axially substituted substitution product for a wide variety of L (eq 2) is consistent with this conclusion.

$$(\mathrm{phen})\mathrm{M(CO)_4} + \mathrm{L} \rightarrow fac\text{-}(\mathrm{L})(\mathrm{phen})\mathrm{M(CO)_3} + \mathrm{CO} \qquad (2)$$

Displacement of acetonitrile from *fac*-$(CH_3CN)(phen)M(CO)_3$ (M = Mo, 0°C; M = W, 22 °C) by ^{13}CO affords stereospecifically labeled *fac*-$(^{13}CO)(phen)M(CO)_3$ products. Reaction of these species with acetonitrile and then with ^{12}CO (Scheme I) affords mixtures of products (Table I) which, when assayed for ^{13}CO, demonstrate that reaction of $(phen)M(CO)_4$ with acetonitrile to afford *fac*-$(CH_3CN)(phen)M(CO)_3$ occurs exclusively via dissociation of an axial CO and that the carbonyls "scramble" statistically during the conversion. There is every reason to ascribe the scrambling process to the five-coordinate species produced via the D path, consistent with obervation for other systems, for which theoretical interpretations have been discussed in detail.[11-17]

The observation that only the *fac*-$(L)(phen)M(CO)_3$ products are obtained and that these products mirror the site of M–CO bond fission is consistent with the "quasi microscopic reversibility" argument (vide supra),[18] which is predicated on the nondiscriminating nature of the $[(phen)Mo(CO)_3]$ intermediates formed via M–CO bond fission.

The results for $(phen)M(CO)_4$ (M = Mo, W) are thus analogous to those for $(phen)Cr(CO)_4$, for which exclusive *axial* loss of CO and statistical scrambling of carbonyls in the resulting five-coordinate intermediate was also observed.[15,16] Thus the identity of the metal atom appears to exert little influence on these features of the ligand-exchange process in such group 6B metal carbonyl complexes.

Acknowledgment. The support of this research by the Robert A. Welch Foundation under Grant No. B-434 and the North Texas State University Faculty Research Fund is gratefully acknowledged. We thank the National Science foundation for an equipment grant which allowed purchase of the FT-NMR spectrometer and Dr. C. R. McDaniel, Jr., for the NMR spectra.

Registry No. $(phen)Mo(CO)_4$, 15740-78-0; $(phen)W(CO)_4$, 14729-20-5.

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Observations on the Structural Characterization of the Di-μ-hydroxo-octaaquodiiron(III) Dimer

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Received May 22, 1980

Morrison et al.[1] concluded from EXAFS (extended X-ray absorption fine structure) work on $Fe(ClO_4)_3$ in 0.023 M $HClO_4$ aqueous solution that the dominant species present is di-μ-hydroxo-octaaquodiiron(III)$[(H_2O)_4Fe(OH)_2Fe(H_2O)_4{}^{4+}]$; this conclusion is in disagreement both with the results of our X-ray work on solutions of similar composition[2] and with our general knowledge of such solutions.

The hydrolysis of iron(III) has been extensively studied. Different authors reached the conclusion that no appreciable amounts of soluble hydrolysis products are present when real equilibrium is established.[3-5] However, attainment of the final equilibrium is very slow in these solutions, requiring several years at 25 °C.[6] Consequently, many of the studies on iron(III) hydrolysis have been performed with supersaturated solutions, i.e., solutions unstable with respect to the precipitation of Fe^{3+} hydroxides. Nevertheless, this fact does not affect the conclusions drawn regarding the equilibria in solutions since the rate of precipitation is negligible as compared to that of complexation. This point has been well outlined by Ciavatta and Grimaldi,[5] who purposely investigated supersaturated solutions of Fe^{3+} in 3 M $NaClO_4$. It is then possible to demonstrate the presence of hydrolysis complexes in supersaturated solutions. Among the various hydrolysis complexes, the above described dimer can be dominant in suitable chemical conditions. Figure 1 shows the distribution of complexes calculated from the equilibrium constants potentiometrically determined by Hedstrom[7] (quoted by Morrison[1]) in 3 M $NaClO_4$ (the use of other reliable constants from Biedermann[8] or Ciavatta,[5] also obtained in 3 M $NaClO_4$, substantially gives the same results). Assuming now that the equilibrium constants are approximately valid for concentrated solutions, an hypothesis that has been proved to hold in many cases,[9] we can see from Figure 1 that neither Morrison's so-

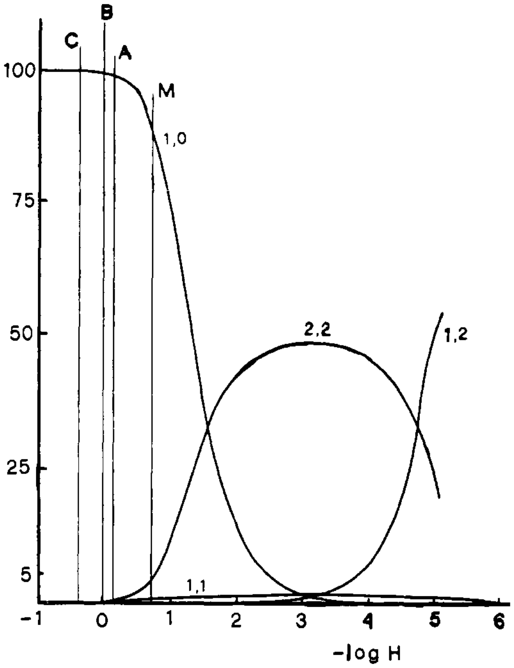

Figure 1. Distribution of Fe^{3+} hydrolysis complexes as a function of the free H^+ concentration with use of the equilibrium constants of ref 7. The various p,q index on the distribution lines refer to the different $Fe_p(OH)_q{}^{3p-q}$ complexes. Vertical lines show the expected complex distributions for the following solutions: M (by Morrison et al.[1]) = 1.819 M $Fe(ClO_4)_3$ –0.023 M $HClO_4$; A = 1.50 M $Fe(ClO_4)_3$ –0.72 M $HClO_4$; B = 2.24 M $Fe(ClO_4)_3$ –1.08 M $HClO_4$; C = 1.825 M $Fe(ClO_4)_3$ –2.56 M $HClO_4$. Since polynuclear complexes are formed, the complex distribution is iron concentration dependent, and the one reported has been evaluated for the chemical conditions of Morrison's solution. The distribution, however, is substantially the same for the other solutions which have been thus indicated by vertical lines on the same figure.

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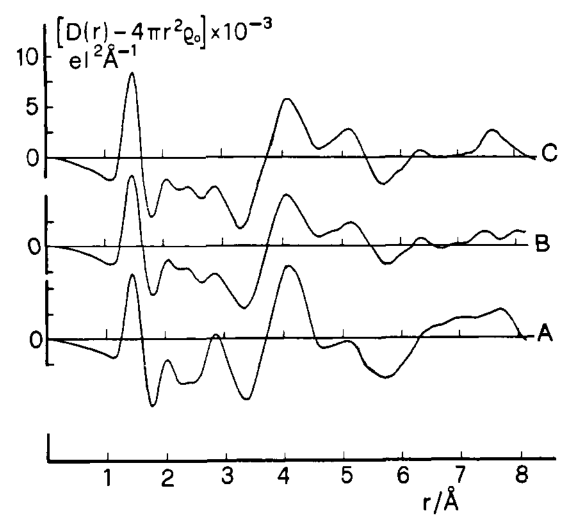

Figure 2. Radial distribution functions of the previously investigated solutions.[2] The compositions of the solutions are given under Figure 1.

lution[1] nor ours[2] seem to contain appreciable amounts of hydrolysis products whatever is the equilibrium situation of these solutions. In Morrison's solution, only about 8% of the total iron concentration is present as dimer (2,2 in the notation of Figure 1) while about 90% is present as nonhydrolyzed ion (1,0 in Figure 1).

X-ray results on three acidic aqueous solutions[2] confirmed the situation shown in Figure 1; Figure 2 shows their radial distribution functions. They do have a peak around 2.8 Å, i.e., where Fe–Fe contacts would occur in the iron(III) dimer; nevertheless, this peak must be ascribed to the typical solvent–solvent interactions since its size decreases with increasing iron concentration (i.e., with decreasing water content). Furthermore our least-squares analysis[2] of the *i*(s) curves, through direct comparison of the experimental *i*(s) data with *i*(s) calculated for various models of the solutions, is consistent with $Fe(H_2O)_6^{3+}$ complexes, in octahedral configuration, and ClO_4^- anions, in tetrahedral configuration being the only important diffracting species present in these solutions.

This behavior of iron(III) with respect to hydrolysis is not restricted to the perchlorate solutions which have been just considered. In all acidic solutions at pH $\leq$1.0, detectable amounts of hydrolyzed complexes are hardly formed. In fact by X-ray similar results to those reported here, i.e., absence of hydrolysis complexes, have been also obtained in solutions of iron(III) sulfate,[9] nitrate,[10] and chloride.[11]

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Structural Characterization of Iron(III) Solutions by EXAFS

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Received December 5, 1980

Recently, Magini et al. have performed X-ray scattering experiments on iron(III) aqueous solutions,[1] and the results of these experiments contradict earlier conclusions reached by Morrison, Reis, et al. in EXAFS experiments.[2] Magini claims that there is no significant amount of di-μ-hydroxo-octaaquodiiron(III) in the solution studied. We believe this claim to be true. We have recently begun to reinvestigate iron(III) solutions by EXAFS techniques, and preliminary results from data obtained at the Stanford Synchrotron Radiation Laboratory[4] are consistent with the conclusions of Magini et al.[1] in that they show no evidence of substantial amounts of dimers of higher multimers in the solutions. (See Figure 1.)

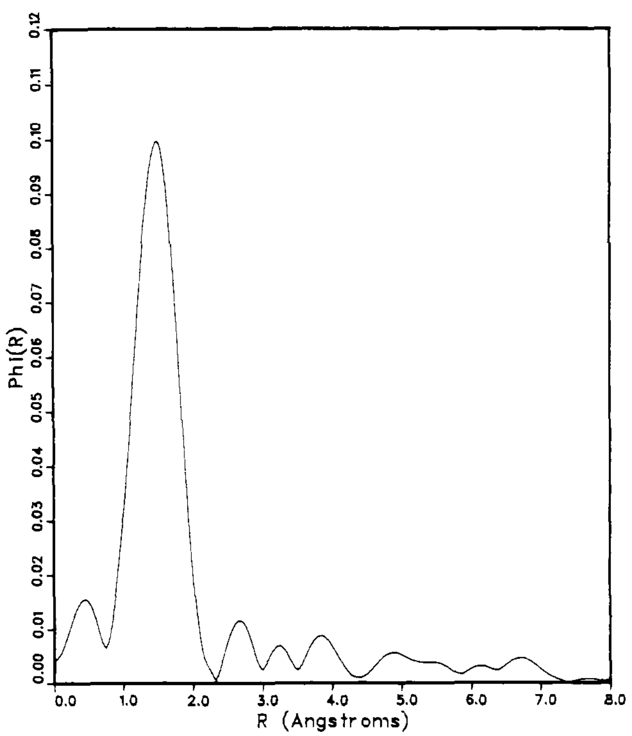

Figure 1. Absolute value of Fourier transform of *k*-weighted EXAFS data obtained on 1 M Fe^{3+} solution at Stanford Synchrotron Radiation Laboratory.

The discrepancies between the early EXAFS conclusions and those reached by Magini et al. (and by us) arise from several factors. First, the early EXAFS experiments were performed on a "in-house" EXAFS spectrometer,[2,3] and the raw data can be seen to have a poor signal-to-noise ratio. The effects of high noise levels have been shown to cause spurious features in the Fourier transform of the EXAFS,[4] and this is undoubtedly a major contribution to the erroneous results obtained. Further, the iron–iron distance was inferred by "eyeballing" the position of the second peak in the Fourier transform of the early EXAFS data and making some questionable approximations concerning the linearity of phase shifts in *R* space.[2] Finally, that there are two frequency components under the first peak in the Fourier transform is indisputable; that these two frequencies represent two real distances is questionable.

We are forced to conclude that the early EXAFS study is in error due primarily to the poor quality of data and to a lack of understanding of the effect of high noise levels and problems of solution chemistry. We shall present the results of new EXAFS experiments performed at SSRL under more optimal

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