toward this interchange process.

Our observations, then, indicate that the molybdenum complexes are generally more labile than the tungsten complexes. These observations are in line with the general trend toward increasing inertness of the heavier transition metals of any group. Good illustrations of this trend are provided by the acid or base hydrolysis of octahedral complexes[23] and the intramolecular, metal-centered inversion of dithiocarbamate complexes.[24]

Although it has been argued that nature's selection of molybdenum in enzymes with the virtual exclusion of tungsten[22,25] arises from differences in the redox properties of these two metals,[4] the differences in the lability of simple molybdenum and tungsten complexes suggest that there may also be a kinetic factor which would make molybdenum a more favorable choice. If dissociation of water or a portion of the peptide chain must occur to provide a coordination site for substrate interaction, molybdenum would be preferred over tungsten based on its more labile nature. Any internal rearrangement of donor atoms during catalysis would similarly occur more readily with molybdenum. The loss or absence of catalytic activity associated with the replacement of molybdenum by tungsten in enzymes may then reflect the kinetic inertness of tungsten as well as its poorer oxidizing strength.

An Additional Observation. It was also found that a rather interesting reaction occurs when solutions of $(PPN)_3WO_3NTA$ in $CHCl_3$ are heated or allowed to stand for several days at room temperature. Large, colorless crystals of $(PPN)_2W_6O_{19}$ are obtained by either method. The same compound is also obtained when $(PPN)_2WO_4$ is allowed to stand in $CHCl_3$. Presumably, traces of water are responsible for the polymerization in each case. Neither $(PPN)_3MoO_3NTA$ nor $(PPN)_2MoO_4$ displays a tendency to polymerize under similar conditions. These observations accord with the well-known, increased susceptibility of W(VI) toward hydrolytic polymerization relative to Mo(VI). Since the reason for this increased susceptibility undoubtedly lies within the province of thermodynamics and not kinetics, no contradictions need occur between these observations and those cited in reference to the dynamics of aminopolycarboxylate complexes of Mo(VI) and W(VI) in solution.

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Registry No. $(PPN)_3(MoO_3NTA)$, 67316-59-0; $(PPN)_3(WO_3NTA)$, 67316-61-4; $(PPN)_2W_6O_{19}$, 67316-62-5; MoO_3IDA^{2-}, 19709-67-2; WO_3IDA^{2-}, 67316-63-6; MoO_3MIDA^{2-}, 67316-64-7; WO_3MIDA^{2-}, 67316-65-8.

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Equilibrium Constants for the Aquated Iron(II) Cation

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Ferrous ion was generated coulometrically in aqueous HCl from vacuum-annealed iron electrodes of 99.999% spectroscopic purity in a closed titration cell quite free of oxygen. At 25 °C the first acid constant of the aquated ferrous ion is $pK_a = 9.2 \pm 0.1$. The solubility product of $Fe(OH)_2$(ppt) at 25 °C is $pK_{sp} = 14.39 \pm 0.05$. Additional measurements at 1 and 40 °C yielded the heat of acid dissociation of $Fe^{2+}{}_{aq}$ as $\Delta H = +8.5 \pm 1.2$ kcal/mol and the heat of dissolution of the hydroxide to ions as $\Delta H = +4.7 \pm 0.4$ kcal/mol. Ferrous hydroxide as ordinarily precipitated was found to be amorphous by X-ray diffraction. Measurements of the ion-pair association constant of $FeHCO_3^+$ place this constant, if it pertains, in the range 10–30 at 25 °C. Directly observed potentials Fe^{2+}/Fe^0 were independent of pH above pH 6 and under these conditions lay between the two values −0.409 and −0.440 V compiled in standard sources.

Introduction

Values of equilibrium constants for several simple but important reactions of the aquated ferrous ion $Fe^{2+}{}_{aq}$ have never been established with certainty. For the solubility product of ferrous hydroxide, for example, numbers ranging from 10^{-16} to 10^{-13} can be found. The acid dissociation constant of the aquated ion was determined by a reliable method in 1 M $NaClO_4$[4] after a number of determinations by incorrect methods; only one thermodynamic value referred to infinite dilution has been available.[10] The potential of the couple Fe^{2+}/Fe^0 has been reported from −0.467 to −0.409 V on the standard hydrogen scale, and the uncertainty in this value appears to affect seriously thermochemical tabulations for many iron-containing species. Although the solubility product of $FeCO_3$ (siderite) is known with good precision, little else is understood concerning the geochemically important

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interactions of Fe^{2+} with carbonate species, such as the formation of the ion pairs $FeHCO_3^+$ and $FeCO_3^0$. References to many of the original investigations of Fe(II) equilibria have been compiled recently by Tremaine et al.[21] and by Cerutti and Hepler.[23]

There are two major experimental problems that must be faced in order to make significant measurements of these equilibria. One is the extraordinary sensitivity of ferrous ion to molecular oxygen in the neutral region in which most of the reactions are accessible to measurement, about pH 6–8. The other difficulty is with the purity of the iron itself, whether as the metal or one of its salts. Several kinds of impurities in solution, including Fe(III) and Cu(II), can give aberrant impressions of hydrolytic properties, and impurity profiles of metallic iron profoundly affect its electrokinetic behavior, particularly the rates of the hydrogen evolution reaction. A commercial "reagent grade" Fe wire of "99.9%" purity was found to contain 965 ppm Cu, 430 ppm Mn, traces of several other transition metals,[14] and easily detectable amounts of C and S.

The rate law for the oxidation of Fe^{2+}_{aq} by O_2 has been found by several groups[3] to be

$$-\frac{d(Fe^{2+})}{dt} = k_{obsd}(Fe^{2+})(O_2)(OH^-)^2$$

with $k_{obsd} = 5.7 \times 10^{13}$ M^{-3} s^{-1} at 25 °C. The strong dependence upon OH^- reflects a very large difference in the kinetic stability of acidic vs. neutral solutions in air. Uncatalyzed pseudo-first-order half-lives of solutions saturated with air can be calculated to be 1×10^9 years at pH 1 and 45 s at pH 8.

It has not always been clear in reports of work on ferrous ion reactions to what extent the conditions of purity and elimination of O_2 and Fe(III) have been met. The intent of the present work was to reexamine some aspects of the behavior of Fe^{2+} using the best iron currently obtainable under conditions of isolation that would still allow titrations and close observation.

Experimental Section

Titration Cell. A closed glass cell of 100-mL capacity was designed and constructed for this work. Blanketing gases were passed through the cell by means of stainless steel needles through rubber septa, which also permitted injection of titrants from plastic/rubber syringes used as weight burets. The content of the cell was stirred with a Teflon-coated magnetic bar and the assembly was surrounded by a thermostated jacket. It was found necessary to boil the septa and the syringes for about 2 h in distilled water just prior to each experiment to remove oxygen dissolved in the rubber.

Electrodes. A Sargent-Welch S-30070-10 combination electrode, which is constructed with a 7/15 inner joint, was used both for pH measurements and as a reference. A platinum counterelectrode was used for the coulometric generation of Fe^{2+}.

Iron electrodes were fabricated from 5-mm diameter spectroscopic rods (described below). Sections of the rod 14 mm in length were turned down to 0.092 in. in diameter for a distance of 6 mm at one end. Machined electrodes were cleaned with carbon tetrachloride, etched for 1 h in 3 M HCl with several changes of acid, rinsed thoroughly with distilled water, and dried in air. Cleaned electrodes were annealed at 720 °C for several hours in evacuated and sealed Vycor tubes. One electrode was further treated to remove hydrogen more completely[20] by cycling between room temperature and 800 °C under an active vacuum of 4×10^{-7} mmHg. Six cycles each consisted of 25 min at temperature, maintained electrically with a cylindrical boat of Ta sheet surrounding the sample, and 5 min at room temperature.

Copper leads were spot-welded to the annealed electrode, and the reduced ends were cemented with epoxy into 0.100-in. glass extension tubes on 7/15 inner joints. Excess epoxy was removed with ethanol so that only a thin edge of epoxy between metal and glass was exposed to solutions. Two years of exposure of this material to dry air did not produce visible corrosion.

pH and Potential Measurements. A Corning Model 12 pH meter was used, which was calibrated with a Data Precision Model 2530A1 digital voltmeter. The latter was also used to measure potential differences between the Ag/AgCl reference and the iron electrode. The pH electrodes were standardized at temperature for several hours prior to each experiment using commercial buffers and published temperature coefficients.

Reagents. The iron from which all ferrous ion was generated was the spectroscopic grade rod manufactured by the Johnson Matthey Co. Their lot analysis identified less than 10 ppm total spectroscopically detectable impurities. About 10 ppm H was also reported (personal communication). Sensible amounts of C and S were absent upon dissolution of gram quantities in acid. Ordinary reagent grade iron wire was used early in the work but was found insufficiently pure.

Ferrous ion was generated coulometrically in the titration cell, under N_2 or Ar. A simple galvanostat was used to pass currents of 10–30 mA between the iron electrode and the platinum counterelectrode. A known excess of standardized 0.1 M HCl was present as the electrolyte. Coulometric and later gravimetric results for the amount of ferrous ion generated typically agreed within 1%. The Pt electrode was raised out of solution after electrolysis was completed. Excess HCl was neutralized (pH 5–6) with deaerated 1 M and 0.1 M NaOH prior to other titrations. In experiments concerned with bicarbonate ion-pair formation, the blanketing gas was at this point changed to CO_2.

Samples of $FeCl_2$ and $Fe(ClO_4)_2 \cdot 6H_2O$ were prepared from the iron rod and used in some of the initial experiments. The method of preparation of pure anhydrous $FeCl_2$ was that given by Winter.[21] The perchlorate was prepared by warming a section of iron rod, which contacted a piece of platinum sheet, in a slight deficiency of 4 M $HClO_4$ protected from air. When hydrogen evolution had ceased, after about 2 days, the solution was filtered in a nitrogen atmosphere and transferred to a simple trap-to-trap distillation apparatus, which was then evacuated. Water was removed by cooling the second trap to dry ice temperature for several hours. Product $Fe(ClO_4)_2 \cdot 6H_2O$ was recovered as greenish white fine crystals. Both the chloride and the perchlorate were free of Fe^{3+} when checked with SCN^-. They were stored in evacuated Schlenk tubes.

Stock solution of NaOH was prepared carbonate-free from reagent grade material in the usual manner and stored in a CO_2-free chamber. Oxygen-free titrants of 0.1 M and 0.004 M NaOH were prepared by volumetric dilution and standardization of this stock. Prepurified grades of CO_2, N_2, and Ar were scrubbed with acidic Cr^{2+} solution prior to passage through the cell. Other materials were all of reagent grade and were used as received.

In the adaptation of the method of Siebert and Hostetler[18] to the determination of K(pair) for $FeHCO_3^+$, a major portion of the coulometrically generated and neutralized ferrous ion solution was withdrawn from the cell into a thoroughly deoxygenated syringe after equilibration of the solution with ca. 1 atm P_{CO_2}. The second titrant was a determinant solution of $NaHCO_3$ or $KHCO_3$, also thoroughly deoxygenated and saturated at the same P_{CO_2} as the cell. Four or five alternate additions of each of these solutions were made to the cell, with attendant precise measurements of pH. (Due to the nature of the data treatment, calibrated pH measurements are not assumed absolute, but the scale of measurement is assumed linear with pH.)

X-ray Powder Diffraction. Powder patterns were obtained with a General Electric diffractometer using filtered copper radiation. The method was used chiefly to determine the nature of the precipitated $Fe(OH)_2(s)$ to which the experimentally derived values of pK_{sp} refer. Stoichiometric amounts of $FeSO_4 \cdot 7H_2O$ (5 mmol) and KOH (10 mmol, corrected for water content) were separately dissolved in 10 mL of 0.005 M H_2SO_4 and 10 mL of H_2O, respectively. The solutions were placed in separate flasks of a simple trap-to-trap distillation apparatus. Air was removed thoroughly by freezing and thawing the solutions repeatedly under vacuum; they were combined in one of the flasks, and the resulting white suspension of ferrous hydroxide was frozen with liquid nitrogen. The sample was freeze-dried by cryogenic pumping for several hours, the sample temperature being raised to 100 °C near the end of this period. A diffraction pattern of the resulting white fluffy powder was obtained immediately upon cooling and opening the flask. The diffraction peaks due to K_2SO_4, slightly broadened due to the method of preparation, were readily identified. The major peaks reported by Bernal et al.[1] for crystalline $Fe(OH)_2$ were absent. Very little oxidation occurred during the period of exposure to air. It appears that $Fe(OH)_2(s)$, as prepared by aqueous precipitation near room temperature without excess base, is amorphous, and that this is the state to which most values of K_{sp} pertain, including those of the present study.

Results and Discussion

Activity Coefficients. Since it was the intent of the work to derive thermodynamic values at infinite dilution for the equilibrium constants, rather than concentration-dependent values, all experiments were arranged such that ionic strengths did not exceed approximately 0.1 and activity coefficients were calculated for each species by means of the Debye–Hückel relationship

$$-\log \gamma_i = \frac{Az_i^2 I^{1/2}}{1 + å_i B I^{1/2}}$$

Values for A and B at each temperature were taken from Robinson and Stokes.[16] The following values of the ion-size parameter, $å_i$, were used: H^+, 9 Å; $FeOH^+$, $FeHCO_3^+$, 5.5 Å; Fe^{2+}, 6 Å. These were taken, or estimated, from the suggestions of Garrels and Christ.[2] The overall results are not particularly sensitive to the choices of $å_i$.

Hydrolysis (or Acid) Constant of Aquated Fe(II). Experimental values for the equilibrium constant, K_a, of the reaction

$$Fe^{2+}{}_{aq} \rightleftharpoons FeOH^+{}_{aq} + H^+ \tag{1}$$

were calculated directly from titrations of solutions of ferrous ion with sodium hydroxide that was rigorously free of oxygen and carbonate. At 0.02 m $Fe(II)_T$, the hydrolysis reaction above can be carried to the right about 3–4% prior to the onset of precipitation of $Fe(OH)_2$ around pH 7.8. The results of the study may be used to calculate that the self-pH of a solution of fully dissociated stoichiometric ferrous salt (chloride or perchlorate) of this concentration is near 5.7 at 25 °C. Thus, the hydrolysis reaction can be studied over a fair range of pH and titrant volume.

Solutions of ferrous ion were adjusted initially to a pH near the stoichiometric point, the amount of base needed for this being accounted for as NaCl or $NaClO_4$ in later calculations of ionic strength. Titrant NaOH was added in increments sufficient to shift pH upward by 0.1–0.2 unit. The pH values resulting were stable within a few seconds and were read for a few minutes thereafter.

The equilibrium constant for eq 1 was evaluated in the form

$$K_a = [H^+](\gamma m_{FeOH^+})/(\gamma m_{Fe^{2+}}) \tag{2}$$

where $\gamma m_{FeOH^+} = [FeOH^+]$ and $\gamma m_{Fe^{2+}} = [Fe^{2+}]$. The two conditions required for calculation are the total charge balance

$$m_{Na^+} + m_{H^+} + 2m_{Fe^{2+}} + m_{FeOH^+} = m_{anion} \tag{3}$$

where a second term on the right for OH^- may be neglected, and the initial salt stoichiometric (or equivalence) condition is

$$2m_{Fe(II)_T} = m_{anion} \tag{4}$$

If only single deprotonation is considered, (4) may be rewritten as

$$2m_{Fe^{2+}} + 2m_{FeOH^+} = m_{anion} \tag{5}$$

The left sides of (3) and (5) may be equated to obtain

$$m_{FeOH^+} = m_{Na^+} + m_{H^+} \tag{6}$$

The concentration of the deprotonated ferrous ion was calculated according to (6) from the amount of titrant NaOH added beyond the equivalence point and from the pH, as $[H^+]/\gamma$. The concentration of aquated ferrous ion was then obtained as

$$m_{Fe^{2+}} = m_{Fe(II)_T} - m_{FeOH^+} \tag{7}$$

Appropriate activity coefficients were applied to $m_{Fe^{2+}}$ and m_{FeOH^+}, and (2) was used to obtain an independent value of K_a for each point in the titration. Exact equivalence was not always obtained prior to titration; the last points, at higher pH, were relatively insensitive to this condition, and the K_a value obtained from them was imposed at the first point to derive a small correction for an excess of deficiency of acid. This correction was then applied to all points. The size of these adjustments to data in the most reliable region (pH 6.8 and above) was 0.1 pK unit and less.

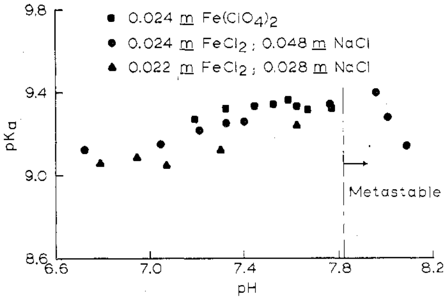

Figure 1. Independent values of the acid dissociation constant of the ferrous ion (expressed as pK_a) at 25 °C in several media as a function of pH. Three values obtained in a region supersaturated with respect to precipitation of the amorphous hydroxide are included. The overall average of the 22 data plotted is 9.23, and the range of dissociation represented is 0.2–4.4% of the total Fe^{2+}.

Data from three experiments at 25 °C are given in Figure 1. At least part of the scatter of the results is due to slight instabilities in the reference portion of the combination electrode, which were more troublesome at higher temperatures. It appears from the small upward trend of the results with pH that reaction 1 may not entirely account for the behavior of the system, although it is a good approximation. Loss of a second proton at the upper end of the range is not indicated prior to the equilibrium precipitation point.

The average result at 25 °C is $K_a = 6 \times 10^{-10}$, or pK_a = 9.2 (1). No significant differences were found between Cl^- and ClO_4^- as counterions in this determination. Although many values for the acidity constant for ferrous ion have appeared in the literature, most of these have been determined by unreliable methods, such as the measurement of the pH of solutions of "pure" salts. A value that has come to be accepted is that due to Hedstrom in 1953,[4] which was determined by a method similar to the one here. His result is pK_a = 9.5 (2) at 25 °C, and it is a concentration constant in 1 M $NaClO_4$. The direction and approximate magnitude of the difference between Hedstrom's result and the present one is what would be expected if activity coefficients appropriate to 1 M $NaClO_4$ were applied. We consider the two studies to be in good agreement. The infinite dilution value reported by Messmer,[10] 9.49 (8), obtained by titration of 0.003 mol kg^{-1} Fe^{2+} solutions, is somewhat higher than that found in the present work and does not agree with Hedstrom's result if the difference in ionic strengths is taken into account.

The average pK_a at 25 °C, 9.23, is equivalent to an association constant for the equilibrium

$$Fe^{2+}{}_{aq} + OH^- \rightleftharpoons FeOH^+{}_{aq} \tag{8}$$

of 6×10^4, or pK_f = −4.8 (1).

Some information concerning the temperature dependence of equilibrium 1 was obtained from additional measurements of pK_a at 1 °C and at 40 °C, the average values found being 9.75 and 8.87, respectively. Higher temperatures were not accessible due to the limitations of the pH-combination electrode. The run-average results are plotted vs. reciprocal absolute temperature in Figure 2. The line of least-squares deviations is shown, from which the enthalpy, $\Delta H_r°$, of the forward reaction in (1) was calculated to be +8.5 (±1.2)

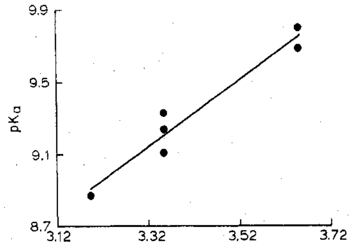

Figure 2. Temperature dependence of the acid dissociation constant of the ferrous ion at 1, 25, and 40 °C. Points plotted are averages for particular runs; the three points at 25 °C are from the data of Figure 1. The line of least-squares fit is shown, and from its slope the heat of acid dissociation is +8.5 (1.2) kcal/mol.

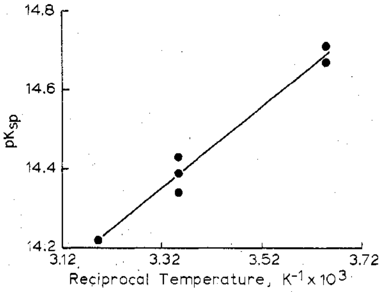

Figure 3. Temperature dependence of the solubility product of amorphous ferrous hydroxide (white) at 1, 25, and 40 °C. The line of least-squares fit is shown and from its slope the heat of dissociation to ions is +4.7 (4) kcal/mol.

kcal/mol. This result, which may be interpreted as the enthalpy of acid dissociation of water molecules bound to Fe(II), may be compared with the enthalpy of dissociation of water itself, +13.34 kcal/mol. For further comparison, the results of McGee and Hostetler[9] have been recalculated by us to yield a heat of dissociation of water bound to Mg^{2+} of +14.9 kcal/mol.

Solubility Product of Ferrous Hydroxide. At the end of each titration for pK_a, small amounts of 0.1 N NaOH were added until a white precipitate of $Fe(OH)_2$ persisted. The pH in the presence of the precipitate became steady within about 1 min, and further small additions of base did not shift this value upward, showing that additional hydroxyl ion is accommodated rapidly by the precipitation reaction. The latter is true only when precipitation is already initiated; prior to the appearance of the precipitate the system can be supersaturated, and ion activity product to K_{sp} ratios as high as 3–4 were easily achieved. Deliberate addition of small amounts of Fe^{3+} to the system prior to precipitation demonstrated that less than 0.1% of the total iron present in this state is sufficient to impart a perceptible green color to the precipitate; green precipitates occur and persist at values of pH lower than the normal value for white ferrous hydroxide (cf. Bernal et al.[1] and Leussing and Kolthoff[8]).

The value of pK_{sp} was calculated as

$$pK_{sp} = pFe^{2+} + 2(pK_w - pH)$$

where the value of pK_w appropriate to each temperature was taken from Olofsson and Hepler,[12] and pFe^{2+} was determined from the total concentration of Fe^{2+} (less the amounts hydrolyzed as $FeOH^+$ and precipitated as $Fe(OH)_2$) and the activity coefficient calculated for the conditions. The amount of Fe^{2+} precipitated with added NaOH did not exceed 20% of the total. The results of these calculations are plotted for experiments at 1, 25, and 40 °C in Figure 3. The average result at 25 °C is $pK_{sp} = 14.39$ (5) or $K_{sp} = 4.1 \times 10^{-15}$, and the heat of dissolution of the hydroxide to ions is calculated from the least-squared line of Figure 3 to be +4.7 (4) kcal/mol. As described in the Experimental Section, these results refer to freshly precipitated *amorphous* $Fe(OH)_2$.

Solubility products at 25 °C have been reported many times previously, but in no case was the physical state of the material to which the data apply also described. The values reported have been summarized by Randall and Frandsen[15] and more recently by Leussing and Kolthoff.[8] The solubility product determined by Randall and Frandsen from their own work, $pK_{sp} = 14.84$ at 25 °C, is somewhat larger than that reported here. It was derived indirectly by means of cell emf measurements, and the value used for the potential Fe^{2+}/Fe^0 was −0.440 V, determined by the same authors.

Of values previously determined by direct methods, that due to Leussing and Kolthoff may be the most reliable. Their average, $pK_{sp} = 15.1$ (2) at 25 °C, refers specifically to precipitates held in contact with the liquor for several days. Their description implies that numerically smaller values (i.e., larger solubility products) would have been obtained for shorter times, which agrees qualitatively with the present findings. Our observations are that the larger solubility product at early times is not an artifact of incomplete precipitation but that equilibrium with respect to the fresh precipitate is established rapidly. Whether the precipitates present in the experiments of Randall and Frandsen and of Leussing and Kolthoff had aged sufficiently to become fully crystalline materials is, unfortunately, not known.

Stability of the Ion Pair $FeHCO_3^+$. The problem of measurement of stability constants for weak ion pairs of the type $MHCO_3^+$ has been successfully approached in several cases by a method described in detail by Siebert and Hostetler.[18] It is found in practice that the values of K(pair) so calculated for various bicarbonate/metal ion concentration conditions generated during an experiment became quite consistent if the value of $pK_0 + pK_1$ (CO_2 dissolution and first ionization constants) is not regarded as known exactly for a particular set of conditions but is allowed to vary slightly ("float") about the value 7.82. This variance is allowed until a value is found which gives the minimum dispersion of values for K for an individual experiment.

The formation constants for the pairs $MgHCO_3^+$ and $MnHCO_3^+$ at 25 °C have been found by this method to be 11.7 (0.8)[18] and 18.8 (1.0),[7] respectively. Each of these values was duplicated within one standard deviation in the present work using the titration cell and pH-combination electrode designed for study of Fe(II).

The results of a dozen experiments with Fe^{2+} failed to show consistent convergence to constant K(pair) values, in contrast to experience with Mg^{2+} and Mn^{2+}. In the latter cases, the value of $pK_0 + pK_1$ at which convergence was achieved for the conditions employed was 7.85 (1). Application of this value in direct calculations of the data for Fe^{2+} gives a range for K(pair) for $FeHCO_3^+$ at 25 °C of 10–30. This range includes most of the interrun as well as intrarun variation. To the extent that this is a reliable estimate of the association between Fe^{2+} and HCO_3^-, the ion pair is approximately as stable as that of Mn^{2+}.

It is in the nature of the technique that no definite result is obtained unless intrarun convergence occurs. In the absence of this condition, it may be questioned whether simple 1:1 ion pairing adequately represents the system. An alternative treatment of the data in which the ion pair formed was assumed to be $FeCO_3^0$ rather than $FeHCO_3^+$ showed a similar failure to converge to a unique value. All runs were made in the pH range 4.9–5.4 and with ratios $Fe^{2+}{}_T/HCO_3^-{}_T$ ranging from 4:1 to 14:1 to eliminate the formation of higher order complexes, $Fe(HCO_3)_n{}^{(2-n)+}$.

Potential of the Couple Fe^{2+}/Fe^0. Two values for the standard potential of this couple have been available from careful measurements of voltages across sealed cells over long periods of time. The earliest is that due to Randall and Frandsen,[15a] −0.440 V; this value was carried in the compilations by Latimer[6] and also in ref 17a. Later, Patrick and Thompson[13] made new measurements on cells incorporating metallic iron electrodes derived from the carbonyl, which were claimed to be free of hydrogen on that account, and they reported the potential as −0.409 V. The reasoning that would explain a shift *toward* the hydrogen potential due to the *absence* of hydrogen in the metal was not discussed. More recent compilations in ref 17a have, nevertheless, accepted the more recent value to the exclusion of the earlier determination. The value −0.467 V determined by Hurlen[5] by extrapolation of forward and reverse kinetic data is probably less reliable, because of the method employed, than the first two values cited.

As is well-known, the major difficulty in making significant measurements of this potential is hydrogen evolution due to the relationship between the potentials $Fe^{2+}|Fe^0$ and $H^+|H_2$. Under most circumstances of purity and acidity a "mixed potential" is obtained resulting from the reactions

$$Fe^0 \rightleftharpoons Fe^{2+} + 2e^-$$

$$2H^+ + 2e^- \rightleftharpoons H_2$$

which occur simultaneously, with the net reactions being to the right. The measured potential (i.e., the potential at which the algebraic sum of currents due to the four reactions is zero) usually lies between the "pure" potentials $Fe^{2+}|Fe^0$ and $H^+|H_2$. Its exact position is determined primarily by the *kinetics* of the hydrogen evolution reaction under particular conditions. Hydrogen evolution becomes slower with increasing pH and with increasing purity of the iron. The "pure" potential $Fe^{2+}|Fe^0$ ought to be independent of pH, unlike the mixed potential. Conversely, a lack of dependence upon pH for observed potentials may be taken as evidence of their significance with respect to the true value for $Fe^{2+}|Fe^0$, provided this independence obtains at pH values below that at which $E(Fe^{2+}|Fe^0) = E(H^+|H_2)$. At unit activities, the latter condition is apparently attained at pH 7.5, but for actual conditions with activities of Fe^{2+} and H_2 much less than unity, it will be higher than pH 8.

The potentials measured in the present work were those of the cell $Fe^0|FeCl_2$ (*ca.* 0.02 *m*)||saturated KCl|AgCl|Ag^0 where the iron half-cell was that resulting from coulometric generation of Fe^{2+} and subsequent titration operations and the reference half-cell was that of the Sargent-Welch pH-combination electrode. Junction-free measurements of the latter against the saturated-calomel electrode (+0.2444 V) placed the reference in the range +0.2015 to +0.2039 V on the standard scale, depending upon the individual combination electrode used. (A value of +0.2000 V was calculated from the standard Ag|AgCl potential (+0.2224 V), the mean molal activity coefficient of saturated KCl, and the assumption of equal activities of K^+ and Cl^- in these solutions.[16]) The effects of liquid junction at the typical ionic strengths of cell solutions was estimated by setting up the half-cell $Ag^0|AgCl|0.100$ mol kg^{-1} NaCl in the titration cell. Comparison of measured differences with those calculated from the Debye–Hückel activity coefficient for Cl^- (0.75) led to apparent liquid junction potentials of not more than 2–3 mV. In view of the uncertainties involved, no corrections for liquid junction potentials were made in the data.

Measured potential differences for the iron–silver cell were further corrected for the value of the Nernst term $(RT/2F)\cdot\ln \gamma_{Fe^{2+}} m_{Fe^{2+}}$ applicable at each experimental point. Under the conditions employed, $\gamma_{Fe^{2+}}$ was usually near 0.4.

A representative series of inferred values of the *apparent* standard reduction potential for the couple $Fe^{2+}|Fe^0$ as a function of pH is shown in Table I.

Table I

pH	$E°(Fe^{2+}\|Fe^0)$, V	pH	$E°(Fe^{2+}\|Fe^0)$, V
1.42	−0.200	6.72	−0.414
2.94	−0.328	7.04	−0.415
3.96	−0.374	7.21	−0.417
5.38	−0.408	7.40	−0.417
5.81	−0.414	7.60	−0.415
6.36	−0.415		

These data were all obtained in a single experiment using iron specially vacuum-annealed to remove H_2; observations were made for periods varying from minutes to hours. It is to be noted that the values above are strongly influenced by pH in the acidic region but that they become independent of pH at 5.8 and above. The constant measured potentials over a 100-fold change in $[H^+]$ indicate that the potentials are no longer "mixed" (in the sense above) but are referable to the $Fe^{2+}|Fe^0$ couple alone in the "plateau" region. With ordinary grades of iron, such as the 99.9% "reagent grade" iron wire referred to previously, no such plateau exists, and all measured potentials are less negative than those above.

In the case of high-purity iron which had been annealed in static vacuum, but not specially degassed, potentials in the plateau region were somewhat more negative; several experiments gave values near −0.435 V. Due to some variability in the performance of the reference electrodes and to the presence of some liquid junction potential, it is not certain that this difference is attributable to differences in the hydrogen content of the metal, but the direction of the change is consistent with the two reports cited.[13,15a]

All potentials measured on high-purity iron lay between the previously established "best" values of −0.409 V[13] and −0.440 V.[15a] We do not propose a new value nor argue for a choice between the two values established in measurements of sealed cells over long periods of time. The principal conclusion of the present work is that under conditions of sufficient purity of the metal and freedom of the system from contamination with Fe(III) and O_2 physically significant potentials can be measured immediately and, further, that the potentials are experimentally independent of pH, in agreement with theory. These points, we believe, have not been previously demonstrated. In the experiments with sealed cells reported in the literature, the pH values were neither known nor controllable; in consequence, it could not be shown that the measured voltages, though constant after some period of time necessary for removal of contaminants, were independent of pH. It is clear that additional careful experimental work is still needed on this important system.

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Registry No. $Fe(OH)_2$, 18624-44-7; $FeHCO_3^+$, 67328-72-7; $FeCO_3^0$, 563-71-3; Fe, 7439-89-6.

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Kinetics and Mechanism of the Ligand-Substitution Reaction of the Copper(II)–4-(2-Pyridylazo)resorcinol Complex with *trans*-1,2-Diaminocyclohexane-*N*,*N*,*N′*,*N′*-tetraacetic Acid with Special Reference to the Effect of Unidentate Ligands

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The kinetics of the ligand-substitution reaction of the copper(II)–4-(2-pyridylazo)resorcinol complex (Cu^{II}-PAR) with *trans*-1,2-diaminocyclohexane-*N*,*N*,*N′*,*N′*-tetraacetic acid (CyDTA) has been studied spectrophotometrically in the presence of unidentate ligands (L = NH_3, CH_3COO^-, N_3^-, SCN^-, Cl^-, Br^-, and I^-) and in the pH range 9.0–10.0 at $I = 1.0$ ($NaClO_4$) and at 25 °C. The rate of the substitution reaction is expressed as $-d[Cu(par)_2^{2-}]/dt = k_1[Cu(par)][cydta'] + k_{OH}\cdot[Cu(par)OH^-][cydta'] + k_L[Cu(par)L][cydta']$, where cydta′ denotes CyDTA not combined with copper ion, and $k_1 = 1.57 \pm 0.03$ mol^{-1} dm^3 s^{-1}, $k_{OH} = 0.491 \pm 0.034$ mol^{-1} dm^3 s^{-1}, $k_{NH_3} = 1.73 \pm 0.014$ mol^{-1} dm^3 s^{-1}, $k_{CH_3COO} = 0.183 \pm 0.006$ mol^{-1} dm^3 s^{-1}, $k_{N_3} = 0.672 \pm 0.020$ mol^{-1} dm^3 s^{-1}, $k_{SCN} = 0.303 \pm 0.008$ mol^{-1} dm^3 s^{-1}, $k_{Cl} = 0.26 \pm 0.11$ mol^{-1} dm^3 s^{-1}, $k_{Br} = 0.70 \pm 0.18$ mol^{-1} dm^3 s^{-1}, and $k_I = 1.33 \pm 0.07$ mol^{-1} dm^3 s^{-1}, all at 25 °C and $I = 1.0$. The reactivity of the mixed-ligand complex (Cu(par)L) is discussed in terms of the electron donation from L.

Introduction

The ligand-substitution reaction often proceeds through an intermediate mixed-ligand complex, in which the central metal ion is simultaneously bonded to both leaving and entering ligands. The rate-determining step of the reaction is the cleavage of the bonds of the metal ion and leaving group. For instance, Ni(edda) and $Ni(nta)^-$ react with PAR to give intermediate mixed-ligand complexes $Ni(edda)par^{2-}$ and $Ni(nta)par^{3-}$, respectively[2] ($edda^{2-}$ = ethylenediamine-*N*,*N′*-diacetate, nta^{3-} = nitrilotriacetate, PAR = 4-(2-pyridylazo)resorcinol (H_2par)). The reaction of $Ni(dien)^{2+}$ and EDTA gives $Ni(dien)edta^{2-}$ as a fast step (dien = diethylenetriamine).[3] Furthermore, a third ligand being incorporated in the mixed-ligand intermediates, the reaction rates are sometimes dramatically accelerated by added ligands.[4–8] Thus, the formation of the mixed-ligand intermediate plays an important thermodynamic and kinetic role in the overall reaction processes.

The kinetic effect of coordinated ligands in the mixed-ligand complexes has also been reported for the dissociation reaction of various nickel(II)–malonate mixed-ligand complexes by Hoffmann and Yeager,[9] and a correlation, except for some ligands, has been found between the dissociation rate and the observed spectral shift of the d–d orbital transition of the mixed-ligand complex.

Zinto et al.,[10] in a study of the aquation of a series of substituted acetatopentaammine chromium complexes ($Cr(NH_3)_5(RCOO)^{2+}$, R = CCl_3, $CHCl_2$, CH_2Cl, CH_3), have related the rate of aquation of NH_3 with the basicity of $RCOO^-$ and suggested the hydrogen bond formation between acetate and NH_3 in the cis position. According to them, the stronger the hydrogen bond, the faster is the rate of ammonia dissociation. However, the increased rate of aquation with increasing basicity of $RCOO^-$ may alternatively be attributable to the increased electron donation from carboxylates.

Nakagawa and Wada[11] have found an accelerating effect of 1,10-phenanthroline (phen) in the ligand-substitution reaction of $Cu(pan)^+$ (pan = 1-(2-pyridylazo)-2-naphthol) with EDTA. They have explained the kinetic data in terms of the structural property of the distorted octahedral mixed-ligand complex Cu(pan)phen.

In previous papers,[7,8] we have reported on the acceleration of the ligand-substitution reaction of certain mercury(II) complexes with *trans*-1,2-diaminocyclohexane-*N*,*N*,*N′*,*N′*-tetraacetic acid (CyDTA) in the presence of halide ions or of ammonia. In this reaction we have mixed halogeno- or hydroxo or ammine complexes of mercury(II). The reaction rate (k_0) is formulated as the product of the formation constant of the mixed-ligand complex (K_M) and the dissociation rate constant (k_d); $k_0 = K_M k_d$. We wish to understand the extent of these two effects. To this end the formation constants of the mixed-ligand complexes of Cu^{II}–PAR with unidentate ligands (L = NH_3, pyridine, CH_3COO^-, N_3^-, SCN^-, Cl^-, Br^-, I^-) have been determined by spectrophotometry.[12] The logarithmic formation constant has been related with both the electron-donor constant (E_n) and the basicity constant (H) of the unidentate ligand. The present paper describes the kinetic results on the substitution reaction

$$Cu^{II}\text{–PAR} + \text{CyDTA} \rightleftharpoons Cu^{II}\text{–CyDTA} + \text{PAR}$$

in the presence of these unidentate ligands.

Experimental Section

Reagents. Methods of preparation and standardization of the reagents (copper(II) perchlorate, unidentate ligands, CyDTA, sodium perchlorate, and sodium hydroxide) have been described previously.[12]

Measurements. The kinetics of the substitution reaction was studied spectrophotometrically by recording the change of absorbance of Cu^{II}–PAR complex at 500 nm as a function of the reaction time with a Toa EPR-100A recorder. The absorbance was measured with a Hitachi 139 UV–vis spectrophotometer with a thermostated 10-mm

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