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Electron Transfer between Sulfur(IV) and Chloroiron(III) and Chlorocopper(II) Ions in Aqueous Chloride Media. Formation of a Sulfur Dioxide Complex with Chlorocopper(I)[1a,b]

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The oxidation of sulfur(IV) by chloroiron(III) in acidic aqueous 1.0 *M* chloride solution is catalyzed by copper(II). The reaction rate is described by $-d[\mathrm{Fe(III)}]/dt = (0.004[\mathrm{Fe(III)}][\mathrm{S(IV)}]/[\mathrm{H^+}]^2)(1 + 20[\mathrm{Fe^{2+}}])$ at 25° in 0.01 *M* Cu^{2+} solutions. The form of the rate law is approximately consistent with the rate-determining step $FeSO_3^+ + H_2O \rightarrow Fe^{2+} + HO^-SO_3^- + H^+$, with $k > 0.5$ for this step. The rate law also suggests rapid Cu(II) reaction with the sulfur(V) species, with competition by Fe^{2+} at high $[Fe^{2+}]$. The oxidation of sulfur(IV) by copper(II) in acidic aqueous 1.0 *M* chloride solution is described by the rate law $-d[\mathrm{Cu(II)}]/dt = [\mathrm{Cu(II)}][\mathrm{S(IV)}]/(1700[\mathrm{H^+}] + 2900[\mathrm{H^+}]^2)$ at 25°. The reaction is retarded by copper(I). Spectral evidence indicates the existence of copper(I)-sulfur dioxide complex in solution.

We have done a kinetic study of the copper(II)-catalyzed reduction of iron(III) by sulfur(IV), as indicated by eq 1.[2]

$$2\mathrm{Fe(III)} + \mathrm{S(IV)} = 2\mathrm{Fe}^{2+} + \mathrm{SO_4}^{2-} \qquad (1)$$

The reactions were carried out in acidic aqueous solutions containing 1.0 *M* chloride. We have already referred to some previous investigations of reaction 1 and have described our general interest in the system.[3] Our specific goal in this particular study was to find a system in which the first Fe(III)-S(IV) electron transfer is completely rate determining, so that this first transfer could be investigated without complications from subsequent steps. Addition of chloride and copper(II) to the system caused this goal to be realized and also provided some additional information about the reactive properties of sulfur(V) radicals.

During the investigation of reaction 1 we became interested in two additional processes that can occur in solutions similar to our reaction mixtures. We extended the study to include a brief investigation of these processes, indicated by eq 2 and 3.

$$2\mathrm{Cu(II)} + \mathrm{S(IV)} = 2\mathrm{Cu(I)} + \mathrm{SO_4}^{2-} \qquad (2)$$

$$\mathrm{Cu(I)} + \mathrm{SO_2} = \mathrm{Cu^ISO_2} \qquad (3)$$

The investigation of eq 3 provided evidence for the existence of a copper(I)-sulfur dioxide complex, possibly containing a Cu(I)-Cl-SO_2 linkage. This evidence is especially interesting in light of the recent X-ray studies of crystalline Pt(II), Ir(I), and Rh(I) complexes containing metal-halide-sulfur dioxide linkages.[4] If the copper-sulfur dioxide complex reported here contains such a linkage, then we believe it is the first to be discovered in aqueous solution and the first to be discovered that involves a first-row transition metal.

Experimental Section

Reagents. The preparations and analyses of iron(III) perchlorate and iron(II) perchlorate were described earlier.[5] The preparation and analysis of aqueous sulfur dioxide solutions has also been described.[6] Sodium chloride was prepared from reagent grade sodium carbonate and hydrochloric acid. Solutions prepared from doubly recrystallized sodium chloride were analyzed by titration of the acid displaced by aliquots of the solution from ion-exchange resin in the H^+ form.

Copper(II) chloride solutions were prepared by dissolution of doubly recrystallized copper(II) chloride in water and were analyzed by the ion-exchange procedure used for the sodium chloride solutions. Copper(I) solutions were prepared from copper(II) chloride and copper metal. The copper(II) chloride was dissolved in 6 *M* hydrochloric acid, copper turnings were added, and the solution was deoxygenated by purging with nitrogen while stirring vigorously. The stirring was continued, and after each day of stirring, the copper turnings were replaced with fresh ones and the solution was purged again. The preparations were carried out in milk dilution bottles fitted with self-sealing rubber caps, and they occurred over a period of about 4 days. The solutions were initially dark green, became dark brown, and then turned colorless. Withdrawals of copper(I) solution were accomplished with a syringe, using a steel needle. The copper(I) solutions were analyzed by titration with cerium(IV), using ferroin as the indicator.

Reagent grade perchloric and hydrochloric acids were used without purification. Laboratory distilled water was redistilled.

Stoichiometry and Rate Measurements. The stoichiometry indicated by eq 1 was confirmed at 25° and 1.0 *M* ionic strength by analysis for dithionate, using the procedure that has been described.[3]

Rate measurements were performed at 25.0° and 1.00 *M* ionic strength. The reactions were allowed to occur in two-necked 10-cm cells positioned in a thermostated cell holder in a Beckman ACTA V recording spectrophotometer. The cells were charged with all the appropriate reagents except sulfur(IV); they were sealed with rubber serum caps and were purged for at least 15 min with nitrogen gas before the sulfur(IV) was added. The purging nitrogen was bubbled through a chromium(II) solution before it was directed into a cell. The nitrogen entered one neck of the cell and exited the other neck by way of steel syringe needles; the needles were prevented from touching the solution, and the nitrogen bubbles agitated the solution. Sulfur(IV) was in excess in each of the reactions and $[H^+]$ was relatively large, so that only the metal ion concentration changed appreciably during any reaction.

The progress of each reaction was followed with the spectrophotometer. Monitoring wavelengths from 400 to 490 nm were used for reaction 1. In this wavelength interval $FeSO_3^+$ and $FeCl^{2+}$ absorb significantly, but the other species present do not. In each experiment designed to measure the rate of reaction 1 the absorbance was measured as a function of time for the entire reaction.

In each experiment designed to measure the rate of reaction 2, the absorbance at 700 nm was measured as a function of time only for a few per cent of reaction, using an expanded absorbance scale. Using the initial slope of the absorbance *vs.* time curve and the measured apparent extinction coefficient for copper(II) (8.34 M^{-1} cm^{-1} in 1.00 *M* chloride) the initial value of $\Delta[\mathrm{Cu(II)}]/\Delta t$ was obtained for each experiment.

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[1] (a) Supported by the Robert A. Welch Foundation. (b) Based on the Ph.D. dissertation of O. F. Z., Texas Tech University. (c) Robert A. Welch Predoctoral Fellow, 1971-1972.

[2] Iron(III), copper(II), and copper(I) are assumed to be involved in complexation equilibria with chloride. The symbols Fe(III), Cu(II), and Cu(I) are used to avoid the implication of a specified degree of complexation. Similarly, SO_2 is in equilibrium with HSO_3^- and SO_3^{2-}; the symbol S(IV) is used to avoid specification of the degree of hydrolysis. Coordinated water molecules are not indicated in formulas for metal ions.

[3] D. W. Carlyle and O. F. Zeck, Jr., *Inorg. Chem.*, 12, 2978 (1973).

[4] (a) M. R. Snow, J. McDonald, F. Basolo, and J. A. Ibers, *J. Amer. Chem. Soc.*, 94, 2526 (1972); (b) M. R. Snow and J. A. Ibers, *Inorg. Chem.*, 12, 224 (1973).

[5] D. W. Carlyle, *Inorg. Chem.*, 10, 761 (1971).

[6] D. W. Carlyle, *J. Amer. Chem. Soc.*, 94, 4525 (1972).

The value $Q_a = [HSO_3^-][H^+]/[SO_2] = 0.043\ M$[7] was used for calculation of $[H^+]$ and $[HSO_3^-]$ in reaction mixtures. This value was measured[7] in 1.00 *m* perchlorate media and so may be slightly in error for our 1.00 *M* chloride solutions. However, the effect of $Q_a \cong 0.043\ M$ on $[H^+]$ was small in all our experiments except those at lowest $[H^+]$ and highest total [S(IV)].

Copper(I)–Sulfur(IV) Complexation. Equilibrium 3 was investigated spectrophotometrically, using either a Cary Model 17 recording spectrophotometer or the Beckman instrument described above. Spectrophotometer cells were charged with the appropriate amounts of all reagents except copper(I) and sulfur(IV). The resulting solutions were thermostated, purged with nitrogen, charged with the copper(I), and positioned in the thermostated cell holder. The absorbance of each solution was measured at 340 nm after each of a series of additions of small volumes of aqueous sulfur dioxide.

Results

Reduction of Iron(III). We attempted to measure the rate of reaction 1 in the absence of copper(II) and in 1 *M* chloride, but we encountered two difficulties. The first problem was poor reproducibility in duplicate solutions containing sodium chloride. This problem occurred even when the duplicate solutions contained NaCl from the same stock solution. Several different sources of NaCl were tried, but the problem persisted. The cause of the erratic behavior was not proven, but we suspect that molecular oxygen was involved in combination with some impurity in our sodium chloride; deliberate additions of very small amounts of oxygen caused an abrupt reduction in the rate of disappearance of iron(III), and merely shaking a solution that was behaving anomalously would occasionally affect the subsequent rate. Thus, we believe that inadequacies in our deoxygenation method prevented reliable measurements in the presence of our sodium chloride. Earlier studies have also indicated rate effects of oxygen.[8]

The second problem encountered in copper-free solutions was a nonintegral order with respect to iron(III) in the rate expression. Measurements of the rate of reaction 1 in 1.0 *M* HCl and in the absence of both Cu(II) and NaCl were reproducible, but the rate of disappearance of iron(III) was between first and second order in iron(III), as in the presence of NaCl. This fractional order suggested that we were *not* measuring only the rate of the initial iron(III)–sulfur(IV) electron transfer as we had hoped to do, and so we turned to the copper-catalyzed system.

The stoichiometry in the copper-catalyzed system was shown by dithionate analyses of product solutions to be in accord with eq 1. A series of four experiments was done; in each experiment the initial iron(III) and copper(II) concentrations were 0.01 *M*. In two experiments at 0.01 *M* initial [S(IV)], $[H^+]$ was 0.07 and 1.0 *M*. In the remaining experiments, [S(IV)] was 0.2 *M* and $[H^+]$ was 0.1 and 1.0 *M*. Throughout the series, the measured S(V) concentrations ranged from less than 0.8 to 2% of the initial [Fe(III)], indicating that sulfate is the dominant sulfur product.

The rate of reaction 1 was measured in 1 *M* chloride with copper(II) present and with a variety of concentration conditions. The rates were increased by the addition of copper(II), as was expected (see ref 3 and references therein). For each of these copper-catalyzed reactions, a plot of log $(A - A_\infty)$ *vs.* time was linear, where A is the absorbance at any time and A_∞ is the absorbance after completion of the reaction. The linearity of the plots shows that the rate of disappearance of iron(III) is described by eq 4; k' is a function of $[H^+]$, [S(IV)], and $[Fe^{2+}]$ as can be concluded from Table I, which shows the results of all the measurements.

$$-d[Fe(III)]/dt = k'[Fe(III)] \tag{4}$$

A set of experiments that were identical, except for the variation of [Cu(II)] from 5×10^{-4} to $1 \times 10^{-2}\ M$, showed the measured k' value to be independent of [Cu(II)] over this range; these experiments are listed in Table I.

The k' values shown in Table I that correspond to experiments done without iron(II) initially present can be correlated by $k' = a[S(IV)]/[H^+]^2$; the value of a was determined by a linear least-squares[9] fit of the data to eq 5. The least-squares fit led to $a = (4.0 \pm 0.14) \times 10^{-3}\ M\ sec^{-1}$, where 0.14×10^{-3} is the calculated standard deviation.

The rigorous $[H^+]^{-2}$ dependence shown above is surprising. Since the dominant aqueous sulfur(IV) species changes from SO_2 to HSO_3^- at $[H^+] = Q_a$, one would expect the order with respect to $[H^+]$ to become less negative as the acidity decreases in that $[H^+]$ region. However, an attempt to fit the data to the equation $k' = \{a'[S(IV)]/[H^+]^2\}\{[H^+]/([H^+] + 0.043)\}$ (equivalent to $k' = a'[SO_2]/[H^+]^2$ if $Q_a = 0.043\ M$) resulted in a distinctly poorer fit than was obtained with the simpler equation.

The k' values that correspond to experiments done with iron(II) added initially, all with 0.01 *M* Cu(II), were graphically fitted to the expression $a[S(IV)]/k'[H^+]^2 = 1 + b[Fe^{2+}]$. The precision of the measurements was poor, but the fit to this expression was better than for other simple expressions, giving b = 16–25 *M*. From this result and those described above, we conclude that k' in eq 4 is described by eq 5,

$$k' = a[S(IV)]/[H^+]^2(1 + b[Fe^{2+}]) \tag{5}$$

where $a = 4.0 \times 10^{-3}\ M\ sec^{-1}$ and $b = 20\ M^{-1}$. The values for k'_{calcd} listed in Table I were obtained from eq 5.

Reduction of Copper(II). The stoichiometry given by eq 2 has been reported to occur in more concentrated solutions;[10] the formation of at least some sulfate in our reaction mixtures was indicated by the formation of barium sulfate upon addition of barium chloride to acidified product solutions.

The initial rate of reaction 2 was measured in a series of experiments listed in Table II. The form of the rate law was assumed to be described by eq 6. The data are so imprecise

$$-d[Cu(II)]/dt = k''[Cu(II)][S(IV)] \tag{6}$$

that it is difficult to judge whether the rate law is more complicated than we assumed. For example, a set of six experiments is shown in Table II for which [S(IV)] = 0.10 *M* and for which [Cu(II)] is varied from 1×10^{-3} to $2 \times 10^{-2}\ M$; the k'' values for these experiments vary considerably based on the assumption that eq 6 is correct. Similarly, a set of four experiments at $1.0 \times 10^{-2}\ M$ Cu(II) and 0.20 *M* H^+, with 0.025–0.20 *M* S(IV), gave varying k'' values. Trends are not apparent in the two sets of experiments described above and other simple rate law assumptions do give trends in rate parameters; we claim that eq 6 is an adequate empirical representation of the data, although unobserved subtle complexities may be present. The lack of precision was caused by the smallness of the absorbance changes used and the changing apparent value of k'' in each experiment as the reaction progressed and inhibition by Cu(I) increased.

The k'' values listed in Table II are inversely dependent on $[H^+]$. The dependence is greater at high $[H^+]$; a plot (not shown) of log k'' *vs.* log $[H^+]$ (for experiments at [S(IV)] = 0.10 *M* and [Cu(II)] = 0.01 *M*) yielded an approximately −2

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[7] M. Frydman, G. Nilsson, T. Rengemo, and L. Sillen, *Acta Chem. Scand.*, 12, 878 (1958). These authors measured $Q_a = 0.043$ *m*.

[8] D. G. Karraker, *J. Phys. Chem.*, 67, 871 (1963).

[9] W. Volk, "Applied Statistics for Engineers," McGraw-Hill, New York, N. Y., 1958, Chapter 8.

[10] R. N. Keller and H. D. Wycoff, *Inorg. Syn.*, 2, 1 (1946).

Table I. Observed and Calculated Rate Constants Defined by Eq 4 and 5 (25°, 1.0–1.1 *M* Ionic Strength)

$[S(IV)]$,[a] *M*	$[H^+]$, *M*	$10^2[Fe(III)]_0$, *M*	$10^2[Fe(II)]_0$, *M*	$10^2[Cu(II)]$, *M*	$10^4k'$, sec^{-1} Obsd	Calcd
0.010	0.036	0.05	None	0.05	340	310
0.010	0.25	0.10	None	0.10	7.0	6.4
0.010	0.50	0.10	None	0.10	1.7	1.6
0.015	0.50	0.10	None	0.10	2.5	2.4
0.025	0.05	0.10	None	0.10	330	400
0.025	0.07	1.0	None	1.0	200	210
0.025	0.10	0.10	None	0.10	120	100
0.025	0.15	0.10	None	0.10	47	44
0.025	0.25	1.0	None	1.0	24	16
0.025	0.50	1.0	None	1.0	4.0	4.0
0.026	1.0	1.0	None	1.0	0.9	1.0
0.05	0.50	0.10	None	0.10	9.0	8.0
0.10	0.14	1.0	None	1.0	250	210
0.10	0.20	1.0	1.0	1.0	70	83
0.10	0.20	1.0	5.0	1.0	50	50
0.10	0.20	1.0	10	1.0	23	33
0.10	0.25	1.0	None	1.0	90	64
0.10	0.50	1.0	None	1.0	26	16
0.10	0.50	1.0	2.0	1.0	23	11
0.10	0.50	1.0	5.0	1.0	13	8.0
0.10	0.50	1.0	10	1.0	6.0	5.4
0.10	0.50	1.0	15	1.0	5.0	4.0
0.10	1.0	1.0	None	0.05	3.6	4.0
0.10	1.0	1.0	None	0.10	3.6	4.0
0.10	1.0	1.0	None	0.20	3.6	4.0
0.10	1.0	1.0	None	1.0	3.5	4.0
0.20	0.15	1.0	None	1.0	360	360
0.20	0.25	1.0	None	1.0	130	130
0.20	0.50	1.0	None	1.0	31	32
0.20	0.50	1.0	1.0	1.0	40	27
0.20	0.50	1.0	3.5	1.0	19	19
0.20	0.50	1.0	7.0	1.0	10	13
0.20	0.50	1.0	14	1.0	8.0	8.4
0.20	1.0	1.0	None	1.0	9.0	8.0
0.40	1.0	1.0	None	1.0	23	16

[a] $[S(IV)]$ represents the total sulfur(IV) concentration.

Table II. Observed and Calculated Rate Constants Defined by Eq 6 and 7 (25°, 1.00 *M* Ionic Strength)

$[S(IV)]_0$, *M*	$[H^+]$, *M*	$10^2[Cu(II)]_0$, *M*	$10^4k''$, M^{-1} sec^{-1} Obsd	Calcd
0.025	0.20	1.0	20	23
0.050	0.20	1.0	30	23
0.10	0.067	1.0	91	90
0.10	0.095	1.0	61	60
0.10	0.10	0.10	48	57
0.10	0.10	0.25	56	57
0.10	0.10	0.50	64	57
0.10	0.10	1.0	39	57
0.10	0.10	2.0	34	57
0.10	0.15	1.0	39	34
0.10	0.20	1.0	24	23
0.10	0.25	1.0	21	17
0.10	0.30	1.0	14	13
0.10	0.40	1.0	7.0	8.7
0.10	0.50	1.0	6.0	6.2
0.10	0.65	1.0	4.1	4.1
0.10	0.80	1.0	2.5	2.9
0.10	0.97	1.0	3.1	2.1
0.10	0.97	1.0	0.4[a]	
0.10	0.97	1.0	0.1[b]	
0.10	0.97	1.0	0.8[c]	
0.20	0.20	1.0	30	23

[a] Initial $[Cu(I)] = 5.7 \times 10^{-3}$ *M*. [b] Initial $[Cu(I)] = 1 \times 10^{-2}$ *M*. [c] Initial $[Cu(I)] = 2.8 \times 10^{-2}$ *M*.

slope at high $[H^+]$; the slope became less negative at lower $[H^+]$ values. Another plot (not shown) of $1/k''[H^+]$ *vs.* $[H^+]$ (for experiments not containing Cu(I) initially) was approximately linear, with intercept and slope of 1700 ± 140 sec and 2900 ± 530 M^{-1} sec, respectively. The slope and intercept were obtained from a linear least-squares treatment[9] of the data; the indicated uncertainties are the calculated standard deviations. These observations indicate that in the absence of Cu(I) the $[H^+]$ dependence of k'' may be represented by eq 7, where $m = 1700$ sec and $n = 2900\ M^{-1}$ sec. The

$$k'' = 1/(m[H^+] + n[H^+]^2) \qquad (7)$$

three experiments listed in Table II for which Cu(I) was initially present show that Cu(I) strongly retards the reaction. As Cu(I) is increased, the value of k'' passed through a minimum. This behavior appeared unusual but occurred again upon repeating the experiments.

Copper(I)-Sulfur(IV) Complexation. The investigation of equilibrium 3 was not extensive but led to the conclusion that Q_3 is small. Four sets of experiments were done with the following molar concentrations, listed in the order $[Cu(I)]_0$, $[H^+]$, maximum $[S(IV)]$: 5.1×10^{-3}, 1.0, 5.95×10^{-2}; 9.9×10^{-3}, 1.0, 3.87×10^{-2}; 20.9×10^{-3}, 1.0, 3.87×10^{-2}; 9.9×10^{-3}, 0.10, 4.11×10^{-2}. For these experiments, plots (not shown) of ϵ_{app} ($\epsilon_{app} = A/l[Cu(I)]$) *vs.* $[S(IV)]$ are linear, with slopes of 280, 220, 210, and 220 M^{-2} cm^{-1}, respectively.

Discussion

Reduction of Iron(III). Empirical eq 4 and 5, based on the data in Table I, indicate that reaction 1 is first order in iron(III), first order in sulfur(IV), and zero order in copper(II) and iron(II) under conditions of low $[Fe(II)]$ and $(0.05\text{–}1.0) \times 10^{-2}$ *M* Cu(II). This result is consistent with the hypothesis that the first electron transfer between iron(III) and sulfur(IV) is rate determining under these conditions. Equation 8 represents an obvious mechanistic suggestion for the first electron transfer. Second-order reactions between the pairs $FeOH^{2+}$-HSO_3^- or Fe^{3+}-SO_3^{2-} are also consistent with eq 4 and 5. However, we think electron transfer between coordinated species is more probable, as we have already argued.[3] Our arguments for the hydrolyzed form of the sulfur(V) species have also been presented.[3]

$$FeSO_3^+ + H_2O \rightarrow Fe^{2+} + HSO_4^{2-} + H^+ \qquad (8)$$

The inverse second-order hydrogen ion dependence indicated by eq 5, even at $[H^+] < 0.1\ M$, is not in accord with eq 8 as the only step influencing the rate law, however, unless Q_a is considerably smaller than 0.043 *M* in 1.0 *M* chloride. Since the acid dependence of k'' is *not* inconsistent with $Q_a = 0.043\ M$, we will continue to assume that the value of Q_a is about the same in chloride as in perchlorate. Reaction 8 agrees with the empirical rate law at high acidity; another pathway with strong inverse acid dependence may account for the failure of k' to show reduced $[H^+]$ dependence at low acidity. Such an additional pathway could be an electron transfer between $FeOH^{2+}$ and SO_3^{2-} or between $FeClOH^+$[11] and SO_3^{2-}. We think a reaction between $FeOH^{2+}$ and SO_3^{2-} is probably not significant, however, because experiments done in perchlorate media[3] did not provide evidence for it.

The role of copper in the mechanism for reaction 1 is not clearly indicated by our data, but our results, together with earlier results, are consistent with the conventional proposal (see ref 3 and references therein) that copper(II) acts as a radical scavenger. Copper(II) is apparently a much more effective radical scavenger in this system than in similar systems not containing chloride.[3] This chloride enhancement of the copper(II) scavenging effect may be caused by one or more

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(11) This ion has recently been characterized by R. Koren and B. Perlmutter-Hayman, *Inorg. Chem.*, 11, 3055 (1972).

of the following: slower Fe(II)–$\cdot SO_3^-$ reaction, slower Fe(III)–$\cdot SO_3^-$ reaction, or faster Cu(II)–$\cdot SO_3^-$ reaction. Since iron(II) is not complexed appreciably by chloride[12] and only about 75% of the iron(III) was complexed in our solutions,[13] but copper(II) is extensively complexed by chloride,[14] we think that complexation of copper(II) may increase the rate of the Cu(II)–$\cdot SO_3^-$ reaction, to account for the improved scavenging ability of the copper. As shown in the next paragraph, our data are consistent with a significant increase in the scavenging ability of copper(II) relative to iron(II) upon changing from perchlorate to chloride media.

The inhibition by large concentrations of iron(II) is consistent with earlier proposals (see ref 3 and references therein) that sulfur(V) is reduced rapidly by iron(II). If we assume the $(1 + b[Fe^{2+}])$ factor in eq 5 arises from competition for radicals by Cu(II) and Fe^{2+} (and evidence for this competition has been presented[3]), then the factor is of the form $(c[Cu^{2+}] + b[Fe^{2+}])$. Since $[Cu^{2+}]$ was 0.01 M in each experiment done with Fe^{2+} present initially, the value of c is computed as $1/0.01 = 100\,M^{-1}$. From this result and from the measured $b = 20\,M^{-1}$, we conclude that the ratio of the second-order rate constants for reaction with radicals by copper(II) and iron(II) in 1.0 M chloride is 100/20, or 5; our results obtained in perchlorate media[3] indicate that the corresponding ratio is 0.15 in perchlorate.

The detailed mechanism of the Cu(II)-S(V) reaction is important because oxidation of radicals by copper(II) is significant in a variety of systems.[15-17] Three limiting mechanisms for the mechanism can be visualized: (a) outer sphere, (b) inner sphere with chloride bridging (this mechanism has been called the ligand-transfer mechanism[15-18]), and (c) inner sphere with a direct copper–sulfur bond or copper–oxygen bond (this has been called the electron-transfer mechanism[15-18]). Each of the inner-sphere mechanisms appears to have many precedents in the copper(II) oxidation of organic radicals.[15,17] Jenkins and Kochi[15c] have observed, however, that *ligand transfer* to organic radicals tends to occur if the radical is soft (as defined by Pearson[19]) and if chloride or other soft ligands are on copper. Conversely, they[15c] have observed that the electron-transfer mechanism is favored if the radical and ligands are hard. These generalizations suggest that the probable mechanism in perchlorate media is inner sphere, with sulfur (or possibly an oxygen atom of the radical) coordinated directly to copper. Similarly, these suggestions predict that the probable mechanism in chloride media is inner sphere and chloride bridged.

If reaction 8 is considered to be correct, then the empirically measured value of a can be used to estimate the product k_8Q', where $Q' = [FeSO_3^+][H^+]/[Fe^{3+}][HSO_3^-]$. Neglecting the results at low acidity, $-d[Fe(III)]/dt = 2k_8Q'[Fe(III)]\cdot[S(IV)]/[H^+](1 + Q''[Cl^-])(1 + [H^+]/Q_a)$, where $Q'' = [FeCl^{2+}]/[Fe^{3+}][Cl^-] = 2.9\,M^{-1}$.[13] Thus, we propose that a in eq 5, in 1.0 M Cl^- and 1.0 M H^+, is equivalent to $k_8Q'/47$. Using this expression for a with the empirically measured value for a we compute $k_8Q' = 0.2\ sec^{-1}$. An upper limit of 0.4 has been established for Q',[5] so that $k_8 = 0.5\ sec^{-1}$. This lower limit for k_8 is the same as was obtained from experiments done in perchlorate solutions,[3] but we view it as considerably more reliable since it is based on fewer empirical numbers and on fewer assumptions.

Reduction of Copper(II). The form of the empirical rate law for reduction of copper(II) by sulfur(IV), given by eq 6 and 7, is consistent with each of a set of four mechanisms. Each of the mechanisms is analogous to that we have just proposed for the copper-catalyzed reduction of iron(III) in chloride media. The individual mechanisms are described by eq 9-12, where Cu(I), Cu(II), and probably $CuSO_3$ are complexed by chloride.

$$CuSO_3 + H_2O \rightarrow Cu(I) + HSO_4^{2-} + H^+ \tag{9}$$

$$Cu(II) + SO_3^{2-} + H_2O \rightarrow Cu(I) + HSO_4^{2-} + H^+ \tag{10}$$

$$Cu(II) + SO_3^{2-} \rightleftharpoons CuSO_3 \tag{11a}$$

$$CuSO_3 + H_2O \rightarrow Cu(I) + HSO_4^{2-} + H^+ \tag{11b}$$

$$Cu(II) + HSO_3^- \rightleftharpoons CuSO_3 + H^+ \tag{12a}$$

$$CuSO_3 + H_2O \rightarrow Cu(I) + HSO_4^{2-} + H^+ \tag{12b}$$

In eq 9 $CuSO_3$ is proposed to be in equilibrium with Cu(II) and HSO_3^-, but in eq 11 and 12, $CuSO_3$ is proposed to be a steady-state species. In each proposal, S(V) is oxidized by a second Cu(II) in a fast step. The mechanisms suggested by eq 9-11 are exactly in accord with the form of eq 6 and 7, but each of these leads to the conclusion that the ratio $m/n = 0.6\,M$ is equal to Q_a. We think this result requires that mechanisms 9-11 be rejected, since Q_a is more than an order of magnitude smaller than 0.6.

The mechanism represented by eq 12 is only approximately in accord with the form of eq 6 and 7. If mechanism 12 is correct, then eq 7 should be of the more complicated form indicated by eq 13, even though the acid-independent denominator term was not detected empirically.

$$k'' = \frac{2}{\dfrac{1}{k_{12a}} + \left(\dfrac{k_{-12a}}{k_{12a}k_{12b}} + \dfrac{1}{Q_ak_{12a}}\right)[H^+] + \dfrac{k_{-12a}}{k_{12a}k_{12b}Q_a}[H^+]^2} \tag{13}$$

The quality of the data is not sufficient to permit a distinction between eq 7 and 13, especially since the calculations of $[H^+]$ made at lowest $[H^+]$ are the most uncertain ones. We suggest that eq 12a and 12b do represent a reasonable mechanism that is consistent with the observed data.

If eq 12a and 12b do indeed describe the mechanism, then $k_{-12a}/k_{12a}k_{12b}$ is about $(2900)(0.043) = 120\,M\ sec^{-1}$, and k_{12a} is about $1/(1700 - 120)(0.043) = 0.015\,M^{-1}\ sec^{-1}$. These numbers are consistent with the assumption that the $1/k_{12a}$ term in eq 13 is small.

We have assumed that the direct reaction between copper(II) and sulfur(IV) is not important in the copper-catalyzed reduction of iron(III). This assumption, which is consistent with the form of rate laws that have been measured for the system, has been included in most[20] of the earlier mechanistic proposals for the copper-catalyzed reduction of iron(III) (see ref 3 and references therein). The slowness of the

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[12] H. N. Po and N. Sutin, *Inorg. Chem.*, 7, 621 (1968).

[13] M. J. M. Woods, P. K. Gallagher, and E. L. King, *Inorg. Chem.*, 1, 55 (1962).

[14] L. G. Sillen, Ed., *Chem. Soc., Spec. Publ.*, No. 17, 285 (1964).

[15] (a) C. L. Jenkins and J. K. Kochi, *J. Org. Chem.*, 36, 3095 (1971); (b) C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, 94, 843 (1972); (c) C. L. Jenkins and J. K. Kochi, *ibid.*, 94, 856 (1972).

[16] J. S. Littler, *Chem. Soc., Spec. Publ.*, No. 24, 383 (1971).

[17] D. C. Nonhebel, *Chem. Soc., Spec. Publ.*, No. 24, 409 (1971).

[18] We are reluctant to follow the earlier nomenclature[15] and call this mechanism *ligand transfer*, because we do not have evidence to show whether chloride is transferred to sulfur. It has already been noted (D. W. Carlyle and J. H. Espenson, *J. Amer. Chem. Soc.*, 91, 599 (1969), and references therein) that ligand transfer need not be a consequence of a bridged, inner-sphere mechanism. We propose that the mechanism should be called simply bridged, inner sphere. Similarly, the term "electron transfer" does not describe the details of a mechanism involving oxidation of a coordinated ligand. We propose that this mechanism should be called simply oxidation of a *coordinated ligand.*

[19] R. G. Pearson, *J. Amer. Chem. Soc.*, 85, 3533 (1963).

direct copper(II)-sulfur(IV) reaction confirms that it is a minor pathway under the conditions employed in our studies. The direct reaction becomes significant at higher [Cu(II)]/[Fe(III)] ratios, however. In 1.0 M H^+, 0.01 M Cu(II), 0.01 M Fe(III), and 0.0 M Fe(II), for example, $-d[S(IV)]/dt$ from eq 6 and 7 is 0.054 times as great as $-d[S(IV)]/dt$ from eq 4 and 5.

The retardation of net reaction 2 by copper(I) indicates that reaction 12b is reversible (assuming that eq 12a and 12b do indeed represent the mechanism). The decreased retardation at the highest Cu(I) used in our experiments is not explained by eq 12; an additional pathway is required, and our data are not sufficiently extensive to warrant speculation.

Copper(I)-Sulfur(IV) Complexation. The linearity of the plots of ϵ_{app} *vs.* [S(IV)] indicates that Q_3 is small; if eq 3 does represent the complexation reaction and if only one complex is formed, then the slope of each line is equal to $\epsilon Q_3[H^+]/(Q_a + [H^+])$, where ϵ is the molar absorbancy coefficient for the complex. Use of this relationship gives an average value $\epsilon Q_3 = 260\ M^{-2}\ cm^{-1}$. Evidence that SO_2 is indeed the complexed species, as written in eq 3, is provided by the constancy of the slopes of the ϵ_{app} *vs.* [S(IV)] plots at 0.10 and 1.0 M H^+. Over this range of $[H^+]$, $[SO_2]/[S(IV)]$, $[HSO_3^-]/[S(IV)]$, and $[SO_3^{2-}]/[S(IV)]$ vary by factors about 1.4, 7.3, and 73, respectively. The composition of the copper(I) complex is at first surprising since most previous studies of metal ion-sulfur(IV) complexes have shown compositions of the form $MSO_3{}^n$, and, indeed, stable $Cu(SO_3)_n{}^{(n-1)-}$ and $Cu(SO_3)_3Cl^{6-}$ complexes have been reported.[21] However, literature precedents can be found for metal-sulfur dioxide complexes containing metal-sulfur bonds and also for metal-halide-sulfur dioxide complexes containing halide-sulfur bonds in crystals.[22] In addition to halide-sulfur dioxide linkages in metal complexes, free $XSO_2{}^-$ complexes containing halide-sulfur dioxide linkages have been characterized in a variety of solvents, including water.[23]

Since copper(I) is extensively complexed by chloride in aqueous chloride media,[14] a Cu(I)-Cl-SO linkage is certainly possible. We think this formulation is as probable as the alternate Cu(I)-SO_2 formulation, but our evidence does not distinguish between the two linkages. We do not plan to pursue the study, but we think this first-row metal-sulfur dioxide complex, stable enough to be detectable in water solution, may be useful in understanding the general set of metal-sulfur dioxide complexes.

Registry No. S(IV), 20681-10-1; Fe(III), 20074-52-6; Fe(II), 15438-31-0; Cu(II), 15158-11-9; Cu(I), 17493-86-6.

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[20] One group of researchers, however, has proposed a mechanism in which reaction 2 is the first step, followed by a rapid reaction between iron(III) and copper(I): I. N. Kuz'minykh and T. B. Bohmshtein, *J. Appl. Chem. USSR*, 26, 1 (1953); *Chem. Abstr.*, 49, 2925 (1955).

[21] (a) V. F. Toropova, I. A. Sirotina, and V. B. Rotanova, *Uch. Zap., Kazan. Gos. Univ.*, 115, 53 (1955); *Chem. Abstr.*, 52, 952 (1958); (b) G. A. Boos, A. A. Popel, and G. A. Merzlikina, *Issled. Elektrokhim., Magnetokhim. Elektrokhim. Metod. Anal.*, No. 3, (1970); *Chem. Abstr.*, 75, 144413 (1971).

[22] The literature reports are well summarized in ref 4b.

[23] D. F. Burow, *Inorg. Chem.*, 11, 573 (1972), and references therein.

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Base Adducts of β-Ketoenolates. VII.[1,2] Electron Paramagnetic Resonance Studies of Some Fluxional 1,1,1,5,5,5-Hexafluoro-2,4-pentanedionatocopper(II) Complexes

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Electron paramagnetic resonance parameters for tetragonal six-coordinate complexes of the type CuO_4N_2 and CuO_n for $n = 4-6$ have been evaluated. Increasing $g_{\parallel}$ and decreasing $A_{\parallel}$ hyperfine parameters are found for a series of similar complexes as the axial ligand field is strengthened. The trend observed correlates well with the shift to lower energies found for the d-d transitions. For both the CuO_4N_2 and CuO_6 complexes, fluxional molecules describable by a dynamic Jahn-Teller formalism have been observed. A correlation between the in-plane σ-bonding coefficients (α) and both the dipolar factor P (which takes into account the radial distribution of the unpaired electron) and the factor κ (which measures the amount of s-electron admixture) has been observed and is presented here for complexes of the type CuO_4N_2.

Introduction

Solution spectra of copper β-diketonates are solvent dependent. Spectral changes arise from coordination of the solvent to the copper atom of the complex. Funck and Ortolano[3] analyzed the effects of single and double coordination of pyridine and water upon the electronic spectrum of $Cu(F_6acac)_2$. Wayland and Garito[4] extended the molecular orbital calculations of Cotton and coworkers[5] to a model for a five-coordinate adduct having coordinates in accord with the known structural changes that occur[6] in $Cu(acac)_2$ upon axial ligation with quinoline. The principal results of this model are that all d-d transitions are shifted to lower energy, while the d energy level ordering is unchanged. Dudley and Hathaway[7] reported the polarized single-crystal

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[1] Abstracted from the Ph.D. thesis of J. Pradilla-Sorzano.

[2] Part VI: J. Pradilla-Sorzano and J. P. Fackler, Jr., *Inorg. Chem.*, 12, 1182 (1973).

[3] L. L. Funck and T. R. Ortolano, *Inorg. Chem.*, 7, 567 (1968).

[4] B. B. Wayland and A. F. Garito, *Inorg. Chem.*, 8, 182 (1969).

[5] F. A. Cotton, C. B. Harris, and J. J. Wise, *Inorg. Chem.*, 6, 909 (1967).

[6] P. Jose, S. Ooi, and Q. Fernando, *J. Inorg. Nucl. Chem.*, 31, 1971 (1969).

[7] R. J. Dudley and B. J. Hathaway, *J. Chem. Soc. A*, 2794 (1970).