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Reactions of $Fe(CO)_5$ and $H_2Fe(CO)_4$ Related to the Water-Gas Shift Reaction

Ralph G. Pearson* and Hieko Mauermann

Contribution from the Chemical Laboratory of the University of California, Santa Barbara, California 93106. *Received June 8, 1981*

Abstract: The reaction of $Fe(CO)_5$ with base to form $HFe(CO)_4^-$ has a rate-determining step $Fe(CO)_5 + OH^- \rightarrow Fe(CO)_4COOH^-$ (k_1) at high base concentration with $k_1 = 70\ M^{-1}\ s^{-1}$ at 25 °C in 70:30 methanol–water. At low base concentration the rate-determining step is $Fe(CO)_4CO_2^{2-} \rightarrow Fe(CO)_4^{2-} + CO_2$ (k_3), with the observed rate depending on the square of the total base concentration. The thermal decomposition of $H_2Fe(CO)_4$ has a rate-determining step of $H_2Fe(CO)_4 \rightarrow H_2 + Fe(CO)_4$ and a stoichiometry in 70:30 methanol–water of $4H_2Fe(CO)_4 \rightarrow 3H_2\uparrow + H_2Fe_3(CO)_{11} + Fe(CO)_5$. In the water–gas shift reaction, $Fe(CO)_5$ is a poor catalyst because of the conflicting pH requirements of the two cyclic processes.

The use of $Fe(CO)_5$ as a homogeneous catalyst for the water-gas shift reaction (WGSR) was suggested by Reppe and Reindl as early as 1953.[1] This suggestion was based on work done even earlier (1930–1945) in the Main Research Laboratories of BASF, the publication of which was delayed by World War II. The proposed catalytic cycle was

$$H_2O + Fe(CO)_5 = H_2Fe(CO)_4 + CO_2 \qquad (1)$$

$$H_2Fe(CO)_4 + CO = H_2 + Fe(CO)_5 \qquad (2)$$

$$CO + H_2O = CO_2 + H_2 \qquad (3)$$

Following the discovery of homogeneous catalysis of the WGSR by other transition metals,[2] the ability of $Fe(CO)_5$ to act as a catalyst has been verified and a number of studies have been made.[3,4] The results are in good agreement with a mechanism first given by Pettit (eq 4–7).[3]

$$Fe(CO)_5 + OH^- \rightarrow HFe(CO)_4^- + CO_2 \qquad (4)$$

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

$$H_2Fe(CO)_4 \rightarrow H_2 + Fe(CO)_4 \qquad (6)$$

$$Fe(CO)_4 + CO \rightarrow Fe(CO)_5 \qquad (7)$$

In 75:25 v/v methanol–water under high-pressure, catalytic conditions, the rate of hydrogen production is first order in iron carbonyl catalyst, independent of CO pressure and sensitive to the pH.[4] Because of the reaction between OH^- and CO to give formate ion, the pH is buffered to a narrow range between 8.6 and 7.4. The overall activation energy is 22 kcal/mol. The turnover number is 2000 mol of H_2/mol of $Fe(CO)_5$ per day at 180 °C.

Since the rate falls as the pH changes from 8.6 to 7.4, it appears that reaction 4 is rate determining in this range.[4] It would be of interest to examine the details of reactions 4 and 6 more closely to see exactly how each is affected by pH. Clearly reaction 4 occurs in more than one step. Reaction 6 is only hypothetical since studies of the evolution of hydrogen from other transition-metal hydrides have revealed quite complex mechanisms.[5,6]

The relatively low turnover number for $Fe(CO)_5$ makes it unlikely to be a practical catalyst, even under ideal conditions. However it seems to be an exemplary model system, and worth studying from that viewpoint. Reactions of coordinated carbon monoxide with nucleophiles and evolution of hydrogen from metal hydrides must be key steps in the operation of any WGSR catalyst. The present work was undertaken to study reactions 4 and 6 separately under noncatalytic conditions. Except for a few cases, this means 25 °C, 1 atm pressure, and no CO initially present.

The solvent used as a mixture of 70% methanol and 30% water by volume. This mixture was selected because we found that a glass electrode gave reliable values of the pH.[7] Since the apparent pK_s of this solvent mixture is known to be 14.2,[8] it was possible to prepare buffer solutions of known pH and known activities of OH^- plus CH_3O^- in this mixture. Fortunately, it turned out that King's catalytic studies were done in a very similar mixture of methanol–water.[4b]

Experimental Section

All procedures involving $Fe(CO)_5$ and $H_2Fe(CO)_4$ were carried out in an atmosphere of nitrogen or argon. Standard bench-top methods using Schlenk apparatus and syringes with valves were used for synthesis, storage, and transfer. $Fe(CO)_5$ and $H_2Fe(CO)_4$ in alkaline solution are extraordinarily sensitive to air. The key to success is to stringently degas all reagents and solvents just before use.

Methanol, CP (Mallinckrodt), was degassed and vacuum distilled into a trap at −7 °C. Distilled water was degassed and vacuum distilled into a trap at −78 °C. $Fe(CO)_5$ (Alfa Products) was vacuum distilled. NaOH, CP (Mallinckrodt), was used without further treatment, as was boric acid. $Ba(OH)_2 \cdot 8H_2O$ (Mallinckrodt) was melted under vacuum and the water largely removed. Tris (Aldrich) was similarly treated.

HCl solutions were made by saturating CH_3OH with HCl gas and vacuum distilling. H_2SO_4 solutions were made from degassed 98% H_2SO_4. Vis-UV cells were placed in a small vessel filled with flowing nitrogen and filled with the reaction mixtures. Teflon stoppers, inserted with pincers, closed the cells which were then transferred to a Cary 118 spectrophotometer.

After flushing with the nitrogen-saturated solutions several times, the syringes of the Durrum Gibson D110 stopped-flow apparatus were ready to measure spectra. Infrared cells were filled under nitrogen and measurements made on a Perkin-Elmer 683 spectrometer. Several studies were made under medium pressure of CO or H_2 with a special infrared cell.[9]

Measurements of pH were made in a nitrogen atmosphere with an Orion 701A pH meter, using a Poly-mark no. 1880 electrode and an Orion Double Junction reference electrode. Gas sample analyses were performed in a Hewlett-Packard 5830A gas chromatograph, calibrated for the appropriate gas. Carbonsieve B columns were used. The carrier gas was a Linde prepared 9.5% H_2–90.5% He mixture.

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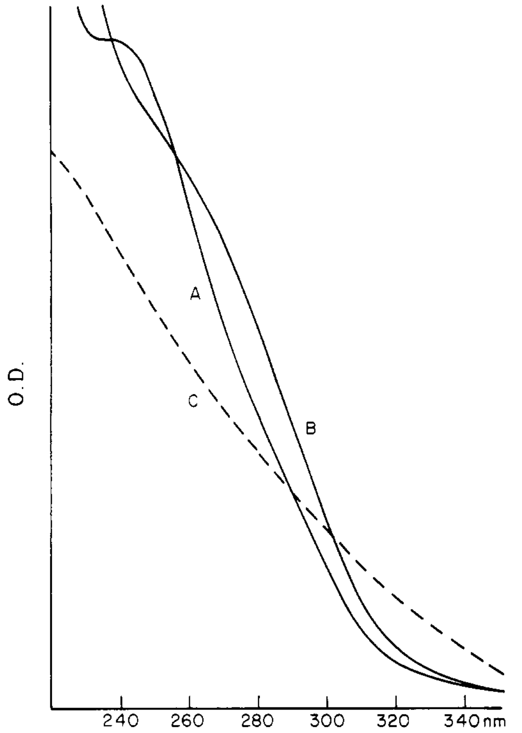

Figure 1. Spectral changes in UV for reaction of $Fe(CO)_5$ with base. (A) $Fe(CO)_5$; (B) H $Fe(CO)_4^-$; (C) spectrum of sample where air has leaked in.

Solutions of $Ba[HFe(CO)_4]_2$ and $NaHFe(CO)_4$ were made in wet methanol from $Fe(CO)_5$ and $Ba(OH)_2$ (1:1.5), or $Fe(CO)_5$, NaOH, and $Ba(OH)_2$ (1:1:1), following Krumholz and Stettiner.[10] After filtering and diluting with water, these solutions could be stored for several days at −78 °C. Preparation of $H_2Fe(CO)_4$ was carried out in three ways. It was made in solution by adding HCl to the salts prepared above. It was made by reacting NaOH in $Fe(CO)_5$ in methanol, adding H_2SO_4, and distilling into a trap at −190 °C. This gave a solution of $H_2Fe(CO)_4$ in methanol, about 0.05 M. It was also made as a pure liquid by following procedures in the literature.[11] There was no difference in the behavior of $H_2Fe(CO)_4$ prepared in any of these ways.

Results

Reaction 4 in more basic media should be written as

$$Fe(CO)_5 + 3OH^- \rightarrow HFe(CO)_4^- + CO_3^{2-} + H_2O \quad (8)$$

This reaction was discovered by Hieber in 1930.[12] In spite of its long history, there does not appear to be any kinetic study of the reaction. Actually reaction 8 is very fast, requiring stopped-flow techniques for base concentrations greater than 1×10^{-3} M.

Figure 1 shows the spectral change that occurs in the UV region for reaction 8. The initial curve is that of $Fe(CO)_5$ and the final curve is due to $HFe(CO)_4^-$. Isosbestic points are at 237.5, 255, and 350 nm and are maintained during the course of the reaction. No evidence is seen for any intermediates. In spite of the small changes in absorption, the UV spectrum is very satisfactory for measuring rates, either in the stopped-flow apparatus or in the Cary spectrometer.

The largest change was at 280 nm, which was the wavelength usually monitored. In several cases rates were also measured at 230 and 246 nm, with no differences found. The concentrations of $Fe(CO)_5$ were about 3×10^{-4} M, and the base concentration was varied from 1.2 to 175 mM using NaOH. The optical density changes obeyed a first-order rate law under these conditions. Figure 2 shows a plot of the pseudo-first-order rate constant for a series of experiments.

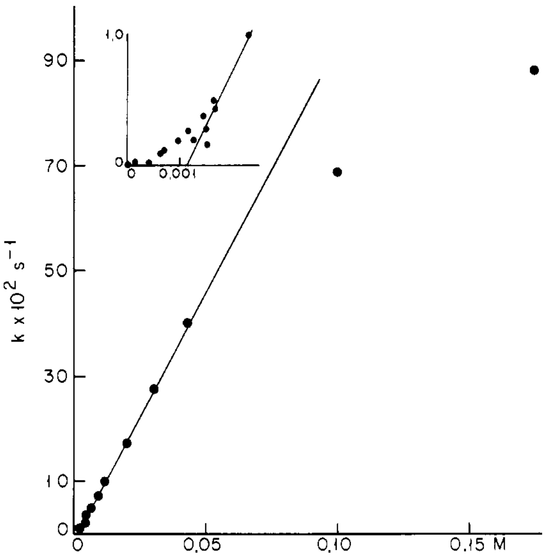

Figure 2. Plot of observed first-order constant vs. concentration of base for $Fe(CO)_5$ + base reaction. (Inset) expanded view of low base concentrations using buffer solutions.

As mentioned, exclusion of air is very important. Even traces of air gave much larger changes in absorbance and unreliable rate constants. Figure 1 shows as a dashed curve the changes in the UV spectrum found when air leaked into the cells. The spectrum is now due largely to $HFe_2(CO)_8^-$.[13]

While Figure 2 seems to go to the origin, a closer examination shows a small negative intercept. To examine the critical region below 1×10^{-3} M base, we made a series of buffer solutions. The most satisfactory were NH_3–NH_4Cl and H_3BO_3–NaOH, but low solubility in the mixed solvent used was a constant problem. The inset in Figure 2 shows the rate constants in the range (0.1–1.0) $\times 10^{-3}$ M base, where base means the sum of OH^- and CH_3O^- determined from a pH measurement.

Ammonia buffers giving a pH of 9, or about 10^{-5} M base, reacted so slowly that no reliable data could be obtained. Also $Fe(CO)_5$ in neutral solution or in weakly acid solution was stable for at least 48 h. The kinetics of reaction 8 in the slower reacting solutions were also checked in the IR spectrometer. The bands due to $Fe(CO)_5$ were steadily replaced by those due to $HFe(CO)_4^-$, again showing no evidence for intermediates. This is in agreement with studies of $Fe(CO)_5$ as a WGSR catalyst, where only the bands of $Fe(CO)_5$ and $HFe(CO)_4^-$ are observed.[4] The rate constants found from their changes were the same as those found from the UV spectrum.

No kinetic studies have been reported for the second reaction we have studied, the thermal decomposition of $H_2Fe(CO)_4$. It is known that the free acid is unstable, lasting only a few minutes at room temperature.[14] The salts containing the anion $HFe(CO)_4^-$ are much more stable in solution, if oxygen is excluded, lasting many hours even at 100 °C. Extra base, which may form $Fe(CO)_4^{2-}$, causes even more stabilization.

In the presence of carbon monoxide, the decomposition of $H_2Fe(CO)_4$ and $NaHFe(CO)_4$ leads to the formation of $Fe(CO)_5$.[1]

$$HFe(CO)_4^- + CO + H_2O \rightarrow Fe(CO)_5 + H_2 + OH^- \quad (9)$$

In the absence of CO, the decomposition products were reported as H_2, $Fe(CO)_5$, and polynuclear iron carbonyls.[14] Our results agree with the stoichiometry

$$4H_2Fe(CO)_4 \rightarrow 3H_2\uparrow + H_2Fe_3(CO)_{11} + Fe(CO)_5 \quad (10)$$

for the decomposition in 70:30 methanol–water at pH values between 3 and 8. The vis–UV spectral changes are consistent with 10. The red color of $H_2Fe_3(CO)_{11}$, due to its absorption maximum at 540 nm,[13] develops smoothly and is useful for kinetic studies.

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The color is actually due to the ion $HFe_3(CO)_{11}^-$, since the acid is completely ionized under these conditions.[13,15] After decomposition of $H_2Fe(CO)_4$ is complete, the infrared spectrum shows bands at 2018 and 1995 cm^{-1} due to $Fe(CO)_5$ and bands at 2065(w), 2000(s), 1975(s), and 1950(w) cm^{-1} due to $HFe_3(CO)_{11}^-$, with relative intensities as expected for equimolar amounts.[16,28]

The gas evolved from 1.0 mmol of $H_2Fe(CO)_4$ in methanol–water was collected in a gas buret, after passing through traps of NaOH solution and dry ice–acetone. The 17.7 mL of gas collected corresponds to 0.72 mol of gas per mol of Fe, or 2.90 mol of gas per 4 mol of Fe. By gas chromatographic analysis, the evolved gas was found to be 97–98% H_2, and the remainder CO. Variable amounts of CO_2 were also evolved if the gases were not trapped. This comes from the synthesis of $H_2Fe(CO)_4$, as in eq 4. In order to study the rate of decomposition of $H_2Fe(CO)_4$ as a function of pH, it was necessary to determine its pK_a in our solvent mixture. Table I shows a series of pK_a values for acetic acid in mixtures of methanol–water. The first values are simply the pH values, measured with a glass electrode, of an equimolar mixture of acetic acid and sodium acetate. These figures may be compared with the accurate data of Grunwald.[17]

With this calibration, the pK_a of $H_2Fe(CO)_4$ in 70% methanol–water was found by preparing solutions of $NaHFe(CO)_4$ half neutralized with HCl and measuring the pH. The half-life for decomposition was long compared to the time necessary to get a stable pH reading. From several experiments, the pK_a of $H_2Fe(CO)_4$ was estimated as 5.88 ± 0.02 at 25 °C. The second ionization constant is too weak to measure. In water the pK_a of $H_2Fe(CO)_4$ is 4.4 at 18 °C.[10]

The kinetics of decomposition of $H_2Fe(CO)_4$ in methanol–water were followed both by monitoring the vis–UV spectrum and by gas evolution method. For $H_2Fe(CO)_4$ concentrations between 1 and 5 mM, the strong increase in absorption at 540 nm was usually followed, but in more dilute solutions the smaller relative changes between 240 and 280 nm were found to give good results. The rate law was strictly first order (eq 11). The first-order rate

$$\text{rate} = k_d[H_2Fe(CO)_4] \tag{11}$$

constant, k_d, was measured over a temperature range from 0 to 45 °C. The results are given in Table II. From these data an activation energy of 26 ± 2 kcal/mol was calculated. The entropy of activation, ΔS^*, is +19 Gibbs.

The gas evolution rates were followed by measuring the volume of gas in a constant-pressure gas buret. The thermostated reaction reaction vessel contained a magnetic stirring bar. Reaction was initiated by adding H_2SO_4 to a solution of NaH $Fe(CO)_4$ by means of a syringe. Plots of ln $(V_\infty - V)$ were linear with time, so that any CO_2 swept out by the product gases was a constant fraction of the whole. There was an initial burst of CO_2 evolution prior to taking the first reading.

The kinetics of decomposition of $H_2Fe(CO)_4$–$HFe(CO)_4^-$ mixtures were studied at 25 °C in buffer solutions of tris(hydroxy)aminomethane in a pH range of 6.5 to 8.0 by following the vis–UV spectrum at 280 or 540 nm. Above pH 8 the reaction was too slow to measure. If eq 11 is the valid rate law, it may be written as

$$\frac{dx}{dt} = \frac{k_d[H^+]}{[H^+] + K_a}(a- x) = k_{obsd}(a - x) \tag{12}$$

where $(a - x)$ is the remaining concentration of the original iron hydride, in both neutral and ionic forms, and x the concentration reacted. The value of k_d was taken as 1.1×10^{-3} s^{-1} (Table II).

Table III shows the observed first-order-rate constants in buffers compared to those calculated from eq 12. Duplicate runs were made at each pH and results agreed within 20%, except at pH 6.5 which is at the limit of the buffer system. It may be concluded that only $H_2Fe(CO)_4$, and not $HFe(CO)_4^-$, can decompose under our conditions. The rate of decomposition of $H_2Fe(CO)_4$ was also measured under CO and H_2 pressures. An experiment with 1 atm of CO was followed in the vis–UV spectrum. No change in rate was found. The solubility of CO in methanol at 1 atm is about 10^{-3} M, but the solution was not equilibrated. Nevertheless enough CO was dissolved so that more $Fe(CO)_5$ and less $H_2Fe_3(CO)_{11}$ was formed, as judged by the 540-nm absorption.

In a second experiment, a high-pressure infrared cell was used with a pressure of 5.4 atm of CO. This resulted in a definite increase in rate, determined by following the growth of the absorption bands at 2000 cm^{-1} (overlapping $Fe(CO)_5$ and $HFe_3(CO)_{11}^-$ peaks). At 28 °C, $k = 2.98 \times 10^{-3}$ s^{-1} compared to 1.8×10^{-3} s^{-1} in the absence of CO. One experiment was performed with a pressure of 13.6 atm of hydrogen. At 28 °C there was no effect on the rate.

Discussion

The results given for the reaction of $Fe(CO)_5$ with base are consistent with the mechanism of eq 13–15. Since the intermediates $Fe(CO)_4COOH^-$ and $Fe(CO)_4CO_2^{2-}$ are not detected, the steady state may be assumed. This gives the rate law

$$Fe(CO)_5 + OH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Fe(CO)_4COOH^- \qquad K_1 \tag{13}$$

$$Fe(CO)_4COOH^- + \text{base} \rightleftharpoons Fe(CO)_4CO_2^{2-} + BH^+ \qquad K_2 \tag{14}$$

$$Fe(CO)_4CO_2^{2-} + H_2O \xrightarrow{k_3} H\ Fe(CO)_4^- + HCO_3^- \tag{15}$$

$$\text{rate} = \frac{k_1k_3K_2[Fe(CO)_5][OH^-][\text{base}]}{k_2 + k_3K_2[\text{base}]} \tag{16}$$

Base refers to either OH^- or CH_3O^-. The equilibrium constant is known at 25 °C.[8] Taking the ratios of activities as ratios of concentrations, this gives $[CH_3O^-] \simeq 8[OH^-]$ (eq 17).

$$\frac{a_{OH^-}a_{CH_3OH}}{a_{OCH_3^-}a_{H_2O}} = 0.13 \tag{17}$$

At high base concentration (16) becomes

$$\text{rate} = k_1[Fe(CO)_5][OH^-] \tag{18}$$

where $k_1 = 70 \pm 5$ M^{-1} s^{-1} from the slope of the straight line in Figure 2. The deviation at higher base concentrations may be attributed to ion pairing, which will reduce the rate. The rate of deprotonation in (14) has been shown to be rapid compared to the reverse of (13) in more basic solutions.[20c]

At low base concentrations the rate law becomes

$$\text{rate} = k_3K_1K_2[Fe(CO)_5][OH^-][\text{base}] \tag{19}$$

which agrees with the data shown inset in Figure 2. The value of $k_3K_1K_2$ is approximately 7×10^4 M^{-2} s^{-1}. The rate goes to an immeasurably small value between pH 10 and 9.

The mechanism given differs from that of Pettit[3] in that $Fe(CO)_4CO_2^{2-}$ loses CO_2 rather than $Fe(CO)_4COOH^-$. If the reverse were true, the rate would be first order in base throughout. The loss of CO_2 from several other metallocarboxylates has been examined. Examples are known where the loss of CO_2 is from the carboxyl form, e.g., $Fe(Cp)(CO)(PPh_3)COOH$[18] and *trans*-$PtCl(PEt_3)_2COOH$.[19] In other cases it is the carboxylate form that loses CO_2, e.g., $Mn(CO)_3(diphos)CO_2^-$.[20a] The species $[(NC)_5FeC(CN)_2(PEt_3)_2COOH]^{4-}$ can lose CO_2 from both forms.[20b]

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Table I. pK_a of Acetic Acid in Water-Methanol Mixtures at 25 °C

vol. % CH_3OH	0	20	40	50	60	70	80	100
pK_a = pH	4.76	5.03	5.36	5.58	5.80	6.15	6.40	
p$K_a{}^{*a}$	4.756	5.011	5.334		5.808		6.500	9.720

[a] Accurate values from ref 17.

Table II. Rates of Decomposition of $H_2Fe(CO)_4$ in 70% Methanol-30% Water

temp, °C	$k \times 10^5$, s^{-1}
0	4.1[a]
2	3.2[b]
20	56.7[b]
25	110,[b] 113[a]
35	576[a]
45	2620[a]

[a] From gas evolution. [b] From vis-UV spectra. Duplicate runs agreed to within 10%.

Table III. Rates of Decomposition of $H_2Fe(CO)_4$ in Tris Buffers, Solvent 70% Methanol, 25 °C

pH	$k_{obsd} \times 10^4$	$k_{calcd} \times 10^4$
6.5	2.10	2.63
7.2	0.68	0.55
7.5	0.25	0.29
7.7	0.20	0.18
8.2	v slow	0.06

Methoxide ion is also expected to add to $Fe(CO)_5$ to form a metallocarboxylic ester[18,19](eq20). These esters are stable in the

$$Fe(CO)_5 + CH_3O^- \underset{k_5}{\overset{k_4}{\rightleftharpoons}} Fe(CO)_4COOCH_3^- \qquad (20)$$

absence of water and will not react further (except to add more methoxide ion). In pure methanol solvent the equilibrium constant for (20) has been measured as 120 M^{-1} at 25 °C.[21] We have verified this equilibrium constant and in addition have measured k_4 and k_5 by stopped-flow experiments.[22]

The value of k_4 is 1.5 M^{-1} s^{-1} at 25 °C, which may be compared to k_1 = 70 M^{-1} s^{-1} for OH^-. The smaller value of k_4 explains why our results in 70:30 methanol are not complicated by reaction 20, in spite of the 8-fold higher concentration of CH_3O^- over OH^-. It is unusual to find OH^- a better nucleophile than CH_3O^-. For organic, substrates, such as alkyl halides and esters, the reverse is true.[23]

The value of k_1 may also be compared with the rate constant for the direct reaction

$$CO + OH^- \xrightarrow{k_6} HCO_2^- \qquad (21)$$

where $k_6 = 2.7 \times 10^{-5}$ atm^{-1} s^{-1} in water solution at 62 °C.[24] Even allowing for the low solubility of CO in water, about 10^{-4} M at 2 atm, it is clear that coordination of CO to the metal has greatly activated it toward nucleophile attack.

The results for the thermal decomposition of $H_2Fe(CO)_4$ are completely consistent with the simple loss of H_2 in the rate-determining step (eq 22). The structures of $H_2Fe(CO)_4$ and $Fe(CO)_4$

$$H_2Fe(CO)_4 \xrightarrow{k_d} H_2 + Fe(CO)_4 \qquad (22)$$

are particularly favorable for this process.[25] The hydrogen atoms in $H_2Fe(CO)_4$ are cis and close to each other,[26] and the $Fe(CO)_4$ residue has the D_{2d} structure predicted for it on theoretical grounds.[27] Reaction 22 is allowed by orbital symmetry.[25]

The failure of CO to inhibit the decomposition of $H_2Fe(CO)_4$ is important in excluding complex mechanisms in which CO is lost. Previous work has shown such mechanisms for $HCo(CO)_4$ and $H_2Os(CO)_4$.[5] Simple loss of H_2 has been shown[6] for $IrH_2(CO)_2L_2{}^+$ and $H_2Co[P(OR)_3]_4{}^+$. The modest acceleration in rate produced by CO is not unexpected. Reppe and Reindl have already shown that high CO pressure increases the rate of decomposition of $NaHFe(CO)_4$ very markedly.[1]

In the presence of CO, the fragment $Fe(CO)_4$ would form $Fe(CO)_5$, as in eq 7. In the absence of CO, the reaction must be with unreacted $H_2Fe(CO)_4$, as in eq 23. The dimeric acid

$$Fe(CO)_4 + H_2Fe(CO)_4 \rightarrow H_2Fe_2(CO)_8 \qquad (23)$$

has been shown to decompose according to eq 24.[28] To be in

$$H_2Fe_2(CO)_8 + HFe_2(CO)_8{}^- \rightarrow H_2 + HFe_3(CO)_{11}{}^- + Fe(CO)_5 \qquad (24)$$

agreement with our observations, reaction 24 should be fast compared to (22). A direct comparison of the rates under acid conditions is not possible, but $NaHFe_2(CO)_8$ decomposes much more rapidly than $NaHFe(CO)_4$.[28] The persistence of the trimeric acid results from its existence as an anion under these conditions.

If $Fe(CO)_4$ is indeed formed, it should be possible to trap it with other potential ligands. We attempted this by decomposing $H_2Fe(CO)_4$ in the presence of PPh_3 and $P(OMe)_3$. The experiments were thwarted by a very rapid substitution reaction (at least 30 times as fast as hydrogen evolution) in which $H_2Fe(CO)_3(PPh_3)$ and $H_2Fe(CO)_3[P(OMe)]_3$, as well as $H_2Fe(CO)_2[P(OMe)_3]_2$, were formed. These unexpected reactions appear to occur by a hydride migration mechanism.[29]

The failure of H_2 to inhibit the decomposition of $H_2Fe(CO)_4$ shows that H_2 is a poor reagent for trapping $Fe(CO)_4$.[30] This is important in the use of $Fe(CO)_5$ as a catalyst for the WGSR. It is of interest to compare our results with those of King et. al. for the catalytic system.[4b] The reported turnover number at 180 °C and pH 8.6 may be converted to a first-order rate constant of 7.1×10^{-8} s^{-1} at 25 °C, using the overall activation energy of 22 kcal. Assuming all of the catalyst is $Fe(CO)_5$, a value of 5×10^{-8} s^{-1} is calculated from 19 for the conversion of $Fe(CO)_5$ to $H_2Fe(CO)_4$. If all of the catalyst is $HFe(CO)_4{}^-$ and its acid, a k_{obsd} of 2×10^{-6} s^{-1} is calculated from 12 for the evolution of hydrogen.

The rate-determining step under catalytic conditions is the reaction of $Fe(CO)_5$ with base, as concluded earlier by King.[4b] The agreement of our calculated rate and the observed value is good, all things considered. This supports the conclusion that it is the species $Fe(CO)_4CO_2{}^{2-}$ which loses CO_2, and not $Fe(CO)_4COOH^-$. We can now calculate the pH at which an optimum catalytic rate can be obtained. This requires equating the rates of both reactions.

$$k_3K_1K_2[B][OH^-] = \frac{k_d[H^+]}{K_a} = \frac{k_dK_s}{K_a[B]}$$

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The value of [B], the total base concentration, is found to be 9.0×10^{-6}, or pH = 9.1. This corresponds to a catalytic rate constant of 31×10^{-8} s^{-1} at 25 °C, or 4 times larger than the 7.1×10^{-8} s^{-1} calculated at pH 8.6.

Thus only a modest improvement in catalytic efficiency can be hoped for by optimizing conditions. $Fe(CO)_5$ is a poor catalyst because the two steps involved in the catalytic cycle have exactly opposite pH requirements. It may be noted that $Fe(CO)_5$ is not a catalyst for the WGSR in acid media,[31] as expected from our results.

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Bistability and Oscillations in the Autocatalytic Chlorite–Iodide Reaction in a Stirred-Flow Reactor[1]

Christopher E. Dateo, Miklôs Orbân,[2] Patrick De Kepper,[3] and Irving R. Epstein*

Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254. *Received July 14, 1981*

Abstract: The reaction between chlorite and iodide in acidic solution (0.08 < pH < 3.75) has been studied in a stirred-tank reactor at 25 °C over a range of flow rates, pH, and input chlorite and iodide concentrations. The system is found to exhibit bistability and, at high $[ClO_2^-]$ and $[I^-]$, sustained oscillations as well. The key reaction which gives rise to these phenomena is $ClO_2^- + 4I^- + 4H^+ = Cl^- + 2I_2 + 2H_2O$, which is autocatalytic in iodine and is inhibited by iodide. The existence of bistability and oscillations in this system is consistent with the "cross-shaped phase diagram" model of Boissonade and De Kepper.

The recent report of the first systematically designed homogeneous chemical oscillator[4] emphasizes the enormous amount that may be learned about the dynamics of complex chemical systems from the study of autocatalytic reactions in a continuous-flow stirred-tank reactor (CSTR). In the above mentioned study, two autocatalytic subsystems, arsenite–iodate and chlorite–iodide, were linked together in a CSTR to give rise to oscillation. The existence of sustained oscillation in that system had been suggested by a model analysis which implied that addition of an appropriate feedback reaction to a system which exhibits bistability in a CSTR should lead to a "cross-shaped phase diagram"[5] in which oscillations appear for a range of input reactant concentrations.

The arsenite–iodate reaction has been thoroughly examined in a CSTR[6,7] and has been found to exhibit bistability under a wide range of conditions. A simple model involving several overall component processes[6] has been shown to give excellent agreement with the experimental observations. Continuing our study of autocatalytic reactions in the CSTR, we report here on the remarkable richness of dynamic behavior exhibited in a flow reactor by the autocatalytic reaction between chlorite and iodide. We have observed not only the expected bistability but also sustained oscillation; the chlorite–iodide system itself is characterized by a "cross-shaped phase diagram". In addition, as we report elsewhere, this reaction forms the basis of an entire new family of oscillating reactions when chlorite- and iodine- containing species (IO_3^-, I^-, or I_2) are combined with a wide variety of reducing[1,4] or oxidizing[8] agents.

Experimental Section

The apparatus employed consists of a thermally regulated stirred tank glass (Pyrex) flow reactor, which has been described in detail elsewhere.[6,9] Potentiometric measurements could be made by using either an Orion iodide-specific electrode or a platinum redox electrode with a $Hg/Hg_2SO_4/K_2SO_4$ electrode as reference. Simultaneous measurement of the absorbance of the solution in the CSTR could also be made. Absorbances were generally monitored at 460 nm, the wavelength at which the I_2 extinction coefficient is a maximum. The path length through the cell was 3.5 cm.

The constraints which are at the disposal of the experimenter are the temperature, which was maintained at 25.0 ± 0.1 °C in this series of experiments, the residence time τ (or flow rate $k_0 = 1/\tau$), and the concentrations $[A_i]_0$ that the input species A_i would reach in the reactor if no reaction were to occur. The input chemical species of importance in these experiments are $[ClO_2^-]_0$, $[I^-]_0$, and $[H^+]_0$. Chorite and iodide solutions were prepared by using doubly distilled water from the highest purity commercially available grades of $NaClO_2$ and KI. Reagent solutions were stored in three separate reservoirs. One contained the chorite, stabilized by 0.001 M sodium hydroxide. The iodide solution was prepared in either sodium acetate or sodium sulfate, and the third reservoir contained the corresponding acid, acetic or sulfuric, depending on the pH desired. Thus when the solutions were mixed in the reactor, an acetic acid–acetate or sulfate–bisulfate buffer of the appropriate pH was generated in situ. The pH was measured directly in the output flow.

The Chlorite–Iodide Reaction in Batch

When solutions of chlorite and iodide are mixed in the absence of flow (bath conditions), an initial slow increase in iodine absorbance soon gives way to a rapid exponential rise. If chlorite is in excess, this rise terminates in an abrupt drop-off, with the disappearance of all trace of iodine color. The iodide concentration is found to decrease slowly at first and then to fall suddenly by more than 5 orders of magnitude at about the time of the peak in I_2 absorbance. This behavior is illustrated for a slight stoichiometric excess of chlorite in Figure 1. With still greater excesses, the absorbance drops to and remains at an essentially zero value.

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