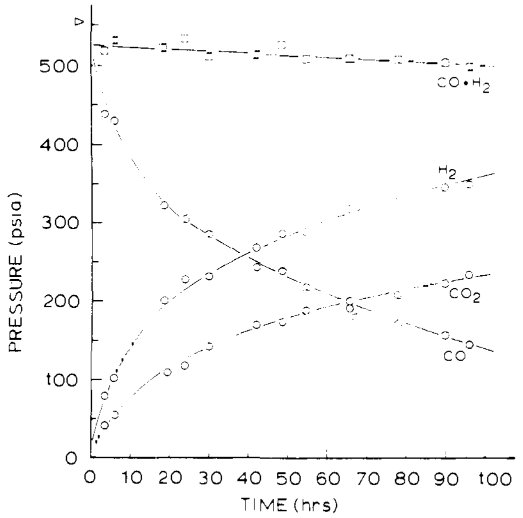

Figure 1. Partial pressures of H_2, CO_2, and CO as a function of time. Catalyst solution: $Fe(CO)_5$ (2.23 mmol), KOH (39 mmol), 200 mL (25% H_2O, 75% CH_3OH). Temperature: 140 °C. Loading pressure of CO corrected to 140 °C: 556 psia.

for injection on the gas partitioner by means of a Pressure-Lok syringe.

All gases used were CP grade or the equivalent having quoted purities of 99.5% or better. Fisher Certified ACS grade methanol and laboratory distilled water were used to make up the various solvent mixtures employed in these studies. Fisher Certified ACS grade potassium hydroxide and practical grade potassium formate were employed as bases. The iron pentacarbonyl was purchased from Alfa Division of Ventron Corp. It had a quoted purity of 99.5% and was used as received with no subsequent purification.

Results and Discussion

Data obtained in these experiments are shown in Figures 1-6 where measured partial pressures of the gases of interest are shown plotted as a function of time over long time spans. The familiar units of "pounds per square inch" rather than SI units have been used to present the data primarily as a matter of convenience. However, an additional benefit is derived from this choice of units, namely, that for systems at 140 °C containing 200-mL liquid loadings such that the gas volume is 500 mL, an increment of 1 psia exactly corresponds to the production of 1 mmol of gas and vice versa. Consequently the ordinates of Figures 1-4 correspond numerically to millimoles produced or consumed for each gas as well as partial pressure.

In a typical experiment, the bomb is loaded with a methanol-water solution containing dissolved KOH and $Fe(CO)_5$ and charged with a CO-Ar mixture to the desired pressure. It is then heated rapidly with stirring during which time the pressure rises owing to thermal expansion of the gas and the increasing vapor pressure of the solvent. At approximately 110 °C the internal pressure ceases to rise, and with large loadings of base even falls for a short time, due to the reaction of CO with base to produce formate.[5] Following this interruption, the pressure again begins to rise and the first traces of H_2 can be detected in gas samples taken from the bomb. The time lapse between this drop in pressure which corresponds to the onset of the shift reaction and the point at which thermal equilibrium is established seldom exceeds 10 min.

Figure 1 shows the results obtained in a typical experiment such as described above. Inspection of these data reveals that the reaction is indeed catalytic in $Fe(CO)_5$ as well as base in that more than 300 mmol of H_2 is produced by a system containing 2.23 mmol of $Fe(CO)_5$ and 39 mmol of base. The line indicating the sum of partial pressures of CO and H_2 is nearly constant indicating that 1 mol of CO is consumed for every mol of H_2 produced during the course of the experiment.[6] Thus it can be inferred that the hydrogen is generated solely as a result of the water gas shift (wgs) reaction rather than a thermal decomposition of the formate present in the system.

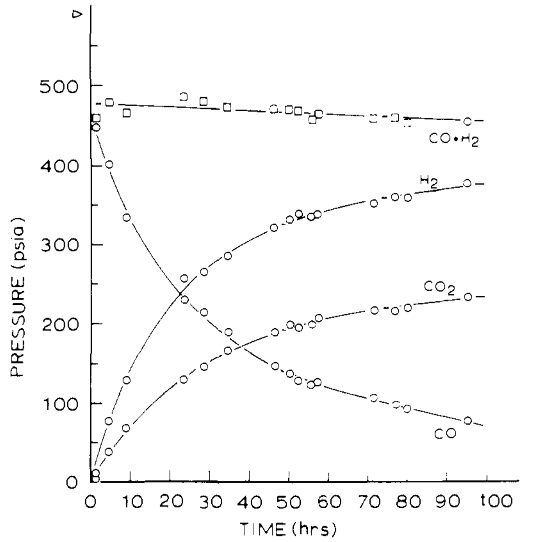

Figure 2. Partial pressures of H_2, CO_2, and CO as a function of time. Catalyst solution: $Fe(CO)_5$ (2.23 mmol), KOH (109 mmol), 200 mL (25% H_2O, 75% CH_3OH). Temperature: 140 °C. Loading pressure of CO corrected to 140 °C; 590 psia.

At time zero the line indicating the sum of the partial pressures of carbon monoxide P_{CO} and hydrogen P_{H_2} shares a common intersection with P_{CO} at a pressure of CO (520 psia) that exists at the beginning of the wgs reaction following the uptake of CO to produce formate. The loading pressure of carbon monoxide when corrected to 140 °C is 556 psia as indicated by the arrow along the Y axis. The discrepancy between these two pressures, 36 psi, indicates that 36 mmol each of CO and OH^- have been consumed to form a like amount of formate prior to the onset of the wgs reaction.

The experiment shown in Figure 2 differs from that of Figure 1 in only one respect; namely, more base (109 mmol) was present in the initial loading. Here the extrapolation of $P_{CO} + P_{H_2}$ yields 480 psia as the partial pressure of CO present at the onset of the wgs reaction. The loading pressure of CO corrected to 140 °C is 590 psia for this experiment. Thus it is seen that 110 mmol of CO and OH^- have been consumed to produce formate in the initial period preceding the initiation of the wgs reaction. Similar experiments using still larger amounts of base (up to 326 mmol of KOH) all yield the same result, namely, that within experimental error (±4 mmol) the initial uptake of CO corresponds to a quantitative conversion of hydroxide ion to formate ion, and only after this reaction is complete does the wgs reaction begin. The rate of hydrogen production is found to be the same in each experiment, however. When sodium formate is substituted for potassium hydroxide as the base there is no initial uptake of CO as might be expected. However, the wgs reaction proceeds in the same manner as if KOH were used as the base.

Figures 1 and 2 show that the vapor concentration of CO_2 is less than that for H_2 at all pressures. A similar discrepancy has been reported in cases where the wgs reaction is carried out in alcohol-aqueous base systems using ruthenium and rhodium carbonyl clusters as catalysts. The suggestion has been made that carbonate formation is largely responsible for the loss of CO_2 in these systems.[4h] The data shown in Figure 1 and 2 reveal that this is not an adequate explanation. Firstly, the loss of CO_2 relative to H_2 exceeds 100 mmol at late times, which is far in excess of the amounts of base used in Figure 1. Secondly, a comparison between the data of Figure 1 and 2 reveals

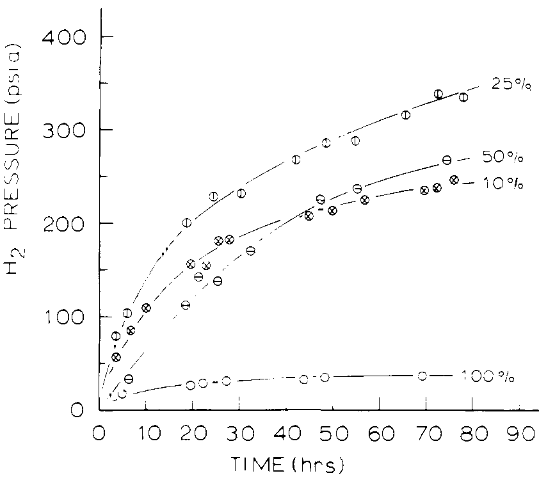

Figure 3. Partial pressure of H_2 as function of time for various solvent mixtures. Catalyst solutions: $Fe(CO)_5$ (2.23 mmol), KOH (39 mmol), 200 mL of H_2O-CH_3OH solutions with compositions ○, 100%; ⊖, 50%; Φ, 25%; ⊗, 10% water by volume. Temperature: 140 °C. Loading pressure of CO corrected to 140 °C: ~550 psia for each experiment.

that the discrepancy between the vapor concentrations of H_2 and CO_2 is largely independent of base concentration. Finally, the ratio of P_{CO_2} to P_{H_2} is found to remain approximately constant over the whole range of each experiment shown in Figures 1 and 2. This indicates that the dominant cause for this discrepancy is the higher solubility of CO_2 relative to H_2 in the aqueous methanol solutions used here. To demonstrate this, a series of reactions were carried out which differed from the conditions employed in Figure 1 with regard to the volume of solvent employed. The ratio of P_{CO_2}/P_{H_2} increased with decreasing volume of solvent. For solvent loadings of 300, 200, and 100 mL the ratios of partial pressures were found to be 0.57, 0.64, and 0.81, respectively. The solubility of H_2 is expected to be an order of magnitude less than that for CO_2 so that, assuming Henry's law to hold, one can easily show that to a good approximation

$$\frac{P_{CO_2}/P_{H_2}}{1 - P_{CO_2}/P_{H_2}} = (RTK_H)^{-1}\left(\frac{V_g}{V_l}\right) \qquad (3)$$

where K_H represents the solubility of CO_2 in the liquid phase at 1 atm pressure. The data above yield a good straight line when plotted according to eq 3, giving a value of 0.021 M atm^{-1} for the solubility of CO_2 in a 25% water-75% methanol mixture at 140 °C.[7]

The preceding discussion has dealt primarily with operational characteristics of the wgs reaction carried out in a closed system. Turning to the kinetics proper it is seen that in the presence of excess water the reaction rate can be expected to depend upon the following variables: (a) the nature of the solvent, (b) pH, (c) amount of $Fe(CO)_5$ present, (d) carbon monoxide pressure, and (e) temperature.

Figure 3 compares the rate of hydrogen production for a series of reactions using methanol-water mixtures of various compositions. The data reveal that a mixture containing 25% water and 75% methanol by volume is the preferred solvent system for the wgs reaction. Pure water is seen to be a very poor choice of solvent. Among the alcohol-water mixtures, it is seen that hydrogen production falls off more abruptly in the mixture containing 10% water than in the solutions richer in water. This is expected since approximately 23% of the water has been consumed over the course of this reaction. Aside from the possible role of polarity on the transition state, it seems likely that the 25% water system represents an optimum balance between water concentration and CO solubility, thus providing the most favorable conditions for the wgs reaction. The solvent system has been used exclusively in all other experiments described here.

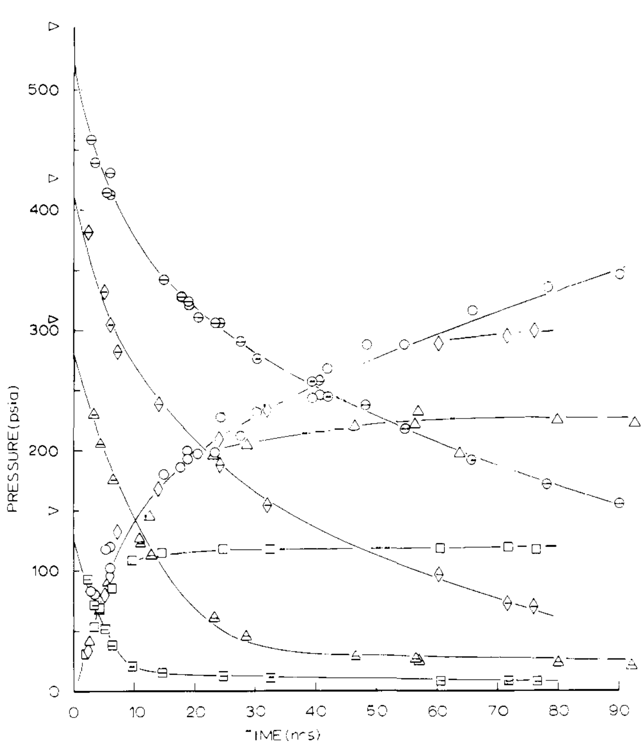

Figure 4. Partial pressure of H_2 and CO as a function of time for series of experiments differing only with respect to loading pressure of CO. Catalyst solution: $Fe(CO)_5$ (2.23 mmol), KOH (39 mmol), 200 mL (25% H_2O, 75% CH_3OH). Temperature: 140 °C. Loading pressures of CO corrected to 140 °C: ○, 556; ◇, 425; △, 309; □, 150 psia.

In order to examine the dependency of reaction rate on the amount of $Fe(CO)_5$ initially present, three experiments were conducted at 160 °C under a carbon monoxide pressure of ~560 psia using 200 mL of 25% water-methanol solutions each containing 39 mmol of KOH and 0.74, 1.48, and 2.23 mmol of $Fe(CO)_5$, respectively. The data (not shown) all resemble that of Figure 1 with initial H_2 production rates as determined over the first 5 h of each run being 0.74 mmol of $Fe(CO)_5$, 20 psi H_2/h; 1.48 mmol of $Fe(CO)_5$, 36 psi H_2/h; 2.23 mmol of $Fe(CO)_5$, 60 psi H_2/h. Thus, within the accuracy of these experiments, the rate of reaction is proportional to the concentration of $Fe(CO)_5$.

Figure 4 compares the hydrogen production for a series of experiments that differ only with respect to the initial CO pressure. The discrepancy between loading pressure of CO and the partial pressure of CO at the onset of the wgs reaction corresponds to a quantitative conversion of hydroxide to formate regardless of the loading pressure. Thus it can be inferred that the composition of the solution phase is the same at the onset of the wgs reaction in each case. The partial pressure of hydrogen produced in the early stages of each reaction is seen to fall on a common curve. However, with the exception of the experiment involving the highest pressure of CO (initial P_{CO} = 556 psia), the hydrogen production abruptly ceases at some point in the reaction. A comparison with the curves describing CO consumption reveals that in each experiment the H_2 production ceases when the CO pressure falls to a value between 50 and 100 psia. Thus it can be concluded that (a) the wgs reaction is zero order in pressure and (b) an abrupt loss in catalytic activity occurs when the pressure of CO falls to a low pressure (50 psia < P_{CO} < 100 psia).

The rate of production of hydrogen increases rapidly with temperature as seen in Figure 5. Again a quantitative conversion of hydroxide to formate occurs prior to each reaction

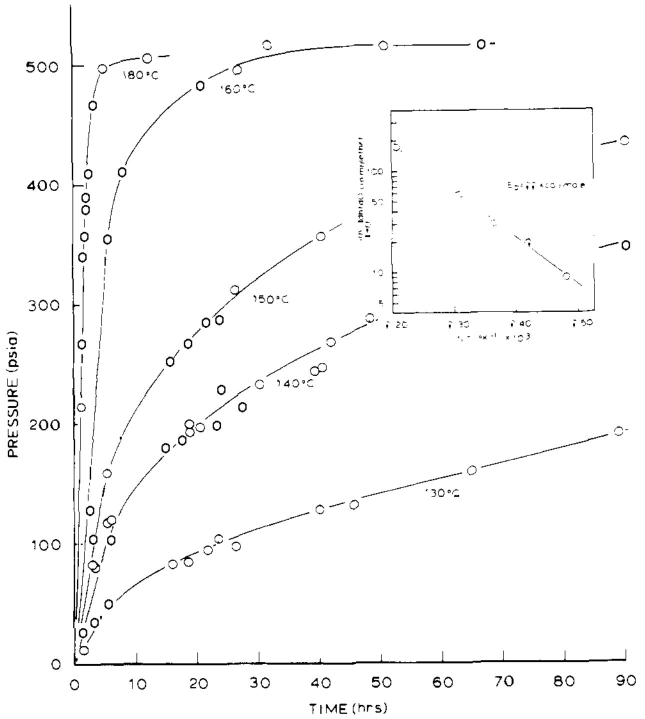

Figure 5. Partial pressure of H_2 as function for a series of experiments varying with respect to temperature. Catalyst solution: $Fe(CO)_5$ (2.23 mmol), KOH (39 mmol), 200 mL (25% H_2O, 75% CH_3OH). Temperatures: 130-180 °C. Loading pressure of CO corrected to the temperature of each experiment: 130 °C, 575 psia; 140 °C, 556 psia; 150 °C, 642 psia; 160 °C, 585 psia; 180 °C, 592 psia.

indicating that the solution-phase composition at the onset of the wgs is independent of temperature. Since the wgs reaction is zero order with respect to CO, it follows that the rates of hydrogen production corresponding to the initial slopes shown in Figure 5 are directly proportional to the rate constant for the wgs reaction. The rates of hydrogen production calculated from these initial slopes are shown as a function of reciprocal temperature in the inset of Figure 5. These data describe a good straight line whose slope corresponds to an activation energy of 22 kcal/mol. Since 2.23 mmol of $Fe(CO)_5$ is used in each of these reactions, the rates of production shown in the inset can be multiplied by 24/2.23 = 11 to yield turnover numbers expressed as mol H_2/mol $Fe(CO)_5$ per day. Thus at 180 °C, the rate of H_2 production, 190 mmol/h, corresponds to a turnover number of 2000 mol H_2/mol $Fe(CO)_5$ per day.

Figure 6 shows the results of two experiments carried out at low CO pressures where a loss of catalytic activity was found previously (Figure 4). Sodium formate is used a base in these experiments. These experiments differ only with respect to the amount of $Fe(CO)_5$ used. In both cases the wgs reaction occurs as indicated by a drop in CO pressure. However, in contrast to previous reactions, the hydrogen produced far exceeds the CO consumed as indicated by the rise in the curve describing the sum of partial pressures of CO and H_2. The difference between this sum and the initial pressure of CO represents hydrogen produced in excess of that derived from the wgs reaction. At the temperature of these experiments (110 °C), 12 and 23 psia correspond to an excess of 13 and 25 mmol of H_2, respectively. The ratios of excess hydrogen to $Fe(CO)_5$ at the end of the reactions are 13/2.23 = 5.8 mol H_2/mol $Fe(CO)_5$ and 23/4.46 = 5.6 mol H_2/mol $Fe(CO)_5$, suggesting that the excess hydrogen results from the decomposition of $Fe(CO)_5$. The solution remaining at the end of these two experiments is colorless, indicating an absence of dissolved $Fe(CO)_5$. Instead a white precipitate of ferrous carbonate is found, indicating that the decomposition of $Fe(CO)_5$ responsible for the stoichiometric production of H_2 terminates with Fe(II).[8] Since ferrous carbonate was also present at the conclusion of each of the three lower pressure experiments shown in Figure 4, it is reasonable to assume that the decomposition of $Fe(CO)_5$ found here is responsible for the loss of catalytic activity seen in Figure 4.

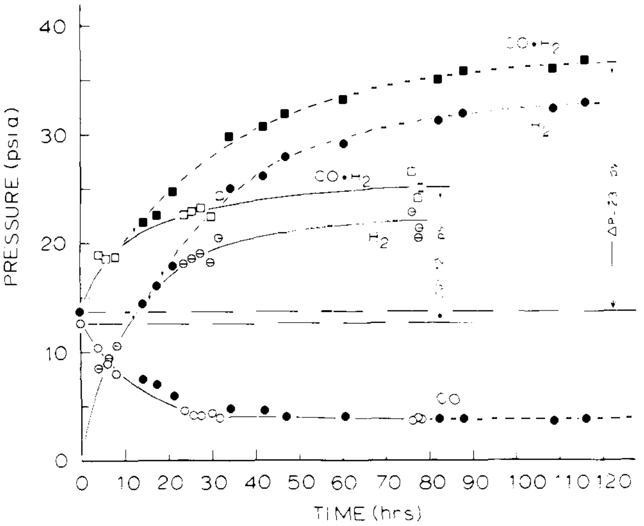

Figure 6. Partial pressures of H_2 and CO as function of time for reactions carried out at low pressures of carbon monoxide. Catalyst solutions: HCOONa (58 mmol), 200 mL (25% H_2O, 75% CH_3OH). Open symbols; $Fe(CO)_5$ (2.23 mmol). Solid symbols; $Fe(CO)_5$ (4.46 mmol). Temperature: 110 °C. Loading pressures of CO corrected to 110 °C: open symbols, 12.6 psia; solid symbols, 13.7 psia.

The liquid phase of the wgs reaction has been examined spectroscopically under conditions of high CO pressure ($P_{CO} \approx 570$ psia, T = 120 °C) using an autoclave-infrared cell (spectroclave) developed in this laboratory.[9] Only two iron carbonyl derivatives can be identified in the reaction mixture, $Fe(CO)_5$ and $HFe(CO)_4^-$. As was found by Wada and Matsuda,[10] the relative intensity of the $HFe(CO)_4^-$ absorption bands decreased in comparison to those for $Fe(CO)_5$ as the temperature rose to 120 °C. The intensities of these two species remained unchanged as the reaction proceeded over a 26-h period at this temperature, indicating that no significant loss of iron carbonyls occurred over this time span.

The pH of solution phases for systems having compositions identical with Figures 1 and 2 has been monitored during the course of the wgs reaction. Here pH measurements were made on small (3 mL) samples of the liquid phase which were withdrawn periodically from the autoclave. At the beginning of the wgs reaction, the pH equals 8.6 indicating that, as expected, potassium formate is the principal base present at the onset of the wgs reaction. The pH falls as the reaction proceeds reaching values of pH ≃7.4 in the late stages of the reaction. This is presumably the result of an acid-base reaction involving CO_2 produced by the wgs reaction:

$$CO_2 + H_2O + HCO_2^- \rightleftharpoons HCO_2H + HCO_3^- \quad (4)$$

The conclusions drawn from the experiments described above can be summarized as follows: (1) the wgs reaction proceeds most rapidly in a moderately polar solvent system; (2) a rapid and, within experimental error, quantitative conversion of hydroxide ion to formate ion occurs prior to the onset of the wgs reaction so that formate is the dominant species of base present during the course of the wgs reaction; (3) the reaction is zero order in CO; (4) the temperature variation of the reaction is characterized by an activation energy of 22 kcal/mol; (5) of the various derivatives possible from $Fe(CO)_5$ in base only $HFe(CO)_4^-$ and the parent compound $Fe(CO)_5$ are present to any appreciable extent during the course of the wgs reaction; (6) decomposition of $Fe(CO)_5$ takes place at low CO pressures in a reaction producing 5.7 mol H_2/mol $Fe(CO)_5$; (7) the pH of the solution phase drops from an initial value of 8.6 immediately following the initial uptake of CO, i.e., the onset of the wgs reaction to a value of 7.4 at late stages of the reaction.

Two mechanisms have been put forth to explain the catalytic role of $Fe(CO)_5$ in the wgs reaction.[4c,e,l] However, the fact that the pH of the solution is so low during the course of the reaction makes the mechanism proposed by Pettit[4c,l] especially attractive. This mechanism considers the reduction of water to occur in a four-step cycle:

$$Fe(CO)_5 + OH^- \rightarrow HFe(CO)_4^- + CO_2 \qquad (5a)$$

$$HFe(CO)_4^- + H_2O \rightleftharpoons H_2Fe(CO)_4 + OH^- \qquad (5b)$$

$$H_2Fe(CO)_4 \rightarrow Fe(CO)_4 + H_2 \qquad (5c)$$

$$Fe(CO)_4 + CO \rightarrow Fe(CO)_5 \qquad (5d)$$

The intermediacy of $H_2Fe(CO)_4$ was necessary to account for the observation made by Pettit that both Reppe hydroformylation and wgs reactions did not proceed to any measurable extent at a pH greater than 10.7 when catalyzed by iron pentacarbonyl. In order for the reaction to be zero order in CO, steps 5a or 5c can be rate determining. However, the fact that the rate of H_2 production falls off with decreasing pH requires that step 5a be the rate-determining step in the sequence above.

Takegami and co-workers[11] have shown that $HFe(CO)_4^-$ will reduce nitrobenzene to aniline with a stoichiometry requiring the transfer of 11 electrons per $HFe(CO)_4^-$ ion. Pettit[4] has interpreted this unusual stoichiometry to indicate that $HFe(CO)_4^-$ and its decomposition products undergo a succession of two electron-transfer steps:

$$\begin{array}{llr}
HFe(CO)_4^- & \longrightarrow Fe(CO)_4 + H^+ + 2e^- & (5e) \\
Fe(CO)_4 + 2OH^- & \longrightarrow Fe(CO)_3 + CO_2 + H_2O + 2e^- & (5f) \\
\vdots & \quad\ \vdots & \\
Fe(CO) + 2OH^- & \longrightarrow Fe^0 + CO_2 + H_2O + 2e^- & (5i) \\
Fe^0 & \longrightarrow Fe^{2+} + 2e^- & (5j)
\end{array}$$

The data of Figure 6 show that a similar reduction of water occurs at pH values of 8.5 or less. Thus the observed loss of catalytic activity observed in Figure 4 can be explained by assuming that, at a partial pressure between 50 and 100 psia, the concentration of dissolved carbon monoxide has fallen to such a low value that CO no longer competes successfully with hydroxide ion for the $Fe(CO)_4$ formed in step 5c. As a result the cycle (5a)-(5d) is broken and $Fe(CO)_4$ enters the series of reductive steps (5f)-(5j) resulting in destruction of the catalyst. When the system is operating in this latter mode, each mole of $Fe(CO)_5$ is capable of producing 1 mol of H_2 by virtue of steps (5a)-(5c) and five more through steps (5f)-(5j) in agreement with the data of Figure 6.

The fact that the catalytic properties of the $Fe(CO)_5$ system depend upon the successful competition of dissolved CO over hydroxide ion for $Fe(CO)_4$ produced in step 5c explains the early loss in catalytic activity that occurs when pure water is used as a solvent (Figure 3). At 25 °C, the solubility of CO in water is less than that in methanol by an order of magnitude.[12] A similar difference in solubility can be expected at 140 °C. Therefore the concentration of CO dissolved in water at a pressure of 500 psia can be expected to be much the same as that present in a methanol-water mixture at 50 psia and therefore below the threshold necessary to sustain the cycle (5a)-(5d).

Conclusion

Iron pentacarbonyl has been shown to be an active catalyst precursor for the water gas shift reaction operating at moderately low temperatures (130-180 °C) using CO gas and water dissolved in base-methanol solutions as reactants. The reaction has been shown to be zero order with respect to carbon monoxide. The increase in reaction rate with temperature corresponds to an activation energy of 22 kcal/mol. The pH of the solution phase is found to be quite low (8.6-7.4) over the course of the reaction. At low pressures of CO, the iron pentacarbonyl is found to lose its activity by reducing water to hydrogen in a stoichiometric reaction leaving $FeCO_3$ as the final product. A threshold CO pressure has been found above which catalytic reduction of water is achieved and below which water is reduced at the expense of the catalyst. The overall kinetics of this reaction including the threshold behavior can be explained in terms of mechanisms proposed by Pettit et al.[4c,l]

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References and Notes

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(5) This was verified by quenching a reaction immediately following this uptake of CO. Infrared analysis of the liquid phase revealed the presence of formate.

(6) The data shown in Figures 1–3 were calculated using external sensitivity factors and measured gauge pressures (method 1 in the Experimental Section). Thus the slight negative slope of the $P_{CO} + P_{H_2}$ line reflects losses due to sampling rather than any subsequent loss of CO to form formate. The slope of the same line determined using Ar as an internal standard is zero.

(7) The solubility of CO_2 in pure methanol has been determined at temperatures ranging from 0 to 75 °C by (a) I. P. Krichevskii and E. S. Lebedeva, *Zh. Fiz. Khim.*, **21**, 715 (1947); (b) K. Ohgaki and T. Katayama, *J. Chem. Eng. Data*, **21**, 53 (1976). These data, expressed as mole fractions, are found to vary linearly with T^{-1}, indicating that the heat of solution is relatively insensitive to temperature. A linear extrapolation yields a mole fraction solubility of $X_{CO_2} = 11 \times 10^{-4}$ atm^{-1} at 140 °C. Likewise a long extrapolation of the density function for methanol found in E. D. Washburn, Ed., "International Critical Tables", Vol. 3, McGraw-Hill, New York, 1928, p 27, yields a value of $\bar{V} = 48$ cm^3/mol for the molar volume of methanol at 140 °C. This can be combined with the mole fraction of CO_2 to yield a solubility of $K_H = X_{CO_2}/\bar{V} = 0.023$ M atm^{-1}, which agrees quite well with the value obtained experimentally for the alcohol–water mixture used here. One can infer from these data that relatively little CO_2 is tied up as bicarbonate ion in the catalyst solutions at the temperatures employed here. While some conversion of CO_2 to bicarbonate must occur as the pH falls from 8.6 to 7.4 according to eq 4, the amount is undoubtedly very small. The amount of CO_2 converted to bicarbonate in order to effect the same pH change in an aqueous solution of formate ion at room temperature can be shown to be only 0.02% of the formate ion originally present, which for a solution containing 39 mmol of formate corresponds to a conversion of $\sim 10^{-2}$ mmol of CO_2.

(8) The standard hexacyanoferrate(III) test and IR analysis were used to confirm that the white precipitates were $FeCO_3$. Gravimetric analysis showed that the $FeCO_3$ formed corresponded to ~70% conversion of $Fe(CO)_5$ originally present.

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