From the activation parameters of the forward and reverse steps we find $\Delta H = -11 \pm 1$ kcal/mol and $\Delta S = -7 \pm 3$ cal deg^{-1} mol^{-1} under the experimental conditions used in this study.

The formation quotient, K_I, is approximately 2–10 times larger than those calculated[6] for a series of pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles. In this work we have shown that the larger stability of the dimethyl sulfoxide complex is reflected in the relatively low specific rate of dissociation of the complex, rather than in a high formation rate. In view of the relatively weak basicity of dimethyl sulfoxide, its strong interaction with the pentacyanoferrate(II) group can only be explained by postulating a covalent bond between DMSO and iron(II) in the complex. The fact that complexes of oxygen bases (*e.g.*, H$_2$O, tetramethylene sulfone) are apparently weak and labile also suggests strongly that the bond is between iron(II) and sulfur.

Conclusion. The existence of a stable, sulfur-bonded DMSO adduct of pentacyanoferrate(II) suggests an important role for M(dπ)–S(dπ) back-bonding in octahedral, low-spin iron(II) complexes. Also, in view of the similar existence of the pentaammine(dimethyl sulfoxide)ruthenium(II) ion, the analogy which has been noted[5] between complexes of pentacyanoferrate(II) and those of pentaammineruthenium-(II) is further extended.

Hydrolytic Precipitation of Iron(III) in 1 *M* (Na)NO₃ Medium

P. R. DANESI,* R. CHIARIZIA, G. SCIBONA, and R. RICCARDI

The hydrolytic precipitation of iron(III) has been investigated at 25° in a 1 *M* (Na$^+$)NO$_3^-$ medium by measuring the acidity of the solutions by glass electrode potentiometry. The hydrolysis process was found to be a very slow one (equilibrium was reached after at least 4 weeks) ending in the formation of a basic precipitate of composition Fe(OH)$_2$(NO$_3$). The data could be explained by assuming only the reaction Fe^{3+} + NO$_3^-$ + 2H$_2$O $\rightleftharpoons$ Fe(OH)$_2$NO$_3$(s) + 2H$^+$ with log $K^* = 2$ log (H$^+$) − log (Fe^{3+}) = −(2.20 ± 0.03) where K^* is the equilibrium constant for the formation of the rather insoluble iron(III) basic nitrate.

Introduction

The hydrolytic behavior of iron(III) ions has attracted the attention of many inorganic chemists. A summary of quantitative conclusions derived from these studies up to 1964 is reported in ref 1. Work performed after 1964 is quoted in ref 2–11. One of the main features of iron(III) hydrolysis is the slowness of the equilibria, a fact recognized as early as 1936[2] when it was stated that the final product of the slow hydrolytic process was the formation of a solid phase leaving no soluble hydrolytic species in equilibrium. Due to this slowness many of the studies carried out seem to have been dealing with nonequilibrium solutions. Nevertheless valuable information has been obtained from physical techniques such as ir and visible spectrophotometry,[5] nmr,[9] esr,[11] and ultracentrifugation.[3] Potentiometric techniques (glass electrodes or redox potentials) have also yielded useful information on composition and formation constants of metastable products forming and dissociating much faster then their transformation to eventually stable products.[12,13] One of the few works dealing with equilibrium data seems to be a potentiometric study[4] of iron(III) chloride solutions. The authors of that paper have in fact applied the mass action law to their potentiometric data only when equilibrium was reached in the hydrolyzed solutions, the time required being of the order of several weeks. In this condition the only reaction required to explain the experimental data was the formation of a precipitate

$$Fe^{3+} + 2.70H_2O + 0.30Cl^- \rightleftharpoons Fe(OH)_{2.70}Cl_{0.30}(s) + 2.70H^+$$
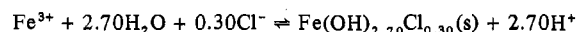
Equilibrium data concerning the hydrolysis process seem still to be lacking for iron(III) nitrate solutions. The slowness of the equilibria has in fact prevented drawing significant conclusions from potentiometric measurements[3] recorded too soon after the starting of the hydrolytic reactions. On the other hand it was shown from ultracentrifuge, dialysis, gel filtration, and chemical analysis that the hydrolysis of ferric nitrate leads to the formation of a high molecular weight polymer, [Fe(OH)$_x$(NO$_3$)$_{3-x}$]$_n$ (where x lies between

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2.3 and 2.5 and $n \cong 900$). This result is, at least qualitatively, in agreement with the more recent esr studies[11] which report the formation of a high molecular weight polymer with a structure similar to that of ferritin. The similarity between ferritin and hydroxyiron was also pointed out in ref 3.

The present work was therefore started with the aim of obtaining stoichiometric information as well as quantitative thermodynamic data on the very slow ferric nitrate hydrolysis equilibria which are still rather poorly known. Glass electrode potentiometry was used in a 1 M (Na)NO$_3$ constant ionic medium to keep activity coefficients constant.

Symbols

B Total iron(III) concentration
H $(NO_3^-) - 3(Fe(III)) - (Na^+)$ = analytical excess of hydrogen ions assuming no hydrolysis
h (H^+) = equilibrium concentration of hydrogen ions
Z $(h - H)/B$ = average number of hydroxyl ions per iron(III) atom in the solution and precipitate.

Experimental Section

Reagents. An iron(III) nitrate stock solution was prepared by dissolving $Fe(NO_3)_3(H_2O)_9$ (Merk p.a.) in water containing a certain amount of nitric acid (Carlo Erba RS-ACS) to prevent hydrolysis. The total iron(III) concentration in this solution was determined gravimetrically.

Stock solutions of $NaNO_3$, HNO_3, and $NaOH$ (Carlo Erba RS-ACS) were prepared, stored, and analyzed as reported previously.[14] By mixing suitable amounts of solutions containing Fe(III), HNO_3, and $NaNO_3$, solutions having the following initial composition were prepared: B M Fe(III), H_0 M H$^+$, $(1.0 - H_0 - 3B)$ M Na$^+$, and 1 M NO_3^-, where B had the values 0.100, 0.050, 0.010, 0.005, and 0.001 M.

H_0 represents the initial hydrogen ion concentration of the unhydrolyzed solution. It was evaluated using an ion-exchange resin, substituting Fe^{3+} ions with H$^+$ ions and then titrating the eluate.

All the solutions were maintained under a slight pressure of purified N_2. Also the potentiometric measurements (see later) were performed under a slow bubbling of N_2.

Method of Investigation. Solutions having the composition B M Fe(III), H M H$^+$, $(1 - H - 3B)$ M Na$^+$, and 1 M NO_3^- (test solutions) have been prepared from the previously reported initial solutions by decreasing H. They have been measured at 25° with the electrochemical cell

Hg, Hg$_2$Cl$_2$ |1 M NaCl|1 M NaNO$_3$ |test solution|glass electrode   (I)
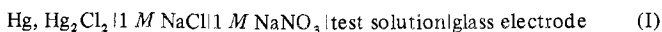
Preliminary experiments, where H was lowered, have shown that a stable potential (within 1 mV) in cell I was only obtained after a period of at least 4 weeks. Because of this long equilibrium time expected on the basis of the previous works,[1-11] the discontinuous technique of measurement[14] was followed. Therefore a certain number of test solutions (generally 10 for each B) were prepared and stored under N_2 at 25°, and the potential of cell I was measured at time intervals of 1 week. Although after 4 weeks no appreciable changes were observed, the potentials after 6 weeks were taken as equilibrium values. To test the reversibility of the hydrolytic reactions, in a few cases H was increased. In this instance the time required to reach equilibrium was at least twice as long. The Z values obtained were falling on the same experimental curve within the limit of the experimental error. The presence of a precipitate in the solution, which in some cases was visually detectable when equilibrium was reached, did not seem to affect appreciably either the time required to attain equilibrium or the reproducibility of the Z values. Knowing the analytical hydrogen ion concentration, H, and obtaining h from the relationship

$$E = E^\circ + E_j + 59.15 \log h \qquad (1)$$

Z was easily calculated as function of $-\log h$. The experimental results are reported in Figure 1.

Equipment. Glass electrode, potentiometer, and liquid junction reference electrode were the same as described,[14,15] the only difference being in the concentration of the ionic medium (1 M NO$_3^-$).

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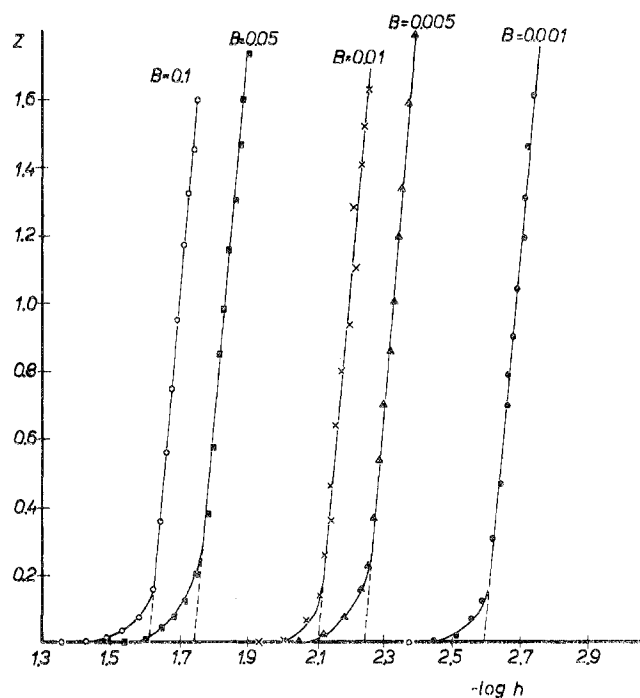
Figure 1. Average number of hydroxyl ions bound to each iron-(III) (Z) *vs.* the logarithm of equilibrium hydrogen ion concentration $(-\log h)$.

The liquid junction (E_j) and the standard potential (E°) of eq 1 were determined[15] immediately before and after each potentiometric determination of the test solutions.

Results and Discussion

The first attempt to interpret the experimental data of Figure 1 has been performed by using the general minimization program LETAGROPVRID[12,13] largely used by the Scandinavian school to calculate hydrolysis constants. The failure to get even a poor fit of the data with any hydrolytic scheme implying the presence of soluble hydrolyzed species, together with the literature indications[3,4,11] showing that the ultimate hydrolysis product is a solid (more or less polymerized), has induced us to try to interpret the experimental results along the pattern

$$Fe(NO_3)_n^{3-n} + (3 - n)OH^- \rightarrow Fe(NO_3)_n(OH)_{3-n}(s) \quad K_e \qquad (2)$$
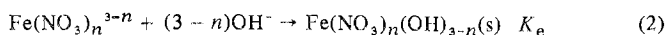
Since in a nitrate medium the complex formation equilibria

$$Fe^{3+} + nNO_3^- \rightleftharpoons Fe(NO_3)_n^{3-n} \quad K_n \qquad (3)$$
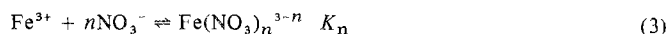
are also present, we obtain for K_e

$$K_e = \frac{\{H^+\}^{3-n}}{K_n K_w^{3-n} \{Fe^{3+}\} \{NO_3^-\}^n} \qquad (4)$$

where $\{\}$ represents activity, the activities of the solid species and H_2O have been set equal to 1, K_e and K_n are formation constants, and K_w is the dissociation constant of H_2O. Since in our experiments (NO_3^-) is constant, eq 4 is further simplified to

$$(H^+)^{3-n}/(Fe^{3+}) = K^* = K_e K_n K_w^{3-n}(NO_3^-)^n \qquad (5)$$

Equilibria 2 and 3 are equivalent to

$$Fe^{3+} + mH_2O \rightleftharpoons Fe(OH)^{3-m}(s) + mH^+ \quad K^* \qquad (6)$$
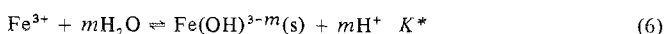
with $3 = m + n$.

If no soluble polynuclear hydrolysis products are present, Z must be equal to zero in a plot of Z *vs.* $\log h$, till the formation of $Fe(NO_3)_n(OH)_{3-n}(s)$ starts to take place. After this point Z must rise very sharply. The trend of the curves of Figure 1 is in agreement with such a mechanism although the

Table I[a]

B, M	$\log h_p$	$\log B$	$m \log h_p$	$\log K^*$
0.100	−1.61	−1.000	−3.22	−2.22
0.050	−1.75	−1.250	−3.50	−2.25
0.010	−2.11	−2.000	−4.22	−2.22
0.005	−2.25	−2.250	−4.50	−2.25
0.001	−2.59	−3.000	−5.18	−2.18

[a] $m = 2$; $\log K^*$ (average) = −(2.20 ± 0.03). Evaluation of precipitate composition and $\log K^*$ is from the experimental data of Figure 1.

initial curvature indicates that small amounts of soluble hydrolysis products can still be present in the solutions.

In order to check the mechanism of formation of this new phase in a more quantitative way and to calculate m and K^* in our ionic medium, equilibrium 6 can be looked upon as a precipitation reaction. For this purpose the values of (Fe^{3+}) and $(H^+)_p$ at the precipitation point must be available. They are easily obtained by setting $(Fe^{3+}) = B$ (before the solubility product is reached all the iron is assumed to be unhydrolyzed) and calculating $(H^+)_p$ from the intercept of the nearly vertical lines of the plot Z *vs.* $-\log h$ of Figure 1. These values are reported in Table I.

Differentiation of eq 5 gives then

$$\frac{d \log (Fe^{3+})}{d \log (H^+)_p} = \frac{d \log B}{d \log h_p} = m \tag{7}$$

Figure 2 shows that the plot of $\log B$ *vs.* $\log h_p$ is rectilinear with a slope $m = 2$. Equation 2 can then be treated as

$$Fe(NO_3)^{2+} + 2OH^- \rightarrow Fe(NO_3)(OH)_2(s)$$
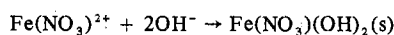
and $\log K^*$ can then be easily obtained from $\log K^* = 2 \log h_p - \log B$. The calculated averaged value of $\log K^*$ is −2.20 ± 0.03 (see also Table I).

The results we have found are in good agreement with the previous finding[4] that the final product of the hydrolysis process is a basic salt precipitate, $Fe(OH)_{2.70}Cl_{0.30}$, with log $K^* = -3.04$. In our case the different stoichiometry of the basic salt precipitated as well as the different log K^* value can be ascribed to the different nature and concentration of the ionic medium. It seems moreover, from the long time
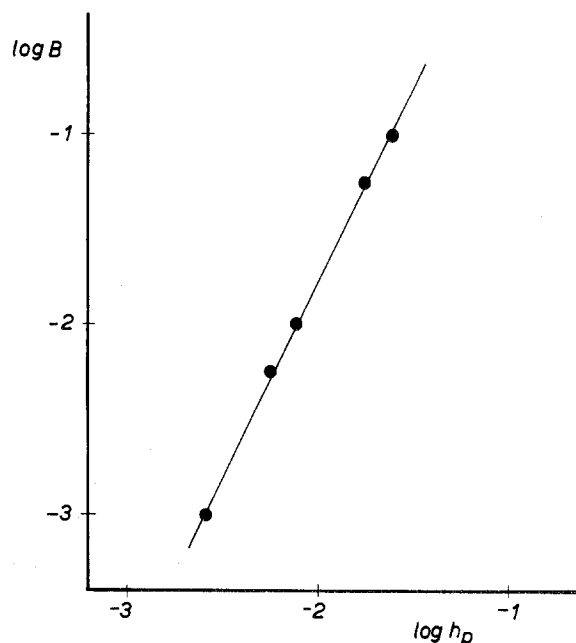

Figure 2. Logarithm of total iron(III) concentration ($\log B$) *vs.* the logarithm of equilibrium hydrogen ion concentration at the precipitation point ($\log h_p$). $\log h_p$ is obtained as the intercept of the dashed lines on the $-\log h$ scale of Figure 1.

required to reach equilibrium, that the previously identified[16,17] low molecular weight species such as $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe_3(OH)_4^{5+}$, and $Fe_2(OH)_2^{2+}$ are probably initially unstable products of the hydrolysis reaction which ends in precipitation of a basic salt (probably polymeric in character) with composition and solubility product value depending on the concentration and nature of the supporting electrolyte.

Registry No. $Fe(NO_3)_3$, 10421-48-4; $Fe(OH)_2(NO_3)$, 39900-57-7.

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Studies in Boron Hydrides. X. Substituent Effects in the Decahydrodecaborate(2−) Ion

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The ^{11}B nmr chemical shifts in two series of phenyl-substituted aryldiazoboranes of the types $XAr-N_2H-B_{10}H_9^-$ and $XAr-N_2-B_{10}H_9^{2-}$ are linearly related to the σ_m and σ_p constants for the substituent groups. These relationships indicate a resonance interaction between the two apical positions in the B_{10} polyhedron. Inductive and resonance effects may operate in the equatorial positions.

Introduction

Previously, we have employed ^{11}B nuclear magnetic resonance spectroscopy to elucidate substituent effects in penta-

borane(9) and phenylboronic acid.[2] We now report results which extend our observations to include substituent effects in the decahydrodecaborate(2−) ion, $B_{10}H_{10}^{2-}$.

The one truly definitive piece of evidence regarding elec-

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