eV, respectively). The higher binding energy of 2p electrons in Cl^- exemplifies the difficulties which arise when attempting to compare binding energies of identical atoms in ionic and covalent compounds. The influence of the crystal field on binding energies has been dealt with elsewhere,[10,44] and it is only necessary here to reiterate the fact that the lattice type has a significant and complex effect on measured core-level energies.

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Metal–Metal Bond Equilibria in Aqueous Solution. I. Zinc Tetracarbonylferrates(–II)[1]

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Abstract: The reaction of the carbonylferrate(–II) anions $Fe(CO)_4^{2-}$ and $HFe(CO)_4^-$ with zinc(II) was studied potentiometrically. On the basis of equilibrium measurements of hydrogen ion concentrations at 20° and a total normality of 1.0 ($NaClO_4$), the equilibrium constants of the following reactions have been evaluated: (A) $Fe(CO)_4^{2-} + Zn^{2+} \rightleftharpoons ZnFe(CO)_4$, (B) $HFe(CO)_4^- + Zn^{2+} \rightleftharpoons ZnHFe(CO)_4^+$, (C) $ZnFe(CO)_4 + Zn^{2+} \rightleftharpoons Zn_2Fe(CO)_4^{2+}$, (D) $2ZnFe(CO)_4 + 2H_2O \rightleftharpoons [HOZnFe(CO)_4]_2^{2-} + 2\,H^+$. The values of the equilibrium constants are, respectively, $(4.0 \pm 0.8) \times 10^8\ M^{-1}$, $21 \pm 3\ M^{-1}$, $30 \pm 3\ M^{-1}$, and *ca.* $2 \times 10^{-16}\ M$. The acid dissociation constants of $H_2Fe(CO)_4$ were redetermined at 20° and 1 *M* $NaClO_4$. $pK_a(H_2Fe(CO)_4) = 4.00 \pm 0.01$; $pK_a(HFe(CO)_4^-) = 12.68 \pm 0.04$.

Heavy-metal derivatives of iron carbonyl hydride of the type $MeFe(CO)_4$, where Me is Hg(II),[2] Cd(II)[3] or Pb(II),[4] are, contrary to the corresponding monomeric derivatives of cobalt carbonyl hydride, *e.g.*, Hg $[Co(CO)_4]_2$,[5] insoluble and very likely polymeric[6] species. An analogous zinc derivative has, hitherto, not been obtained. Hieber and Fack[7] prepared the ammine complex $(NH_3)_3ZnFe(CO)_4$, which dissolves in methanol to form weakly conducting solutions. An earlier observation[3] suggests the existence of a water-soluble cadmium derivative. The ammine complex $(NH_3)_2CdFe(CO)_4$ dissolves in aqueous acetic acid without liberation of the carbonyl hydride. $CdFe(CO)_4$ is precipitated when this solution is heated to boiling.

With the aim of elucidating the nature of such soluble metal carbonyl species, it was decided to investigate further the reaction of the carbonylferrate anions $Fe(CO)_4^{2-}$ and $HFe(CO)_4^-$ with heavy metal ions. It was hoped that formation constants of the respective metal–metal-bonded species could, eventually, be obtained. In this paper we report the results of a potentiometric study of the reaction of the carbonylferrate anions with zinc(II) in aqueous solution.

Experimental Section

All of the manipulations with the highly oxygen-sensitive carbonylferrate solutions were performed under an atmosphere of high-purity nitrogen. All solutions were made up using water triply distilled in an all-glass still. The concentration of hydrolytic impurities was evaluated from the change in pcH (= –log $[H^+]$) on the addition of increasing amounts of acid and base.[8] The values given below and used in the calculations of the equilibrium constants refer to the pcH range 8.2–5.5 (mean initial and final pcH of the experiments with $Na[HFe(CO)_4]$). All solutions were standardized to within ±0.1% according to accepted methods.

A 4.5 *M* stock solution of sodium perchlorate was prepared according to Biedermann[9] and adjusted to pcH 6–6.3 at 1 *M*. The concentration of hydrolytic impurities in the deaerated 1 *M* solution was $(5 \pm 2) \times 10^{-6}\ M$. A 0.50 *M* solution of zinc perchlorate was prepared from reagent grade zinc oxide and perchloric acid, so that after tenfold dilution with 1 *M* $NaClO_4$ the pcH was 5.5. Hydrolytic impurities were within the limits indicated for $NaClO_4$ alone. The two solutions were used in the titration experiments with $Na[HFe(CO)_4]$. In the experiments with $Na_2[Fe(CO)_4]$, solutions were used which were, respectively, 0.25 and 0.0625 *M* in zinc and 1.00 *M* in $NaClO_4$.

Solutions of sodium hydridotetracarbonylferrate(–II) were prepared by the procedure described earlier,[10] slightly modified to ensure a low carbonate content and absence of dissolved $Fe(CO)_5$. Freshly distilled $Fe(CO)_5$ (1.95 g, 9.95 mmol), measured with a Gilmont micrometer syringe, was added to 100 ml of an aqueous solution containing 11.00 mmol of $Ba(OH)_2$ and 8.00 mmol of NaOH, placed in a 150-ml Schlenk tube. The tube was shaken for 3 hr

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(1) Abstracted in part from the Ph.D. Thesis of F. Galembeck, Universidade de São Paulo, Brazil, 1970.

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and the contents were filtered through a low-porosity glass frit into another Schlenk tube. The so-prepared, faintly yellow solution contains an excess of *ca.* 1% alkali over $HFe(CO)_4^-$, which is neutralized before each titration experiment (see later). At 0° and in the dark, solutions can be kept for a week without discoloration. Of the carbonylferrate, 80% is present as sodium salt and 20% as barium salt. Since in the pcH region of interest (*ca.* 4.5–9.5), the amount of barium present has no noticeable effect on the pH of the reaction mixtures, the presence of barium will be neglected altogether. Neglecting minor volume changes, the carbonylferrate content can be calculated from the stoichiometry of the reaction as one-third of the difference between the total alkalinity of the mixed hydroxide solution (0.300 *F*) and the excess of alkali in the final solution (*vide supra*). Direct determination of iron yields a value *ca.* 0.3% lower. The concentration of hydrolytic impurities was estimated to $(1.5 \pm 0.5) \times 10^{-5}$ *M*.

Apparatus. The titration assembly was designed to permit quick exchange of titration cells while maintaining all other desirable characteristics. The titration cell is a cylindrical glass jar, 50 mm wide and 110 mm high, closed with a tightly fitting lucite cover which holds the glass electrode, the salt bridge, a combined gas inlet and outlet tube, a thermometer, and two glass capillaries with 0.5-mm polyethylene tips, which connect through $^1/_8$-in. tygon tubing to the burets. Metrohm 5-ml piston burets were used for the addition of NaOH and $Zn(ClO_4)_2$ and were found to be reproducible to within ±0.003 ml. The titration cell is loosely placed in an open water jacket mounted on a magnetic stirrer. Burets and storage vessels were kept permanently under nitrogen pressure.

The salt bridge is an inverted U-tube with two different arms. One arm is an open glass capillary of 0.7-mm bore and connects to the titration cell. The other, shorter arm is a 4-mm glass tube closed with a medium-porosity glass frit and connects to the reference electrode. The bridge is filled with 1.00 *M* $NaClO_4$. The capillary can be flushed by opening the stopcock connecting to a $NaClO_4$ reservoir. The reference electrode is an electrolytic type silver|silver chloride electrode in a solution, 0.05 *M* in NaCl and 0.95 *M* in $NaClO_4$. The electrode vessel has a fused-on water jacket and connects to the salt bridge *via* an open side arm. The capillary liquid junction proved very stable and reliable. Flushing the capillary hardly produces a detectable (0.001) change in the pcH.

The emf was measured with a Corning Model 12 expanded-scale pH meter, recalibrated to within ±0.1 mV or 0.1% of full scale with a Leeds and Northrup Type K 3 potentiometer.

Care and Standardization of Glass Electrodes. Corning and Coleman all-purpose glass electrodes were used throughout this work. The pH meter was set to read directly in pcH using a solution 4.50×10^{-3} *M* in $HClO_4$ and 1.00 *M* in total perchlorate as the primary pcH standard. A CO_2-free solution, 0.025 *M* in $Na_2B_4O_7$ and 0.95 *M* in $NaClO_4$, was used as secondary standard (pcH 8.930 at 20°). Up to pcH 11.7, the sodium ion error was negligible. At pcH 12.2, it amounted to *ca.* 0.02. In carbonylferrate solutions, glass electrodes are rapidly fouled and, unless properly treated, soon give an erratic response. After every two experiments, the electrode was kept for *ca.* 12 hr in 0.01 *M* (occasionally 0.1 *M*) HCl and then immersed for several hours in either the acid or the alkaline standard solution (whichever came closer to the pcH range of the next experiment). After 20–30 experiments, the response of the electrode became sluggish and, eventually, erratic, and the electrode had to be discarded.

Technique of Potentiometric Measurements. All experiments were made in a constant-temperature room, 20 ± 1°. The titration cell and the reference electrode were thermostated at 20.0 ± 0.1°. Unless otherwise stated, the total equivalent concentration (normality) of ions of either sign, *N*, in the reaction mixtures was kept close to 1.00 using sodium perchlorate as background electrolyte. Before each titration experiment, the glass electrode was standardized with one of the standard solutions. The initial volume of the carbonylferrate solutions was 50.0 ml. The required amount of $NaClO_4$ solution and water was placed in the titration cell, a magnetic stirring bar was supplied, and nitrogen, which was equilibrated with 1 *M* $NaClO_4$, was bubbled through the solution for 40 min. Then the $Na[HFe(CO)_4]$ solution was transferred from the Schlenk tube to the titration cell with the help of a pipet provided with a capillary tip and a side tube at the upper end, which was connected to a gas-tight syringe. After purging pipet and syringe with nitrogen, the carbonylferrate solution was aspirated to the mark and then blown out with nitrogen into the titration cell. Next, enough 0.2 *M* $HClO_4$ was added to bring the pcH to within ±0.1 of the value calculated for stoichiometrically pure $Na[HFe(CO)_4]$ (8–8.4, depending on the concentration). When the presence of $Na_2[Fe(CO)_4]$ was desired, the required amount of NaOH was added and sufficient time allowed to elapse (5–15 min) to reach a steady pcH reading. Finally, the gas inlet tube was raised above the level of the liquid, the introgen flow was reduced to *ca.* 1 bubble/sec, and addition of the reagent, $Zn(ClO_4)_2$ or $HClO_4$, was started. At a stirring rate of *ca.* 5 rev/sec, the desired volume of reagent was added within 10–20 sec with the buret tip lowered into the solution. Then the tip was withdrawn from the liquid and the stirring rate reduced to half; pH readings were taken every 30 sec (*vide infra*). At the end of the experiment, the glass electrode was once more standardized with the standard solution. Initial and final calibration agreed within 0.005–0.01 pcH unit, depending on the pcH range covered in the experiment.

Iron Carbonyl Hydride Losses and Precision of pcH Measurements. In addition to the lability of the carbonylferrates toward oxygen, the instability and, particularly, the volatility of $H_2Fe(CO)_4$ present serious problems to the precise determination of the pcH. When acid or zinc salt is added to a solution of $Na[HFe(CO)_4]$ that was being stirred slowly, the pcH shows, after a fast initial descent (30–90 sec), a uniform upward drift of *ca.* 0.02/min. The magnitude of this drift is roughly independent on the pcH of the solution. In unstirred solutions, the pcH drift is smaller but quite erratic. Apparently, this drift is caused by the loss of $H_2Fe(CO)_4$, chiefly by evaporation, the rate of loss of the hydride being approximately proportional to its concentration.

Extrapolation of pcH readings taken every 30 sec, after the drift has become uniform, to zero time of mixing permits the evaluation of the correct pcH value with an accuracy of *ca.* ±0.005. When a second addition of reagent is made, the loss of hydride in the preceding addition must be taken into account. Approximately, this loss can be expressed

$$\Delta H_2X \approx k[H_2X]\Delta t \approx k'[H^+][HX^-]\Delta t \qquad (1)$$

where X stands for $Fe(CO)_4$, and $[H_2X]$, etc., are average concentrations, *e.g.*, at half the elapsed time, Δt. After the second addition of reagent, the same amount of hydride would have been lost in

$$\Delta t_2' \approx \frac{[H^+]_1[HX^-]_1}{[H^+]_2[HX^-]_2}\Delta t_1 \qquad (2)$$

where indices refer to the first and second addition of reagent, respectively. Thus, the loss of hydride in the first addition can be accounted for by extending the extrapolation of the pcH readings after the second addition by $\Delta t_2'$. In principle, the same procedure can be applied to further additions of acid or zinc salt. However, successive pcH readings must differ by at least 0.5, and Δt be kept as short as possible, to keep the uncertainty of the extrapolated pcH values below ±0.01.

When zinc(II) is allowed to react with $Na[HFe(CO)_4]$ and $Na_2[Fe(CO)_4]$ at pcH <8, an upward drift of the pcH is, eventually, observed, which increases with decreasing pcH up to a maximum value of *ca.* 0.01/min. On the other hand, the time necessary for the drift to become uniform increases in the opposite direction and was, occasionally, as long as 10 min. At pcH >8, readings come within 30–60 sec to within ±0.005 of the final, steady pcH value which is reached in 2–5 min.

In the reaction of $Na[HFe(CO)_4]$ with acid or zinc salt, extrapolated pcH values of duplicate experiments agreed on the average within 0.01. In the reaction of zinc(II) with $Na[HFe(CO)_4]$ and $Na_2[Fe(CO)_4]$, results agreed within 0.01–0.03 pcH, the latter value referring to regions around the inflection points of the titration curves (see Figure 1).

Determination of the Dissociation Constants of Iron Carbonyl Hydride. Since published values[10,11] of the dissociation constants of $H_2Fe(CO)_4$ refer to different experimental conditions, these constants were redetermined. The first acid dissociation constant, $K_a(H_2Fe(CO)_4) = K_{a1}$, was evaluated from the pcH of solutions which were $0.3\text{–}2.5 \times 10^{-2}$ *M* in $Na[HFe(CO)_4]$ and had received additions of $1.0\text{–}8.0 \times 10^{-4}$ mol/l. of $HClO_4$, allowing for the presence of hydrolytic impurities (*vide supra*). Since acidities were low enough to not exceed the solubility of $H_2Fe(CO)_4$, and $K_{a1}/K_{a2} \approx 10^9$, K_{a1} may be evaluated in a straightforward manner. The second acid dissociation constant of $H_2Fe(CO)_4$, $K_a(HFe(CO)_4^-) = K_{a2}$, was evaluated from the pcH of solutions which were

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0.5–4.0 × 10^{-2} M in $Na[HFe(CO)_4]$ and had received additions of 0.5–2.0 × 10^{-2} mol/l. of NaOH. The ionic product of water, necessary for the evaluation of K_{a2}, was determined in separate experiments; $pK_w = 13.965 \pm 0.01$ (at 20° and $N = 1.00$ ($NaClO_4$)). Under the same conditions, the acid dissociation constants of $H_2Fe(CO)_4$ were found to be: $K_{a1} = (1.01 \pm 0.03) \times 10^{-4}$ M and $K_{a2} = (2.1 \pm 0.2) \times 10^{-13}$ M.

The Reaction of Tetracarbonylferrate(−II) Anions with Zinc(II). The reaction of zinc(II) with $Na_2[Fe(CO)_4]$ (in presence of $Na[HFe(CO)_4]$) was investigated with the main purpose of obtaining qualitative evidence for the formation of stoichiometric zinc–carbonylferrate species. Solutions of $Na[HFe(CO)_4]$, *ca.* 0.5–4.0 × 10^{-2} M, that had received additions of varying amounts of sodium hydroxide, and were (formally) 0.25–2.0 × 10^{-2} M in $Na_2[Fe(CO)_4]$ and 0.1–2.0 × 10^{-2} M in $Na[HFe(CO)_4]$, were titrated with zinc perchlorate in the manner described before. At pcH <7.5, additions of zinc(II) were made so that the pcH of successive titration points differed by at least 0.3 (*vide supra*). The reaction of zinc(II) with $Na[HFe(CO)_4]$ was studied to determine the stability constants of the zinc–carbonylferrate species. Three series of potentiometric experiments were made which differed in the initial concentration of $Na[HFe(CO)_4]$, $C_X{}^0$, which was *ca.* 4.0 × 10^{-3}, 8.0 × 10^{-3}, and 2.5 × 10^{-2} M, respectively. The total analytical concentration of zinc, C_{Zn}, was varied in the first two series from *ca.* 5 × 10^{-4}–4.6 × 10^{-2} M, *i.e.*, over a 100-fold range. In the last series, the highest value of C_{Zn} was *ca.* 4 × 10^{-3} M. At still higher concentration, iron carbonyl hydride appeared as a second phase. Not more than two consecutive additions of zinc perchlorate were made in one experiment (*vide supra*). Since the maximum concentration of zinc–carbonylferrate species formed in the reaction was well below 10^{-2} M, N remained constant within 1%.

Calculation of Equilibrium Constants. The species considered in the reaction of $Na[HFe(CO)_4]$ with zinc(II) are $ZnFe(CO)_4$, $Zn_2Fe(CO)_4{}^{2-}$, and $ZnHFe(CO)_4{}^-$. Mass balance relationships were set up as follows

$$C_X = [X] + [HX] + [H_2X] + [ZnX] + [Zn_2X] + [ZnHX] \quad (3)$$

$$C_{Zn} = [Zn] + [ZnX] + 2[Zn_2X] + [ZnHX] \quad (4)$$

$$C_H = C_X - \Delta OH = [H] - [OH] + [HX] + 2[H_2X] + [ZnHX] \quad (5)$$

where C_X and C_{Zn} are the total analytical concentrations of carbonylferrate and zinc, respectively, and ΔOH is the concentration of acid-consuming hydrolytic impurities (charges are omitted for the sake of simplicity). In the pcH range of the experiments, [X] and [OH] are small and can be safely neglected. The following equilibrium constants are considered: $K_{ZnX} = [ZnX][H]/([Zn]\cdot[HX])$, $K_{Zn_2X} = [Zn_2X]/([Zn][ZnX])$, $K_{ZnHX} = [ZnHX]/([Zn][HX])$, and $K_{a1} = [HX][H]/[H_2X]$.

If $ZnFe(CO)_4$ were the only zinc–carbonylferrate species, K_{ZnX} could be calculated in a straightforward manner from the analytical and the experimental pcH data. In that case, it is helpful to express this constant, $K_{ZnX}{}^0$, according to

$$K_{ZnX}{}^0 = \frac{[H]^2[1/K_{a1} - 1/[HX] - \Delta OH/([HX][H])]}{[Zn]} \approx \frac{[H]^2}{K_{a1}[Zn]} \quad (6)$$

Similarly, if $Zn_2Fe(CO)_4{}^{2+}$ were the only species, an approximate expression for $K_{Zn_2X}{}^0$ is

$$K_{Zn_2X}{}^0 \approx \frac{[H]^2}{K_{a1}[Zn]^2} \quad (7)$$

When all three zinc–carbonylferrate species are present, one deduces the approximate expression

$$K_{ZnX} \approx \frac{[H]^2}{K_{a1}[Zn](1 + K_{Zn_2X}[Zn])} \quad (8)$$

The system of the simultaneous equilibria involving the species $ZnFe(CO)_4$, $Zn_2Fe(CO)_4{}^{2+}$, and $ZnHFe(CO)_4{}^+$ was resolved in the following manner. The equilibrium constant of the primary species, K_{ZnX}, is calculated by using trial values of K_{Zn_2X} and K_{ZnHX}, which are varied until the standard deviation of K_{ZnX} over the whole range of experimental concentrations is reduced to the lowest possible value. The equilibrium concentrations necessary for the evaluation of K_{ZnX} were obtained by an iterative procedure by using the following expressions deduced from eq 3, 4, and 5 and the expressions for K_{Zn_2X}, K_{ZnHX}, and K_{a1} (*vide supra*).

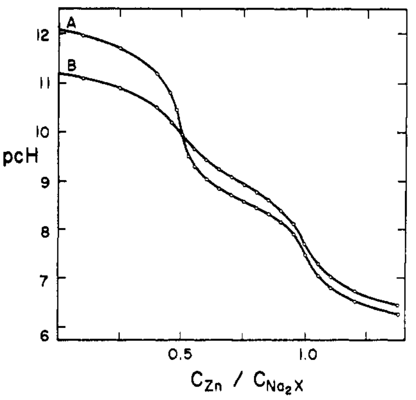

Figure 1. Potentiometric titrations of solutions containing $Na_2[Fe(CO)_4]$ and $Na[HFe(CO)_4]$ with zinc perchlorate. Initial analytical concentrations: (A) $C_{Na_2X}{}^0 = 2.02 \times 10^{-2}$ M, $C_{NaHX}{}^0 = 1.98 \times 10^{-2}$ M; (B) $C_{Na_2X}{}^0 = 2.54 \times 10^{-3}$ M, $C_{NaHX}{}^0 = 1.96 \times 10^{-2}$ M. Temperature = 20°; $\mu_c = 1.0$ ($NaClO_4$).

$$[HX] = \frac{C_X - [H] - \Delta OH}{1 + 2[H]/K_{a1} + K_{ZnHX}[Zn]} \quad (9)$$

$$[ZnX] = \frac{[H][HX]/K_{a1} + [H] + \Delta OH}{1 + K_{Zn_2X}[Zn]} \quad (10)$$

$$[Zn] = \frac{C_{Zn} - [H][HX]/K_{a1} - [H] - \Delta OH}{1 + K_{ZnHX}[HX] + K_{Zn_2X}[ZnX]} \quad (11)$$

Since an approximate value of K_{ZnX} can be obtained by an extrapolation procedure (see Discussion), eq 8 can be used to obtain a first value of [Zn], necessary to start the iteration calculations. At high zinc concentration, where $[Zn] \approx C_{Zn}$, eq 8 allows one to calculate an approximate value of K_{Zn_2X}. Finally, when C_{Zn} is small and C_X is large, one can use the easily deduced expression

$$K_{ZnX} \approx K_{ZnX}{}^0(1 + K_{ZnHX}C_X) \quad (12)$$

to obtain an approximate value of K_{ZnHX}. A program was written for a Burroughs 3500 computer and the equilibrium concentrations were computed to a consistency of 0.1%.

The zinc–carbonylferrate species considered in the approximate treatment of the reaction of zinc(II) with $Na_2[Fe(CO)_4]$ (in the presence of $Na[HFe(CO)_4]$) are $ZnFe(CO)_4$ and $[HOZnFe(CO)_4]_2{}^{2-}$. Mass balance relationships were set up as follows.

$$C_X = [X] + [HX] + [H_2X] + [ZnX] + 2[(HOZnX)_2] \quad (13)$$

$$C_{Zn} = [Zn] + [ZnX] + 2[(HOZnX)_2] \quad (14)$$

$$C_{OH} = C_{Na_2X} = [ZnX] + 4[(HOZnX)_2] + [OH] + [X] - [H] - [H_2X] - \Delta OH \quad (15)$$

$$C_{NaHX} = C_X - C_{OH} \quad (16)$$

C_{OH} is the (formal) analytical concentration of sodium hydroxide in the experimental solutions. In the pcH range 8–9.5, terms like [H], [OH], $[H_2X]$, [X], and ΔOH are small and are neglected. The equilibrium between $ZnFe(CO)_4$ and the dimeric hydroxo species $[HOZnFe(CO)_4]_2{}^{2-}$ can then be expressed according to

$$K_{hydr} = \frac{[(HOZnX)_2][H]^2}{[ZnX]^2} = \frac{(1 - R)[H]^2}{2(2R - 1)^2 C_{OH}} \quad (17)$$

where R is the ratio C_{Zn}/C_{OH}.

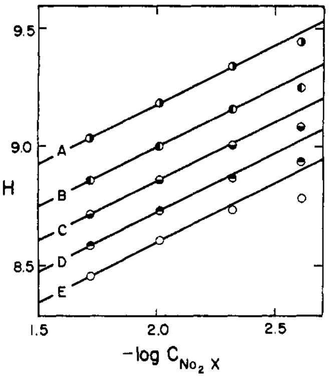

Figure 2. Plots of pcH *vs.* $-\log C_{Na_2X}$ for the reaction of zinc(II) with $Na_2[Fe(CO)_4]$ in the presence of $Na[HFe(CO)_4]$. $C_{HX}^0 = (1.96 \pm 0.02) \times 10^{-2}$ *M*. C_{Zn}/C_{Na_2X}: (A) 0.60; (B) 0.65; (C) 0.70; (D) 0.75; (E) 0.80 *M*. Temperature = 20°; μ_c = 1.0 ($NaClO_4$). The straight lines are drawn with the theoretical slope of $^1/_2$.

Results and Discussion

The pcH profile of titration of solutions containing $Na_2[Fe(CO)_4]$ and $Na[HFe(CO)_4]$ with zinc perchlorate, shown in Figure 1, provides direct evidence for two consecutive reaction steps in which zinc(II) and $Na_2[Fe(CO)_4]$ have reacted in the ratio of 1:2 and 1:1, respectively. The inflection points of the titration curves remain within 1% of these stoichiometric relations when the concentration of $Na_2[Fe(CO)_4]$ is varied from *ca.* 0.25 to 2.0 × 10^{-2} *M*. Over the same concentration range, $Na[HFe(CO)_4]$ has no noticeable influence on the position of the equivalence points. Since $Fe(CO)_4^{2-}$ is hydrolyzed to a large extent

$$Fe(CO)_4^{2-} + H_2O \rightleftharpoons HFe(CO)_4^- + OH^- \qquad (18)$$

the aforementioned stoichiometries may as well refer to OH^-. However, under no circumstances was the precipitation of zinc hydroxide observed. Thus, except at pcH >11, where $Zn(OH)_2$ becomes appreciably soluble,[12] the carbonylferrate anion $Fe(CO)_4^{2-}$ must have directly participated in the reaction with zinc(II). Considering the small value of the solubility product of $Zn(OH)_2$ ($pK_{so} \approx 15.5$[13]), one is led to conclude that the zinc–carbonylferrate species are reasonably stable. Any species of the composition $Zn_n[Fe(CO)_4]_{n-m}(OH)_m$ ($m < n$) and $Zn_n[Fe(CO)_4]_{2n-m}(OH)_m$ ($m < 2n$), respectively, will comply with the aforementioned stoichiometries. Since in the region between the two equivalence points, the pcH at constant ratio $C_{Zn}:C_{Na_2X}$ (X = $Fe(CO)_4$) depends on the concentration of $Na_2[Fe(CO)_4]$ (see Figure 1), and thus on C_{Zn}, polynuclear species must be present. Over a limited range of concentrations, the hydrogen ion concentration is roughly proportional to the square root of the carbonylferrate concentration, *i.e.*, pcH $\approx -^1/_2 \log C_{Na_2X}$ + constant (see Figure 2). This points to an equilibrium (compare eq 17)

$$2ZnFe(CO)_4 + 2H_2O \overset{K_{hydr}}{\rightleftharpoons} [HOZnFe(CO)_4]_2^- + 2H^+ \qquad (19)$$

By using eq 17 and the data in Figure 1, one obtains for the equilibrium constant of reaction 19 the approximate value $K_{hydr} \approx 2 \times 10^{-16}$ *M*. One notices in Figure 2 that at low values of C_{Na_2X}, the pH is lower than expected, especially when the ratio $C_{Zn}:C_{Na_2X}$ comes close to one. This is what is to be expected if the dimeric hydroxo species is in equilibrium with the corresponding monomer

$$[HOZnFe(CO)_4]_2^{2-} \rightleftharpoons 2HOZnFe(CO)_4^- \qquad (20)$$

Martell and coworkers[14] have shown that hydrolytic equilibria of the type represented by eq 19 and 20 are quite common among metal chelates. Therefore, it seems reasonable to conclude that these equilibria make, at least, a major contribution to the reaction of zinc(II) with $Na_2[Fe(CO)_4]$. A more detailed analysis of this reaction is beyond the scope of the present study.[15]

In order to confirm the existence of zinc tetracarbonylferrate(−II), $ZnFe(CO)_4$, and to obtain information on its stability, the reaction of zinc(II) with $Na[HFe(CO)_4]$ was investigated in some detail. Since this reaction proceeds at a pcH well below 7, it was hoped that complications caused by the presence of hydroxo species could be avoided.

Addition of zinc perchlorate to a solution of $Na[HFe(CO)_4]$ results in a decrease of the pcH and the simultaneous formation of $H_2Fe(CO)_4$ which can be driven out by a stream of nitrogen and identified by its reaction with $HgCl_2$.[16] Eventually, the solution becomes saturated with the slightly soluble (*ca.* 8 × 10^{-4} *M* at 20° in 1 *M* $NaClO_4$) hydride which separates out in the form of a yellow turbidity which soon becomes red by decomposition. Inspection of the data in Table I shows that,

Table I. Equilibrium Data for the Zn^{2+}–$HFe(CO)_4^-$ Reaction (Eq 21)[a]

$C_{Zn} \times 10^4$, *M*	$C_X \times 10^3$, *M*	$[H^+] \times 10^6$, *M*	$K_{ZnX}^0 \times 10^5$, *M*	$K_{ZnX} \times 10^5$, *M*
5.01	4.04	1.75	7.8	8.34
9.93	4.00	2.57	7.9	8.34
19.48	3.92	3.78	8.4	8.54
50.15	4.04	6.53	9.2	8.78
103.3	3.96	9.64	9.6	8.03
197.8	3.88	15.21	12.5	8.50
200.7	3.85	15.14	12.2	8.25
334.6	3.73	21.90	15.2	8.25
337.7	3.67	22.02	15.6	8.24
460.5	3.66	27.90	17.9	8.22
462.1	3.56	27.90	17.9	8.17
5.01	7.90	1.62	7.4	8.45
9.93	7.82	2.45	7.7	8.75
19.48	7.66	3.56	8.1	8.47
50.15	7.88	6.15	8.5	8.55
103.3	7.74	9.55	9.6	8.52
197.8	7.59	14.86	11.7	8.64
200.7	7.52	15.45	12.8	9.14
334.6	7.29	21.84	14.6	8.56
337.7	7.18	21.84	14.4	8.42
460.5	7.16	27.75	17.5	8.34
462.1	6.93	28.50	18.4	8.72
5.01	24.63	1.10	5.4	8.05
9.93	24.39	1.76	5.6	8.10
19.48	23.92	2.75	5.8	8.24
28.67	23.47	3.60	6.3	8.75
37.50	23.04	4.27	6.5	8.72

[a] Temperature = 20.0°, μ_c = 1.00 ($NaClO_4$).

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(12) See, *e.g.*, J. W. Fulton and D. F. Swinehart, *J. Amer. Chem. Soc.*, **76**, 864 (1954).

(13) W. Feitknecht and E. Häberli, *Helv. Chim. Acta*, **33**, 922 (1950).

(14) R. C. Courtney, R. L. Gustafson, J. Chabarek, Jr., and A. E. Martell, *J. Amer. Chem. Soc.*, **81**, 519 (1959); R. L. Gustafson and A. E. Martell, *ibid.*, **81**, 525 (1959); M. M. T. Khan and A. E. Martell, *ibid.*, **84**, 3037 (1962).

(15) A detailed treatment of the reaction of zinc(II) with $Na_2[Fe(CO)_4]$ will be presented in a forthcoming publication.

(16) F. Feigl and P. Krumholz, *Monatsh. Chem.*, **59**, 314 (1932).

at low zinc concentrations, the hydrogen ion concentration is roughly proportional to the square root of C_{Zn}. This points to the equilibria (see eq 6, taking $[Zn] \propto C_{Zn}$)

$$HFe(CO)_4^- + Zn^{2+} \overset{K_{ZnX}}{\rightleftharpoons} ZnFe(CO)_4 + H^+ \qquad (21)$$

$$HFe(CO)_4^- + H^+ \overset{K_{a1}}{\rightleftharpoons} H_2Fe(CO)_4 \qquad (22)$$

As a first approximation, it was assumed that $ZnFe(CO)_4$ is the unique zinc–carbonylferrate species formed in the reaction. Values of the equilibrium quotient of eq 21 calculated on this assumption ($= K_{ZnX}{}^0$), with $K_{a1} = 1.01 \times 10^{-4}$ M, are listed in Table I. It is apparent that $K_{ZnX}{}^0$ depends on the concentrations both of zinc and of the carbonylferrate. However, as can be clearly seen in Figure 3, $K_{ZnX}{}^0$ tends toward a constant value of *ca.* 8×10^{-5} when both C_{Zn} and C_X go to zero. Now, the apparent increase of $K_{ZnX}{}^0$ with increasing C_{Zn} indicates that there is another reaction which causes the true equilibrium concentration of $ZnFe(CO)_4$ to be lower than that calculated on the assumption that Zn $Fe(CO)_4$ is the unique complex species. Similarly, the decrease of $K_{ZnX}{}^0$ with increasing C_X is indicative of a reaction which lowers the equilibrium concentration of zinc(II). The reactions

$$ZnFe(CO)_4 + Zn^{2+} \overset{K_{Zn_2X}}{\rightleftharpoons} Zn_2Fe(CO)_4{}^{2+} \qquad (23)$$

$$HFe(CO)_4^- + Zn^{2+} \overset{K_{ZnHX}}{\rightleftharpoons} ZnHFe(CO)_4{}^+ \qquad (24)$$

are obvious choices.

As explained in the Experimental Section, the simultaneous equilibria of the reactions 21, 22, 23, and 24 were solved by computing K_{ZnX} with the help of K_{a1} (determined independently) and of trial values of K_{Zn_2X} and K_{ZnHX} which were varied until K_{ZnX} became as nearly independent as possible on C_{Zn} and C_X.

The best values of K_{ZnX} listed in Table I were obtained by using $K_{Zn_2X} = 30$ M^{-1} and $K_{ZnHX} = 21$ M^{-1}. The average of the values of K_{ZnX} in Table I is $(8.45 \pm 0.3) \times 10^{-5}$ (standard deviation). A variation of K_{Zn_2X} or K_{ZnHX} by 10% produces a 2% variation of the average value of K_{ZnX} and increases the standard deviation by *ca.* 20 and 10%, respectively. Considering the probable error of the values of K_{Zn_2X} and K_{ZnHX} (*ca.* 10–15%) and of K_{a1} and ΔOH, used in the computation of K_{ZnX}, one obtains $K_{ZnX} = (8.45 \pm 0.8) \times 10^{-5}$. Finally, using the independently determined value of $K_a(HFe(CO)_4^-) = (2.1 \pm 0.2) \times 10^{-13}$ M, one obtains the stability constant of $ZnFe(CO)_4$ (at 20° and in 1 M $NaClO_4$)

$$K_{ZnX}{}^0 = \frac{[ZnFe(CO)_4]}{[Zn^{2+}][Fe(CO)_4{}^{2-}]} = (4.0 \pm 0.8) \times 10^8\ M^{-1} \qquad (25)$$

Preliminary measurements in a 1 M chloride medium provide further evidence for the real existence of the equilibria of eq 23 and 24. Compared with the results in 1 M perchlorate, K_{Zn_2X} and K_{ZnHX} increase by a factor of *ca.* 8 and 3, respectively, while K_{ZnX} is affected to a much lesser degree. This increase is most likely due to the formation of the neutral chloro complexes $(ClZn)_2Fe(CO)_4$ and $ClZnHFe(CO)_4$. The first complex is analogous to the well-known mercury derivative $(ClHg)_2Fe(CO)_4$.[2]

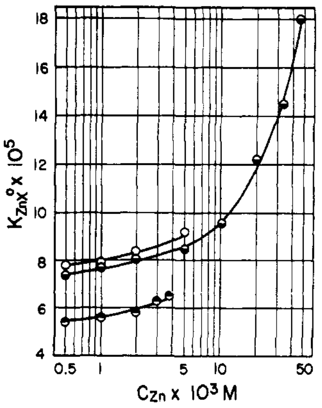

Figure 3. The influence of C_{Zn} and C_X on the equilibrium quotient $K_{ZnX}{}^0$ (see text). Initial analytical concentrations of $Na[HFe(CO)_4]$: (○) $C_X{}^0 = 4.1 \times 10^{-3}$ M; (◒) $C_X{}^0 = 8.0 \times 10^{-3}$ M; (◓) $C_X{}^0 = 2.49 \times 10^{-2}$ M. Temperature = 20°; $\mu_c = 1.0\ (NaClO_4)$.

Attempts to rationalize the experimental data in terms of an equilibrium involving a dimeric species, $(ZnFe(CO)_4)_2$, were unsuccessful. A detailed analysis of the reaction of zinc(II) with $Na[HFe(CO)_4]$ and $Na_2[Fe(CO)_4]$[15] shows that such dimer, if present at all, cannot make a significant contribution to the reaction of zinc(II) with $Na[HFe(CO)_4]$ alone.

Conclusion

The existence of water-soluble, monomeric zinc–tetracarbonylferrate(–II) species of the stoichiometric composition $ZnFe(CO)_4$, $Zn_2Fe(CO)_4{}^{2+}$, and $ZnHFe(CO)_4{}^+$ seems firmly established. There may be little doubt that in these compounds, just as in $Zn[Co(CO)_4]_2$,[17] zinc is directly bonded to the transitional metal. Because only one σ bond can be formed between each zinc and the iron, a semipolar structure, such as $Zn^+–[Fe(CO)_4{}^-]$ must be assigned to $ZnFe(CO)_4$, unless dπ–pπ bonding involving vacant p orbitals[18] on zinc is invoked. The existence of the ammine complex $(NH_3)_3ZnFe(CO)_4$[7] in which, apparently, zinc is tetracoordinate, *i.e.*, the vacant p orbitals on zinc are already used in σ bonding, makes the π-bonding proposition less probable. By the same token, a formulation of zinc tetracarbonylferrate as $(HOZn)HFe(CO)_4$[19] seems rather unlikely.

Burlitch[20] has recently shown that metal–metal bonds are readily broken when species such as $Zn[Co(CO)_4]_2$ are dissolved in water or in polar organic solvents. The rapid and reproducible establishment of glass electrode potentials in aqueous solutions containing zinc(II) and the carbonylferrate anions shows now that the formation of the metal–metal bond is a fast and reversible process. Except for the difficulties resulting from the instability and volatility of $H_2Fe(CO)_4$, the carbonylferrate anions behave in the potentiometric titrations as any ordinary ligand.

(17) B. Lee, J. M. Burlitch, and J. L. Hoard, *J. Amer. Chem. Soc.*, **89**, 6362 (1967).

(18) Strong dπ–pπ interaction between iron and indium in $Br_2InFe(CO)_4^-$ has been postulated by J. K. Ruff, *Inorg. Chem.*, **7**, 1499 (1968).

(19) Equilibrium measurements provide no information on the number and nature of bonded water molecules.

(20) J. M. Burlitch, *J. Amer. Chem. Soc.*, **91**, 4562 (1969).