containing unusual ligands in the axial site has been initiated. As will be reported elsewhere, the use of $[\mathrm{TPPFe(I)}]^-$ has allowed, for example, the formation of a product containing an iron–tin bond.

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# Electron Transfer between Sulfur(IV) and Tris(1,10-phenanthroline)iron(III) Ion in Aqueous Solution[1]

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**Abstract**: The electron-transfer reaction between tris(1,10-phenanthroline)iron(III) and sulfur(IV) species occurs rapidly, according to the rate law $-d[\mathrm{FeL_3}^{3+}]/dt = (k_1 + k_2/[\mathrm{H}^+] + k_3[\mathrm{HSO_3}^-])[\mathrm{HSO_3}^-][\mathrm{FeL_3}^{3+}]$. The rate constants are correlated by the activation parameters $\Delta H_1^{\ddagger} = 9.7$, $\Delta H_2^{\ddagger} = 7.4$, and $\Delta H_3^{\ddagger} = 14$ kcal/mol; $\Delta S_1^{\ddagger} = -20$, $\Delta S_2^{\ddagger} = -31$, and $\Delta S_3^{\ddagger} = 6$ eu. The $k_1$ and $k_2$ terms are interpreted as resulting from reaction of $\mathrm{FeL_3}^{3+}$ with $\mathrm{HSO_3}^-$ and $\mathrm{SO_3}^{2-}$, respectively. The $k_3$ term is interpreted as reaction of $\mathrm{FeL_3}^{3+}$ with $\mathrm{S_2O_5}^{2-}$, or with S(IV) to form an intermediate, followed by reaction with a second S(IV) species.

A kinetic study of reaction 1[2] is the subject of this paper. Net reactions of sulfur(IV) with metal ion

$$2\mathrm{FeL_3}^{3+} + \mathrm{HSO_3}^- + \mathrm{H_2O} = 2\mathrm{FeL_3}^{2+} + \mathrm{SO_4}^{2-} + 3\mathrm{H}^+ \quad (1)$$

oxidants have the unusual feature (not apparent in reaction 1) that both one- and two-electron net oxidations may occur. Thus, the sulfur product may be sulfate, dithionate, or, more often, a mixture.[3] Dithionate is thermodynamically unstable with respect to disproportionation,[4] but is kinetically stable with respect to both disproportionation and oxidation,[3] and so is not oxidized further by most oxidants. Stoichiometry data for a large number of oxidants have already been reported; some representative data are listed in ref 3, 5–8.

The stoichiometry of oxidation of sulfur(IV) to sulfur(VI) by an oxidant undergoing net one-electron change may be rationalized in terms of one of four simple and fundamentally different mechanisms.[9,10] Two of these,[9] one involving a one-step termolecular mechanism and the other an initial disproportionation of oxidant, are not consistent with kinetic data available for these systems.[6,7,10–16] In the third mechanism,[9] sulfur(IV) is oxidized in a two-electron step; the resulting unstable reduced oxidant reacts in a one-electron step with fresh oxidant to complete the sequence. This mechanism does not account for rate observations, such as inhibition by reduced oxidant in some systems[6,15,16] and of catalysis by copper(II)[6] in some systems. The fourth mechanism,[9] two one-electron oxidations, with sulfur(V) as an intermediate is consistent with kinetic observations and is generally accepted.[6,7,10–16] Dithionate formation is then accounted for by the reasonable postulate that sulfur(V) radicals may combine before the second one-electron oxidation occurs.[6]

It has been suggested that the sulfur(V) species may be coordinated to a metal ion[7,17] and thus need not be a free radical. Convincing esr evidence for coordination between metal ions and other simple radicals has been reported,[18,19] but esr evidence that free sulfur(V) radicals can be formed in aqueous solution has also been presented.[20,21]

The work that is being reported here is part of a larger effort to discover the mechanisms of oxidation of sulfur(IV). The original purpose of this particular study was to learn about the mechanism of oxidation of sulfur(IV) by an oxidant that does not coordinate to sulfur(V) species. It was reasoned that if a sulfur

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intermediate could be formed, it would be a free radical, and the free radical–coordinated radical ambiguity[7, 17] would not exist. The metal ion $FeL_3^{3+}$ appeared to be a satisfactory choice of oxidant because of its substitutional inertness.[22]

## Experimental Section

**Reagents.** Tris(1,10-phenanthroline)iron(III) was prepared by cerium(IV) oxidation of the $FeL_3^{2+}$ sulfate.[23] The iron(III) complex was taken at least three times through the cycle of precipitation with sodium perchlorate, washing with dilute sodium perchlorate solution, and dissolution in perchloric acid. The final product was dissolved in concentrated perchloric acid and was stored at $-15°$ in the dark.[24] Solutions of the $FeL_3^{3+}$ sulfate were prepared in the same way, but the final $FeL_3^{3+}$ perchlorate salt was dissolved and stored in 4–9 *M* sulfuric acid. The solutions of $FeL_3^{2+}$ ion used to prepare $FeL_3^{3+}$ were the reagent grade 0.025 *M* aqueous sulfate or were prepared from reagent grade ferrous ammonium sulfate and reagent grade 1,10-phenanthroline monohydrate.[24] Solutions were analyzed for $FeL_3^{3+}$ by reduction to $FeL_3^{2+}$ with sulfur(IV) or aquoiron(II), followed by spectrophotometric measurement of the absorbance at 510 nm.[25]

Air-free aqueous sulfur(IV) solutions were prepared by transfer of gaseous sulfur dioxide into sealed bottles, as described earlier.[26] The gas was obtained by distilling from a cylinder of anhydrous liquid sulfur dioxide or by adding sulfuric acid to sodium sulfite as before.[25] Sulfur(IV) solutions were analyzed iodometrically.[26]

Lithium sulfate was prepared by reaction of the carbonate with sulfuric acid, followed by crystallization and recrystallization. Lithium sulfate solutions were analyzed by titration of the acid displaced by aliquots from ion-exchange columns in the hydrogen ion form. Sodium perchlorate was prepared and analyzed as described earlier.[26] Reagent grade sulfuric acid and perchloric acid were diluted with water and used directly. The water used was redistilled from laboratory distilled water.

**Stoichiometry Measurements.** Owing to the limited solubility of $FeL_3^{3+}$ and $FeL_3^{2+}$ in perchlorate solutions, the stoichiometry was measured in 0.5 *M* sulfuric acid solution. With excess $FeL_3^{3+}$, the stoichiometry was determined by the decrease in absorbance at 650 nm, where $\epsilon(FeL_3^{2+}) = 0$, and $\epsilon(FeL_3^{3+}) = 514$. Mixing of reactants was done in a spectrophotometer cell.

With excess sulfur(IV), the stoichiometry was determined by analysis for dithionate and the assumption that dithionate and sulfate are the only sulfur-containing products. Mixing of reactants was done with the stopped-flow[26] mixing chamber. The analysis was accomplished by oxidation with excess chromium(VI), after removal of metal ions by ion exchange and removal of sulfite by bubbling with nitrogen. The oxidation occurred in 1.08 *M* sulfuric acid solution, during 3 hr in a boiling water bath. The absorbance of the excess chromium(VI) was measured at 348 nm, and concentration was then obtained from a calibration curve. The curve, relating absorbance to dithionate concentration, was obtained from measurements on solutions containing a fixed initial concentration of potassium dichromate and known, variable concentrations of dithionate. The dithionate stock solution used in construction of the curve was prepared by dissolution of reagent grade sodium dithionate in water; the solution was analyzed by oxidation with excess cerium(IV), followed by back-titration with iron(II) solution.[27] The calibration curve was reproducible; adding and removing sulfur dioxide, or $FeL_3^{2+}$ ions, did not affect the results. The curve was not linear, however, showing an apparent increase in $\epsilon(Cr(VI))$ as [Cr(VI)] decreased. The method can be used to measure dithionate concentrations as low as $2 \times 10^{-5}$ *M*.

**Rate Measurements.** Measurement of the rate of reaction 1 was accomplished spectrophotometrically, by observing the decrease in optical absorbance at 650 nm. Reactions with half times greater than 5 sec were made to occur in 10-cm spectrophotometer cells. The cells were charged with the appropriate reagents, except for sulfur(IV) solution, and were sealed with rubber serum caps. The sealed cells were bubbled with nitrogen while in a temperature-controlled water bath. The nitrogen was cleansed of oxidizing impurities and saturated with water vapor, by passage through chromium(II) solution, and entered the cell through a Teflon syringe needle. Contact between the cap and the solution was prevented, because some of the serum caps were found to reduce $FeL_3^{3+}$. Bubbling of the cell contents was stopped after 15 min; sulfur(IV) was added *via* a volumetrically calibrated syringe, the cell contents were mixed, and the cell was positioned in a thermostated cell holder in a Beckman ACTA V recording spectrophotometer. The recorder chart drive was used to measure time. The concentration of sulfur(IV) was always at least 12-fold greater than the concentration of $FeL_3^{3+}$. The concentration of each reactant was calculated from the measured dilution of the stock solution.

The rates of reactions with half times smaller than 5 sec were measured with the stopped-flow instrument described earlier.[26] Reactions were initiated by mixing $FeL_3^{3+}$ solution with sulfur(IV) solution; the method for handling the air-free sulfur(IV) and iron(III) solutions has been described.[26]

## Results

**Competing Reactions.** In some preliminary experiments at 25°, the absorbance of a reaction mixture in a spectrophotometer cell was monitored continuously at 510 nm. The absorbance first increased, then decreased, presumably due to the formation, then aquation, of $FeL_3^{2+}$. In experiments with $FeL_3^{3+}$ in excess over sulfur(IV), the aquation step was faster than in experiments with excess sulfur(IV). For example, results for three experiments at 25°, with data listed in the order $[FeL_3^{3+}]_0$, $[FeL_3^{2+}]_0$, $[S(IV)]_0$, $[H_2SO_4]$, $k_{\text{aquation}}$, were (molar concentrations): $7.6 \times 10^{-4}$, 0.0, $2.8 \times 10^{-4}$, 0.50, $1.9 \times 10^{-4}$ sec$^{-1}$; $1.6 \times 10^{-5}$, 0.0, $8.75 \times 10^{-4}$, 0.50, $7.5 \times 10^{-5}$ sec$^{-1}$; 0.0, $6 \times 10^{-6}$, 0.0, 0.96, $7.1 \times 10^{-5}$ sec$^{-1}$. The first reaction mixture, containing excess $FeL_3^{3+}$, gave a significantly larger aquation rate than the other mixtures. The measured rate constants for aquation in the absence of excess $FeL_3^{3+}$ agree with $7.5 \times 10^{-5}$ sec$^{-1}$, measured previously under similar conditions.[22]

Not only is a different $FeL_3^{2+}$ aquation rate observed in the presence of $FeL_3^{3+}$, but an observable reaction between $FeL_3^{2+}$ and $FeL_3^{3+}$ occurs. This reaction was demonstrated in a series of four experiments at 25°, with 0.50 *M* $H_2SO_4$, 0.0 *M* S(IV), and with data listed in the order $[FeL_3^{3+}]_0$, $[FeL_3^{2+}]_0$, initial absorbance increase or decrease at 510 nm: $0.18 \times 10^{-4}$, $0.19 \times 10^{-4}$, decrease; $3.3 \times 10^{-4}$, $0.93 \times 10^{-4}$, increase; $6.7 \times 10^{-4}$, $0.93 \times 10^{-4}$, increase; $10 \times 10^{-4}$, $0.19 \times 10^{-4}$, increase. All of the solutions had initial absorbance increases, except the solution with lowest $[FeL_3^{3+}]_0$; these increases occurred over periods of from one to several hours, before the expected decrease to zero began. After the absorbance increases began, the solutions had the brown color that is characteristic[22] of the dimeric $Fe_2OL_4^{4+}$ or $Fe_2(OH)_2L_4^{4+}$. Conditions for subsequent measurements of stoichiometry and kinetics were chosen to prevent $FeL_3^{3+}$ and $FeL_3^{2+}$ from being together in significant concentration for more than a few minutes.

It was further observed that attempts to measure the rate of reaction 1 gave non-first-order rates of absorbance change at 510 nm, but first-order rates at 650 nm [the dimeric iron(III) species does not absorb above 590 nm[22]], and that the isosbestic "point" observed during repetitive scans of a reaction mixture moved from about 384 nm near the start of the reaction to about 382 nm near the end of the reaction. The spectra

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**Table I.** Calculated and Observed Rate Constants, $Sec^{-1}$

| | | $k' \times 10^2$ | | | | $k' \times 10^2$ | |
|---|---|---|---|---|---|---|---|
| $[H^+]$[a] | $10^2[S(IV)]$[a] | Obsd | Calcd | $[H^+]$[a] | $10^2[S(IV)]$[a] | Obsd | Calcd |
| 0.050[b] | 0.050 | 0.94[c] | 0.89 | 0.05 | 0.200 | 3.6 | 3.6 |
| 0.05 | 0.500 | 11 | 9.5 | 0.10 | 0.050 | 0.34 | 0.37 |
| 0.10 | 0.200 | 1.5 | 1.5 | 0.10 | 0.500 | 4.3[c] | 4.0 |
| 0.20 | 0.050 | 0.15 | 0.15 | 0.20 | 0.200 | 0.65 | 0.61 |
| 0.20 | 0.500 | 1.6 | 1.6 | 0.40 | 0.200 | 0.27 | 0.25 |
| 0.40 | 0.500 | 0.60 | 0.66 | 0.40 | 1.00 | 1.4 | 1.4 |
| 0.40 | 1.50 | 3.2 | 2.3 | 0.40 | 2.00 | 4.1 | 3.3 |
| 0.60 | 0.200 | 0.14[c] | 0.15 | 0.60 | 2.00 | 3.0 | 1.9 |
| 1.0 | 0.200 | 0.073 | 0.082 | 1.00 | 0.500 | 0.22 | 0.21 |
| 1.0 | 0.500 | 0.22[d] | 0.21 | 1.00 | 1.00 | 0.44 | 0.44 |
| 1.0 | 2.00 | 1.0 | 0.97 | 1.00 | 4.00 | 3.2 | 2.3 |
| 0.20[b] | 5.31 | 33 | 42 | 0.20 | 10.6 | 130 | 130 |
| 0.10[b] | 0.050 | 0.57 | 0.66 | 0.20 | 0.050 | 0.25 | 0.26 |
| 0.20 | 0.500 | 2.5 | 2.9 | 0.40 | 0.500 | 1.3 | 1.2 |
| 0.40 | 1.00 | 2.3 | 2.5 | 1.00 | 0.500 | 3.5 | 3.7 |
| 0.05[b] | 1.73 | 150 | 130 | 0.10 | 0.050 | 0.98 | 0.95 |
| 0.10 | 0.10 | 1.9 | 1.9 | 0.10 | 2.59 | 93 | 93 |
| 0.10 | 6.65 | 510 | 420 | 0.10 | 13.3 | 2000 | 1400 |
| 0.15 | 0.135 | 1.5 | 1.5 | 0.15 | 3.50 | 91 | 82 |
| 0.15 | 8.97 | 440 | 390 | 0.15 | 17.9 | 1700 | 1400 |
| 0.20 | 0.17 | 1.6 | 1.3 | 0.25 | 0.051 | 0.30 | 0.28 |
| 0.25 | 0.100 | 0.56 | 0.56 | 0.25 | 0.205 | 1.2 | 1.2 |
| 0.25 | 10.9 | 310 | 250 | 0.25 | 13.6 | 280 | 370 |
| 0.25 | 27.2 | 1200 | 1300 | 0.40 | 0.155 | 0.45 | 0.48 |
| 0.40 | 0.310 | 0.93 | 1.0 | 0.40 | 0.620 | 2.0 | 2.1 |
| 0.986 | 0.050 | 0.063 | 0.052 | 0.986 | 0.100 | 0.11 | 0.11 |
| 0.986 | 0.200 | 0.22 | 0.21 | 0.986 | 0.500 | 0.53 | 0.55 |
| 1.00 | 0.100 | 0.12[d] | 0.10 | 1.00 | 10.0 | 19 | 23 |
| 1.00 | 24.2 | 85 | 97 | | | | |

[a] Initial molar concentrations. The initial concentration of $FeL_3^{3+}$ was 4–8 × $10^{-5}$ in all experiments. [b] The first group of 22 experiments, the second group of 2, the third group of 6, and the final group of 27 listed above were done at 0.0, 2.9, 14.5, and 25.0°, respectively. [c] Average of two experiments. [d] 0.01 *M* $Cu(ClO_4)_2$ was present.

of $FeL_3^{3+}$ solutions from several preparations each exhibited the shoulder at 355 nm that is diagnostic of the iron(III) dimer.[22] To check the suspicion that an iron(III) dimer reaction, observable at 510 nm but not at 650 nm, accounted for the different rate behavior, a solution of $FeL_3^{3+}$ containing a slight excess of cerium(IV) was prepared. Quickly, without taking time to purify the $FeL_3^{3+}$ solution, some was used in a rate measurement at 510 nm, some in a measurement at 650 nm, and finally the spectrum of the remaining $FeL_3^{3+}$ solution was measured. Both rate experiments gave the same first-order rate constant, in agreement with the value measured at 650 nm using other $FeL_3^{3+}$ solutions, and the spectrum did not have a shoulder at 355 nm. In other rate experiments, the initial presence of $Ce^{3+}$ or $Ce^{4+}$, and the particular $FeL_3^{3+}$ solution chosen, had no effect on the value of the rate constant measured at 650 nm. It is concluded that rate constants measured at 650 nm apply only to reaction 1, but those measured at 510 nm are affected by another reaction.

Three other potential reactions did not occur significantly during the experiments reported here. Reaction of $FeL_3^{3+}$ with $OH^-$ [22,28] was avoided by using a hydrogen ion concentration of at least 0.05 *M* in every solution; aquation of $FeL_3^{3+}$ is slow[22] relative to the reactions studied in this work, and an acidic, iron-free solution containing 1,10-phenanthroline and sulfur(IV) did not undergo spectral changes within 20 min of mixing.

**Stoichiometry.** A solution containing 0.50 *M* $H_2SO_4$, 1.03 × $10^{-4}$ *M* S(IV), and 10.0 × $10^{-4}$ *M* $FeL_3^{3+}$ was prepared. The absorbance at 650 nm in a 5-cm cell, before adding S(IV), was 2.638; the absorbance after completion of the reaction (500 sec after mixing, at room temperature) and after correction for the dilution caused by addition of S(IV) solution, was 2.104. The absorbance decreased by 20.2%, so that $\Delta[FeL_3^{3+}]/\Delta[S(IV)]$ was $(2.02 \times 10^{-4})/(1.03 \times 10^{-4})$, or 1.96.

A second reaction was carried out at room temperature, using 0.50 *M* $H_2SO_4$, 0.12 *M* S(IV), and 7.2 × $10^{-4}$ *M* $FeL_3^{3+}$. In duplicate attempts to analyze dithionate, none was found. In a control sample, prepared to contain 0.65 × $10^{-4}$ *M* dithionate, the concentration was determined accurately, using the calibration curve described earlier. The results of spectrophotometric analysis, and the dithionate analysis, require the stoichiometry shown in eq 1.

**Rate Measurements.** The results of rate measurements, conducted in 1.00 *M* $HClO_4$–$NaClO_4$ solutions, are shown in Table I. The data are described by eq 2–4. The quotient $Q' = [SO_2(aq)]/[H^+][HSO_3^-] =$

$$-d[FeL_3^{3+}]/dt = k'[FeL_3^{3+}] \tag{2}$$

$$k' = (k_1 + k_2/[H^+] + k_3[HSO_3^-])[HSO_3^-] \tag{3}$$

$$[HSO_3^-] = [S(IV)]/(1 + Q'[H^+]) \tag{4}$$

12.5, 18.2, and 23.2 $M^{-1}$ at 0, 14.5, and 25°, respectively, was evaluated from the data of Sillen[29] and from $\Delta H(Q') = 4.0$ kcal/mol,[30] as before.[26]

The data in Table I were fitted to eq 3, and to the absolute rate theory equation, using a nonlinear least-squares computer procedure.[31] The calculated param-

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**Table II.** Calculated Rate Parameters for Reaction 1 in 1.00 *M* Perchlorate

| Path | Value at 0.0° | Value at 14.5° | Value at 25.0° | $\Delta S^{\ddagger}$, eu[b] | $\Delta H^{\ddagger}$, kcal/mol[b] |
|---|---|---|---|---|---|
| $k_1$[a] | 4.2 | 11 | 20 | $-20 \pm 3$ | $9.7 \pm 0.7$ |
| $k_2$[a] | 1.2 | 2.5 | 4.2 | $-31 \pm 3$ | $7.4 \pm 0.9$ |
| $k_3$[a] | 760 | 2900 | 7200 | $6 \pm 4$ | $14 \pm 1$ |

[a] Time unit is seconds. [b] The indicated uncertainty is the calculated[31] standard deviation.

eters are shown in Table II. The data at high $[HSO_3^-]$ at 25° suggest that $k_3$ may have an inverse $[H^+]$ dependence, but the data at 0° do not. Owing to uncertainty in $\Delta H'$, the acid dependence of $k_3$ remains uncertain.

In addition to the experiments described in Table I, some stopped-flow measurements were made at 25°, using 0.5 *M* sulfate solutions; as for perchlorate solutions, both first- and second-order [S(IV)] and inverse $[H^+]$ dependences were observed. For example, in 0.5 *M* $H_2SO_4$, the form of $k'$ was approximately $k' = 20 \cdot [S(IV)] + 430[S(IV)]^2$, and in 0.3 *M* $H_2SO_4$, 0.2 *M* $Li_2SO_4$, it was approximately $k' = 80[S(IV)] + 3300 \cdot [S(IV)]^2$. Since neither $Q'$ nor the extent of acid dissociation of $HSO_4^-$ has been measured in these media, quantitative comparisons with the perchlorate results have not been attempted. One experiment was done at 25°, with 0.1 *M* $Cl^-$, $2.06 \times 10^{-4}$ *M* $HSO_3^-$, 1.00 *M* $H^+$, and $8 \times 10^{-5}$ *M* $FeL_3^{3+}$ present initially. The measured rate constant was 1.7 times that calculated from the parameters in Table II.

The effect of impurities was tested in several experiments. For example, the product $FeL_3^{2+}$ retards the reaction under some conditions. Using the initial concentrations 0.500 *M* $H_2SO_4$, 0.06 *M* S(IV), $18 \times 10^{-5}$ *M* $FeL_3^{3+}$, and $18 \times 10^{-5}$ *M* $FeL_3^{2+}$, at 25°, the rate was reduced to 0.3 times the rate in an identical experiment but without $FeL_3^{2+}$ added initially.

Dissolved oxygen slows the reaction. In 1.00 *M* $HClO_4$, 0.005 *M* S(IV), at 0°, the initial rate for an air-saturated solution was smaller by the factor 0.47 than for an identical air-free solution. Moreover, as the air-saturated solution continued to react, the apparent first-order rate became even smaller. In 0.09 *M* $H_2SO_4$, 0.41 *M* $Li_2SO_4$, $1.91 \times 10^{-3}$ *M* S(IV), at 25°, the rate increased by the factor 0.79 upon saturation with air, but deviation from pseudo-first-order behavior did not occur.

In 0.50 *M* $H_2SO_4$ and 0.12 *M* S(IV), 0.0144 *M* Cu(II) increased the rate by a factor of 1.2. In perchlorate, however, 0.01 *M* $Cu^{2+}$ had a negligible effect (see Table I).

## Discussion

The mechanism described by eq 5, in which solvation

$$FeL_3^{3+} + S(IV) \longrightarrow FeL_3^{2+} + S(V) \quad (5a)$$

$$FeL_3^{3+} + S(V) \longrightarrow FeL_3^{2+} + S(VI) \text{ (fast)} \quad (5b)$$

and protonation details have been omitted, is consistent with the considerations listed in the introduction, with the observed stoichiometry, and with the first two terms of the observed rate law. Using the value $\Delta G = 10$ kcal/mol[17] for $Fe^{3+} + S(IV) = Fe^{2+} + S(V)$, together with oxidation potentials for $Fe^{2+}$[4] and $FeL_3^{2+}$,[32] one can estimate that the value of $\Delta g$ (5a) is only about 3 kcal/mol. If eq 5 represents the mechanism, then $k_1$ and $k_2$ in eq 3 likely correspond to S(IV) = $HSO_3^-$ and $SO_3^{2-}$, respectively, and the activation parameters listed in Table II are reasonable.

A modification of eq 5 is possible, in which the S(V) being oxidized adds to a phenanthroline ligand of the oxidant, rather than forming sulfate.[33] Evidence against this modification is: the visible spectrum of reduced $FeL_3^{3+}$ is not dependent on whether $Fe^{2+}{}_{(aq)}$ or S(IV) is the reducing agent, and the aquation rate of the product of the S(IV) reduction (in the absence of excess $FeL_3^{3+}$) is the same as for authentic $FeL_3^{2+}$. This evidence can be circumvented, however, by proposing a relatively fast desulfonation reaction to bring the net reaction in accord with eq 1. Though desulfonation reactions do occur,[34] and though visible spectral differences between $FeL_3^{2+}$ and $FeL_2LSO_3^{2+}$ may not be large, no positive evidence for the sulfonation–desulfonation sequence has been obtained in this study.

The observed second-order S(IV) dependence is consistent with mechanism 6 or 7, where $(FeL_3 \cdot S)^{VII}$ is

$$2HSO_3^- = S_2O_5^{2-} + H_2O \quad Q_{6a} < 1^{35} \quad (6a)$$

$$FeL_3^{3+} + S_2O_5^{2-} \longrightarrow FeL_3^{2+} + S_2O_5^- \quad (6b)$$

$$\text{fast steps} \quad (6c)$$

$$FeL_3^{3+} + S(IV) = (FeL_3 \cdot S)^{VII} \quad \text{fast, } Q_{7a} \quad (7a)$$

$$(FeL_3 \cdot S)^{VII} + S(IV) \longrightarrow FeL_3^{2+} + S(V) + S(IV) \quad (7b)$$

$$FeL_3^{3+} + S(V) \longrightarrow FeL_3^{2+} + S(VI) \text{ (fast)} \quad (7c)$$

an outer-sphere Fe(III)–S(IV) or Fe(II)–S(V) complex. Outer-sphere metal ion–sulfur(IV) or -(V) interactions could also be postulated in mechanism 5; thus, a conclusive demonstration of uncomplexed radicals cannot be claimed.

The observed inhibition (of disappearance of $FeL_3^{3+}$) by oxygen can be understood in terms of scavenging of a radical. However, the oxygen-caused decrease in the rate to less than half the uninhibited rate, in a reaction first-order in S(IV), requires more than simply prevention of reaction 5b. The "extra" decrease may be caused by oxidation of $FeL_3^{2+}$, by species formed after the first S(V)–$O_2$ reaction. An observation pertinent to this suggestion is that $FeL_3^{2+}$ is not oxidized by acidic $H_2O_2$ but is oxidized by a reacting $H_2O_2$–$Fe^{2+}{}_{(aq)}$ mixture.

Inhibition by $FeL_3^{2+}$ is in accord with the proposed mechanisms, only if the reverse of the radical-forming step occurs to a significant extent in the presence of excess $FeL_3^{2+}$. Reversibility would require a more complex rate law than was observed; low initial concentrations of $FeL_3^{3+}$ were used for the experiments reported in Table I, however, and the conformity of those experiments to pseudo-first-order behavior suggests that, in the presence of small amounts of product, the reverse reactions occurred to a negligible extent.

The absence of Cu(II) catalysis in perchlorate is consistent with each of the mechanisms. The very small catalysis in sulfate is not explainable by any of the mech-

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(31) The program is based on Report LASL-2367 + Addenda, Los Alamos Scientific Laboratory, Los Alamos, N. Mex., 1959.

(32) G. F. Smith and F. P. Richter, *Ind. Eng. Chem., Anal. Ed.*, **16**, 580 (1944).

(33) J. S. Littler, ref 19, p 407.

(34) E. G. Gilbert, "Sulfonation and Related Reactions," Interscience, New York, N. Y., 1965, Chapter 8.

(35) R. M. Golding, *J. Chem. Soc.*, 3711 (1960), and references cited therein.

anisms, unless a radical-forming step is reversible. A separate rate term may exist, however, of the form $k$-$[Cu(SO_4)_n^{2-n}][S(IV)]$. A similar Cu(II) term can contribute significantly to the slower sulfur(IV) reduction of chloroaquoiron(III) complexes, in 1 $M$ chloride media,[36] but was not observed in the sulfur(IV) reduction of sulfatoaquoiron(III) complexes in sulfate media.[6]

Oxidation of sulfur(IV) by a pathway second order in sulfur(IV) is unusual. The previous observation of a second-order path, in the oxidation by chromium(VI), probably involves reaction between a sulfitochromate(VI) ester and a second sulfur(IV) species.[37] Mechanism 7 is similar to that proposed for the chromium system,[37] except for the structure of the intermediate; ester formation by $FeL_3^{3+}$ does not appear possible. A mechanism analogous to 6 could not account for the exact form of the rate law in the chromium system,[37] rate = $k[Cr(VI)][S(IV)]^2[H^+]/(1 + a[S(IV)])$, owing to the small value[35] of $Q_{6a}$.

Limiting mechanisms 6 and 7, representing approach to the transition state by two sulfur atoms, either in a single species (6), or separately (7), cannot be distinguished by the observations made in this study. The positive entropy of activation appears consistent with either mechanism. If mechanism 6 is correct, then comparatively great reactivity of $S_2O_5^{2-}$ in this system is implied; second-order terms could perhaps be found in other systems, including anion oxidants such as $IrCl_6^{2-}$, for which ion pairs or specific sulfur–ligand interactions are unlikely.

If mechanism 7 is correct, then one can question whether the species $(FeL_3 \cdot S)^{VII}$ is only an ion pair or if a more specific interaction between inner- and outer-sphere ligands exists. An experimental approach to this question would include attempts to detect the complex, or other $ML_3 \cdot S$ complexes, and studies of reaction with other metal ion oxidants, especially highly charged ones. It has been suggested[38] that anion catalysis of the $Fe(H_2O)_6^{2+}$–$FeL_3^{3+}$ reaction may involve specific interaction between a bridging anion and the phenanthroline ligand.

The unexpected results of this work are the suggestions that $S_2O_5^{2-}$, potentially a two- to four-electron reducing agent, may react rapidly in a one-electron step and an alternate possibility that decomposition of $(FeL_3 \cdot S)^{VII}$ to $FeL_3^{2+}$ and S(V) can be accelerated by S(IV).

(36) O. F. Zeck and D. W. Carlyle, unpublished results.

(37) G. P. Haight, Jr., E. Perchonock, F. Emmenegger, and G. Gordon, *J. Amer. Chem. Soc.*, **87**, 3835 (1965).

(38) N. Sutin and A. Forman, *ibid.*, **93**, 5274 (1971).

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# Synthesis and Properties of Tetraaza[14]tetraene and Tetraaza[14]hexaene Macrocyclic Complexes

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**Abstract:** An efficient nontemplate synthesis of the new macrocycle 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene ($H_2(MeHMe(en)_2)$, **11**) is described. This compound reacts with metal(II) acetates or with other metal(II) salts under conditions of nonaqueous chelation to afford the macrocyclic 12-$\pi$ complexes $M(MeHMe(en)_2)$ (**13**, M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II)), whose electronic properties are consistent with planar coordination. Treatment of the Ni(II) and Cu(II) complexes with 3 equiv of trityl tetrafluoroborate in acetonitrile results in oxidative dehydrogenation, yielding the 15-$\pi$ cations [M(MeHMe-2,9-diene)]$^+$ (**15**) which were isolated as their tetrafluoroborate salts. Conductivity, spectrophotometric, and epr results indicate that the nickel complex exists in a paramagnetic monomer $\rightleftarrows$ diamagnetic dimer equilibrium in solution. The nickel and copper cations are reduced by sodium borohydride in ethanol to the neutral 16-$\pi$ complexes M(MeHMe-2,9-diene) (**14**). Voltammetric studies of these complexes in acetonitrile have established the existence of a three-membered electron-transfer series **14** (16-$\pi$) $\rightleftarrows$ **15** (15-$\pi$) $\rightleftarrows$ **16** (14-$\pi$). Members of the series are interconverted by reversible one-electron redox processes considered to alter the ligand oxidation level such that the terminal oxidized member, [M(MeHMe-2,8,10-triene)]$^{2+}$ (**16**), contains a $(4n + 2)$-stabilized ring system. 16-$\pi$ Ni(II) complexes **26** derived from several recently reported dihydrooctaaza[14]annulene macrocycles have been prepared. These and the 16-$\pi$ Ni(II) complexes **1** were found to undergo two-electron oxidations, presumably yielding the 14-$\pi$ species **27** and **28**, respectively.

Attempts to relate electronic properties and reactivities of synthetic macrocyclic complexes to those of naturally occurring macrocycles, such as porphyrins and corrins, continue to promote considerable interest in their design and preparation. Work in this area has resulted in substantial progress in the development of cyclization reactions, usually involving metal ions, which have led to a variety of new macrocycles.[1] In addition, development of systematic transformations, particularly hydrogenation and dehydrogenation reac-

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