Contribution from the Department of Chemistry,
Texas Tech University, Lubbock, Texas 79409

# Electron Transfer between Sulfur(IV) and Hexaaquoiron(III) Ion in Aqueous Perchlorate Solution. Kinetics and Mechanisms of Uncatalyzed and Copper(II)-Catalyzed Reactions[1a]

DAVID W. CARLYLE* and OTTO F. ZECK, Jr.[1b]

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The oxidation of sulfur(IV) by iron(III) occurs at moderate rates in aqueous acidic perchlorate media at 25°. In solutions containing excess sulfur(IV) the empirical rate law is $-d[\mathrm{Fe(III)}]/dt = k'[\mathrm{Fe(III)}]^2$, with $k' = a[\mathrm{HSO_3^-}]/[\mathrm{H^+}]^2[\mathrm{Fe^{2+}}] + (b[\mathrm{HSO_3^-}]^2/[\mathrm{H^+}]^2[\mathrm{Fe^{2+}}])/(c + [\mathrm{SO_2}])$, $a = 1.7 \times 10^{-6}\ M\ \mathrm{sec^{-1}}$, $b = 5.7 \times 10^{-5}\ M\ \mathrm{sec^{-1}}$, and $c = 0.19\ M$. In solutions containing excess iron(III), the rates are about an order of magnitude larger than predicted by the above equation. In solutions containing copper(II) and excess sulfur(IV), the empirical rate law is $-d[\mathrm{Fe(III)}]/dt = k'_{\mathrm{Cu}}[\mathrm{Fe(III)}]$, with $k'_{\mathrm{Cu}} = [\mathrm{Cu^{2+}}][\mathrm{HSO_3^-}][\mathrm{H^+}]/(m[\mathrm{Fe^{2+}}] + n[\mathrm{Cu^{2+}}] + p[\mathrm{Cu^{2+}}]^2/[\mathrm{H^+}])$, and $m$, $n$, and $p$ are 14.1, 2.16, and 0.83 sec, respectively. This rate law also describes the behavior in solutions containing copper(II) and excess iron(III), except that at low $\mathrm{Fe^{2+}}$ and $\mathrm{Cu^{2+}}$ concentrations the calculated rates are larger than the observed. These results are interpreted in terms of a multistep mechanism involving electron transfer within the inner-sphere complex $\mathrm{FeSO_3^+}$, formation of free sulfur(V) intermediate, and competition among $\mathrm{Fe^{3+}}$, $\mathrm{Cu^{2+}}$, and $\mathrm{FeOH^{2+}}$ for the intermediate.

We are reporting a kinetic study of the oxidation of sulfur(IV) by hexaaquoiron(III) ion. This oxidation occurs according to net reactions 1[2] to give a mixture of sulfate and

$$2\mathrm{Fe^{3+}} + \mathrm{HSO_3^-} + \mathrm{H_2O} = 2\mathrm{Fe^{2+}} + \mathrm{SO_4^{2-}} + 3\mathrm{H^+} \tag{1a}$$

$$2\mathrm{Fe^{3+}} + 2\mathrm{HSO_3^-} = 2\mathrm{Fe^{2+}} + \mathrm{S_2O_6^{2-}} + 2\mathrm{H^+} \tag{1b}$$

dithionate.[3-10] It has been reported that an excess of iron reactant results in sulfate as the principal product, and an excess of bisulfite reactant results in dithionate as the principal product.[4,7-9]

Several pertinent mechanistic studies have been performed already. Higginson and Marshall[7] measured the rate of reaction 1a in sulfate media in the presence of copper(II) and suggested the mechanism indicated by eq 2-6. This mechanism predicts that copper(II) increases sulfate formation, as has been observed.[7,8] Pollard, *et al.*,[8] measured rates in sulfate media in the absence of copper(II), did not get results in agreement with the proposed[7] mechanism, and suggested that dithionate may be formed in an additional way. (A suggestion had been made earlier[10] that $\mathrm{S_2O_5^{2-}}$ may be oxidized in a two-electron step to $\mathrm{S_2O_6^{2-}}$.) Karraker[9] measured rates in perchlorate media and obtained results consistent with the proposed[7] mechanism. Karraker proposed that the sulfur(IV) species is in the inner coordination sphere of iron(III) when the first electron is transferred. More recently it was pointed out that the S(V) intermediate may remain coordinated to iron(II) until further reaction occurs.[11,12]

$$\mathrm{Fe(III)} + \mathrm{S(IV)} \rightleftarrows \mathrm{Fe(II)} + \mathrm{S(V)} \tag{2}$$

$$2\mathrm{S(V)} \rightarrow \mathrm{S_2O_6^{2-}} \tag{3}$$

$$\mathrm{Fe(III)} + \mathrm{S(V)} \rightarrow \mathrm{Fe(II)} + \mathrm{SO_4^{2-}} \tag{4}$$

$$\mathrm{Cu(II)} + \mathrm{S(V)} \rightarrow \mathrm{Cu(I)} + \mathrm{SO_4^{2-}} \tag{5}$$

$$\mathrm{Cu(I)} + \mathrm{Fe(III)} \xrightarrow{\text{fast}} \mathrm{Cu(II)} + \mathrm{Fe(II)} \tag{6}$$

Our purpose in beginning additional measurements of this system was to obtain more accurate and extensive rate data; this has been accomplished by the use of a spectrophotometric method that is now commonly available, rather than use of the much more laborious sample, quench, separate, and analyze sequence that was employed earlier. We have used these data to extend and test the understanding of the mechanisms of reactions 1.

## Experimental Section

**Reagents.** The preparations and analyses of iron(III) perchlorate, iron(II) perchlorate, sodium perchlorate, and perchloric acid solutions were described earlier.[13] The preparation and analysis of aqueous sulfur dioxide solutions have also been described.[14] A copper(II) perchlorate solution was prepared from reagent grade copper(I) oxide and perchloric acid. After addition of the acid, copper metal was removed by filtration, and copper(II) perchlorate was crystallized and recrystallized from water. The copper(II) perchlorate crystals were dissolved in water; the Cu(II) content of the solution was determined by titration of the acid displaced from ion-exchange resin in the $\mathrm{H^+}$ form by aliquots of the solution. Laboratory distilled water was redistilled before use in any solution.

**Rate and Stoichiometry Measurements.** Reactions for stoichiometry measurements were allowed to occur in 160-ml milk dilution bottles, each capped with a rubber disk. All the appropriate reagents except sulfur(IV) were added to the bottle, including enough sodium perchlorate to achieve a final ionic strength of 1.00 *M*. The bottles were purged with nitrogen *via* steel syringe needles and immersed in a 25.0° water bath. After temperature equilibration, aqueous $\mathrm{SO_2}$ was added by syringe. Dithionate analyses were done on the product mixtures using the method described earlier,[14] after hydrogen peroxide oxidation of excess sulfur(IV), iron(II) reduction of excess peroxide, and ion-exchange (1 cm × 5 cm column of Dowex 50W-X8 200–400 mesh resin) removal of metal ions. The uncertainty of the resulting dithionate determination is estimated to be about 10%.

Rate measurements were done at 25.0° and 1.00 *M* ionic strength, using 5- or 10-cm cells and a Beckman ACTA V or Cary Model 17 recording spectrophotometer, with the procedure described before.[14] Monitoring wavelengths were chosen from the interval 320–443 nm, where the species $\mathrm{FeSO_3^+}$ absorbs appreciably.[13] Reaction mixtures containing excess iron(II) and no copper(II) gave initial rate behavior that was anomalous. These mixtures were treated with a small quantity of sulfur(IV) at least 10,000 sec before adding a second quantity of sulfur(IV) and measuring the rate of the subsequent reaction.

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[1] (a) Supported by the Robert A. Welch Foundation. (b) Robert A. Welch Predoctoral Fellow, 1971-1972.

[2] Coordinated water molecules will be omitted from formulas.

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The $H^+$ and $HSO_3^-$ ion concentrations in reaction mixtures were calculated from the amounts of analyzed stock solutions added, using $Q_7 = 0.043\,M$[15] (see eq 7).

$$SO_2(aq) + H_2O = HSO_3^- + H^+ \quad Q_7 \tag{7}$$

The iron(III) and sulfur(IV) reactant concentrations were chosen to provide a significant excess of one reactant in each experiment. In addition, the hydrogen ion concentration was always 0.03 *M* or greater, to allow reasonably accurate calculation of the concentration. The upper limits of hydrogen ion concentrations were chosen to avoid extremely slow reactions and extremely small absorbance changes.

## Results

**Stoichiometry.** The results of our stoichiometry measurements are presented in Table I. The series of experiments with $[Fe(III)]_0 = 1.09 \times 10^{-2}\,M$, with $[H^+] = 0.10\,M$, and with $[S(IV)]_0$ increasing in the range $1.09 \times 10^{-2}$ to $12.3 \times 10^{-2}\,M$ gave an increasing trend in S(V) produced, in agreement with earlier reports;[4,7-9] the effect is not large in that concentration range, however. Also in agreement with earlier reports,[7,8] addition of copper(II) (in experiments at $[Fe(III)]_0 = 1.09 \times 10^{-2}\,M$, $[S(IV)]_0 = 12.3 \times 10^{-2}\,M$, $[H^+] = 0.10\,M$, $[Cu^{2+}] = 0.003$ and $0.01\,M$) did significantly reduce S(V) production.

Attempts to verify the reported[4,7-9] decrease in S(V) production with increasing $[Fe(III)]_0$ were not successful. The seventh and eighth experiments listed in Table I show a slight increase in S(V) product upon doubling $[Fe(III)]_0$, with S(IV) in excess in both experiments. The last four experiments listed in Table I, together with the second experiment listed, each with $[S(IV)]_0 = 1.09 \times 10^{-2}\,M$ and $[H^+] = 0.10\,M$, constitute a series in which $[Fe(III)]_0$ was varied from $0.545 \times 10^{-2}\,M$ (S(IV) in excess) to $2.73 \times 10^{-2}\,M$ (Fe(III) in excess). The results appear scattered just outside the estimated uncertainty of the measurements.

Increasing acidity reduced S(V) production in the first four experiments and also in the series of experiments 13-15 in Table I. Possible effects of low concentrations of $Fe^{2+}$ and $SO_4^{2-}$ were not revealed by the experiments referred to by notes *d* and *e* in Table I.

**Rates of Uncatalyzed Reactions.** The rates of reactions 1 were measured in a series of copper-free solutions containing excess sulfur(IV). The results are given in the first 25 entries of Table II. The $[S(IV)]_0/[Fe(III)]_0$ ratio was greater than 10 in each experiment (except the fifth and sixth experiments listed in the table), and the $[Fe(III)]_0/[Fe(II)]_0$ ratio was greater than 5 in each experiment (greater than 10 in most experiments). For individual experiments, plots of $1/(A - A_\infty)$ *vs.* time were linear, where $A$ is the absorbance at a particular time and $A_\infty$ is the absorbance at completion of the reaction. Thus, the rate of a particular reaction is described by eq 8. It is apparent from the results listed in Table II that

$$-d[Fe(III)]/dt = k'[Fe(III)]^2$$

$k'$ is a function of $[H^+]$, $[Fe^{2+}]$, and $[S(IV)]$. The functionality is approximately that given by

$$k' = \frac{1}{[Fe^{2+}]}\left[\frac{a[HSO_3^-]}{[H^+]^2} + \frac{b[HSO_3^-]^2/[H^+]^2}{c + [SO_2]}\right] \tag{9}$$

where $a = (1.7 \pm 0.2) \times 10^{-6}\,M\,\text{sec}^{-1}$, $b = (5.7 \pm 0.9) \times 10^{-5}\,M\,\text{sec}^{-1}$, and $c = 0.19 \pm 0.04\,M$. These values for the empirical constants were obtained from a least-squares fit[16] of $k'[Fe^{2+}][H^+]/[HSO_3^-]$ to the function of $[HSO_3^-]$ and

**Table I.** Dithionate Production (25.0°, 1.00 *M* Ionic Strength)

| $10^2[Fe(III)]_0$[a] | $10^2[S(IV)]_0 \times 10^2$ | $[H^+]$[b] | $10^2[S(V)]_\infty$[c] | $[S(V)]_\infty/[Fe(III)]_0$ |
|---|---|---|---|---|
| 1.09 | 1.09 | 0.0322 | 0.65 | 0.60 |
| 1.09 | 1.09 | 0.10 | 0.50 | 0.46 |
| 1.09[d] | 1.09 | 0.10 | 0.56 | 0.51 |
| 1.09 | 1.09 | 0.50 | 0.15 | 0.14 |
| 1.09 | 2.46 | 0.10 | 0.73 | 0.67 |
| 1.09 | 4.92 | 0.10 | 0.88 | 0.81 |
| 1.09 | 7.38 | 0.10 | 0.85 | 0.78 |
| 2.18 | 7.38 | 0.10 | 1.9 | 0.87 |
| 1.09 | 12.3 | 0.10 | 0.90 | 0.83 |
| 1.09[e] | 12.3 | 0.10 | 0.92 | 0.85 |
| 1.09[f] | 12.3 | 0.10 | 0.61 | 0.56 |
| 1.09[g] | 12.3 | 0.10 | 0.33 | 0.30 |
| 1.09 | 12.3 | 0.0712 | $1.0_3$ | 0.95 |
| 1.09 | 12.3 | 0.0827 | $1.0_0$ | 0.92 |
| 1.09 | 12.3 | 0.50 | 0.73 | 0.67 |
| 0.545 | 1.09 | 0.10 | 0.35 | 0.65 |
| 1.64 | 1.09 | 0.10 | 0.61 | 0.56[h] |
| 2.18 | 1.09 | 0.10 | 0.48 | 0.44[h] |
| 2.73 | 1.09 | 0.10 | 0.62 | 0.57[h] |

[a] All concentrations units are moles per liter. [b] The concentration of $H^+$ was calculated with the value $Q_7 = 0.043\,M$ as described in the text. [c] [S(V)] is reported as gram-atoms of S(V) per liter rather than gram-ions of $S_2O_6^{2-}$ per liter. [d] Initial $[Fe^{2+}]$ was 0.01 *M*. [e] Initial $[SO_4^{2-}]$ was 0.019 *M*. [f] Initial $[Cu^{2+}]$ was 0.003 *M*. [g] Initial $[Cu^{2+}]$ was 0.01 *M*. [h] Iron(III) was in excess in these reactions; the reported ratio is $[S(V)]_\infty/S(IV)]_0$.

**Table II.** Observed and Calculated Rate Constants, Defined by Eq 8 and 10 (25°, 1.00 *M* Ionic Strength)

| $10^3[S(IV)]_0$[a] | $10^3[Fe(III)]_0$ | $[H^+]$[b] | $10^3 \times [Fe^{2+}]_0$ | $[HSO_3^-]/[H^+]$[b] | $10^3k$[c] Obsd | $10^3k$[c] Calcd[d] |
|---|---|---|---|---|---|---|
| 23.2 | 0.309 | 0.043 | 1.69 | 0.270 | 17 | 19 |
| 46.4 | 0.309 | 0.129 | 1.69 | 0.090 | 2.8 | 1.9 |
| 186 | 0.155 | 0.129 | 1.69 | 0.360 | 18 | 16 |
| 309 | 0.155 | 0.129 | 1.69 | 0.600 | 39 | 33 |
| 2.00 | 0.513 | 0.043 | 3.37 | 0.0232 | 0.31 | 0.31 |
| 4.30 | 0.513 | 0.043 | 3.37 | 0.050 | 0.70 | 0.80 |
| 6.00 | 0.309 | 0.043 | 3.37 | 0.070 | 1.1 | 1.2 |
| 11.6 | 0.309 | 0.043 | 3.37 | 0.135 | 3.2 | 3.1 |
| 20.0 | 0.309 | 0.043 | 3.37 | 0.232 | 7.7 | 7.3 |
| 23.2 | 0.309 | 0.043 | 3.37 | 0.270 | 10 | 9.3 |
| 35.0 | 0.155 | 0.043 | 3.37 | 0.407 | 22 | 18 |
| 46.4 | 0.309 | 0.043 | 3.37 | 0.540 | 26 | 30 |
| 80.0 | 0.052 | 0.044 | 3.37 | 0.920 | 63 | 73 |
| 46.4 | 0.309 | 0.086 | 3.37 | 0.180 | 3.6 | 3.5 |
| 12.0 | 0.513 | 0.129 | 3.37 | 0.0232 | 0.17 | 0.14 |
| 25.8 | 0.513 | 0.129 | 3.37 | 0.050 | 0.40 | 0.40 |
| 46.4 | 0.309 | 0.129 | 3.37 | 0.090 | 1.2 | 0.96 |
| 92.8 | 0.309 | 0.129 | 3.37 | 0.180 | 3.0 | 2.8 |
| 309 | 0.309 | 0.129 | 3.37 | 0.600 | 14 | 17 |
| 23.2 | 0.309 | 0.043 | 6.74 | 0.270 | 4.8 | 4.7 |
| 46.4 | 0.513 | 0.129 | 6.74 | 0.090 | 0.57 | 0.48 |
| 309 | 0.513 | 0.129 | 6.74 | 0.600 | 7.8 | 8.4 |
| 464 | 0.513 | 0.215 | 6.74 | 0.360 | 2.8 | 2.3 |
| 186 | 0.513 | 0.129 | 8.42 | 0.360 | 2.8 | 3.2 |
| 11.6 | 0.309 | 0.030 | 10.1 | 0.229 | 2.4 | 2.8 |
| 0.2 | 4.7[e] | 0.043 | 1.69 |  | 0.22 |  |
| 0.2 | 4.7 | 0.043 | 3.37 |  | 0.45 |  |
| 0.2 | 4.7 | 0.043 | 6.74 |  | 0.22 |  |
| 0.3 | 4.55 | 0.086 | 3.37 |  | 0.44 |  |
| 0.3 | 9.55 | 0.086 | 1.69 |  | 0.15 |  |
| 0.3 | 9.55 | 0.086 | 3.37 |  | 0.15 |  |
| 0.3 | 19.6 | 0.086 | 3.37 |  | 1.4 |  |

[a] All concentration units are moles per liter. [b] Calculations of $[H^+]$ and $[HSO_3^-]$ were done using $Q_7 = 0.043\,M$.[15] [c] The first 25 values are for $k'$, eq 8, and the units are $M^{-1}\,\text{sec}^{-1}$; the last 7 values are for $k''$, eq 10, and the units are $\text{sec}^{-1}$. [d] See text for the bases of the calculations. [e] The value listed for each of the last 7 experiments is the concentration remaining after 50% reaction.

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(15) M. Frydman, G. Nilsson, T. Rengemo, and L. Sillen, *Acta Chem. Scand.*, 12, 878 (1958). These authors reported $Q_7 = 0.043\,m$.

(16) A computer program, based on Report LASL-2367 + Addenda, Los Alamos Scientific Laboratory, Los Alamos, N. M., 1959, was used.

$[SO_2]$ suggested by eq 9, using the weighting factor $(k'[Fe^{2+}] \cdot [H^+]/[HSO_3^-])^{-2}$ for each datum; the indicated uncertainties are the calculated[16] standard deviations. The 25 calculated values listed in Table II were calculated from eq 9, using the values for $a$, $b$, and $c$ listed above. The average deviation between the observed and calculated $k'$ values is 12% of the observed value.

The last seven entries in Table II list the results of a series of experiments done with iron(III) as the reagent in excess. Two features of these measurements caused the results to be of low precision. The first difficulty was with the small total absorbance changes, superimposed on large initial absorbances. The second difficulty was apparently caused by an impurity initially present in the solution; plots of log $(A - A_\infty)$ *vs.* time that were obtained after addition of the first small volume of S(IV) solution had initial curvature toward less negative slopes. The slopes became approximately constant after about $1 \times 10^{-4}$ *M* S(IV) had been consumed. Addition of the second small volume of S(IV) normally[17] led to an approximately linear plot. The measured rate constants were assumed to be defined by eq 10. The factor 0.5 arises from

$$-d[S(IV)]/dt = -0.5d[Fe(III)]/dt = k''[S(IV)] \qquad (10)$$

the assumption that sulfate is the dominant sulfur product in these experiments with excess iron(III) and very low [S(IV)].

The measured values of $k''$ may be compared with those expected from the $k'$ measurements in the following way. At the $[HSO_3^-]/[H^+]$ ratios used in these experiments, the calculated contribution from the second term in eq 9 is negligible. Consideration of only the first term in eq 9, together with eq 8 and 10, yields the relation $k'' = 0.5aQ_7[Fe^{3+}]^2 \cdot [Fe^{2+}]^{-1}[H^+]^{-2}(Q_7 + [H^+])^{-1}$. Use of this equation yields values of $k''$ that are about an order or magnitude smaller than the observed values. The precision of the measured $k''$ values is poor, and we have not attempted to write a rate law more detailed than eq 10 based on those seven numbers. However, the apparent disagreement between the results in excess iron(III) and the results in excess sulfur(IV) is not unreasonable and is discussed later in this paper.

**Rates of Copper(II)-Catalyzed Reactions.** The rate of reaction 1a was measured using a variety of concentration conditions. The results obtained from solutions containing excess sulfur(IV) are given in the first 43 entries in Table III. The value of $k'_{Cu}$ for each experiment was obtained from the linear plot of log $(A - A_\infty)$ *vs.* time, where $k'_{Cu}$ is defined by

$$-d[Fe(III)]/dt = k'_{Cu}[Fe(III)] \qquad (11)$$

The relationship between $k'_{Cu}$ and various concentrations is described by eq 12, where $m = 14.1 \pm 0.8$ sec, $n = 2.16 \pm$

$$k'_{Cu} = \frac{[Cu^{2+}][HSO_3^-]/[H^+]}{m[Fe^{2+}] + n[Cu^{2+}] + p[Cu^{2+}]^2/[H^+]} \qquad (12)$$

0.09 sec, and $p = 0.83 \pm 0.07$ sec. These values for $m$, $n$, and $p$ were obtained from a least-squares fit[16] of $[HSO_3^-]/[H^+]k'_{Cu}$ to the function of $[Fe^{2+}]/[Cu^{2+}]$ and $[Cu^{2+}]/[H^+]$ suggested by eq 12, using the weighting factor $([HSO_3^-]/[H^+]k'_{Cu})^{-2}$ for each experiment. The indicated uncertainties for $m$, $n$, and $p$ are the calculated[16] standard deviations. The first 43 calculated values in Table III were calculated from eq 12, using the values for $m$, $n$, and $p$ shown above. The average deviation between the observed and calculated $k'_{Cu}$ values is 8.5% of the observed value; the deviations do not appear to be systematic

The last nine experiments listed in Table III were done with solutions containing excess iron(III). The precision of the results of this series of experiments is low, owing to difficulties described for the corresponding experiments done with copper-free solutions. The initially larger rate described above was not observed in these measurements, however. The absorbance decreases occurred in these experiments according to a first-order process; the rate constants reported in Table III are defined by eq 13. The assumption that eq

$$-d[S(IV)]/dt = -0.5d[Fe(III)]/dt = k''_{Cu}[S(IV)] \qquad (13)$$

11 and 12 are valid for these experiments leads to eq 14; eq 14 is the basis for the calculated $k''_{Cu}$ values given in Table

$$k''_{Cu} = \frac{0.5[Cu^{2+}][Fe^{3+}][H^+]^{-1}Q_7/(Q_7 + [H^+])}{m[Fe^{2+}] + n[Cu^{2+}] + p[Cu^{2+}]^2/[H^+]} \qquad (14)$$

III, using the $m$, $n$, and $p$ values calculated for the experiments using excess S(IV). For those solutions containing iron(II) initially, the agreement between eq 14 and the observed $k''_{Cu}$ values is remarkably good, considering the long extrapolation in conditions. For solutions not containing iron(II) initially, the agreement is poor; eq 14 predicts that the numerator and denominator $Cu^{2+}$ terms nearly cancel, but the observed $k''_{Cu}$ values are dependent on $[Cu^{2+}]$.

## Discussion

**Mechanisms.** The empirical rate law given by eq 8 and 9 for the uncatalyzed reactions 1 in excess sulfur(IV) is complex, and the agreement with observation is only fair. Owing to these facts we cannot be confident that even 8 and 9 do not represent an oversimplification, even within the concentration ranges studied. However, the features of the empirical rate law indicated by eq 8 and 9 almost certainly do exist and are consistent with mechanism A (reactions 15-20) and with mechanism B (reactions 15, 16, 21-24).[18]

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+ \quad Q_{15} = 1.65 \times 10^{-3}\,M^{19} \qquad (15)$$

$$Fe^{3+} + HSO_3^- = FeSO_3^+ + H^+ \quad Q_{16} \leqslant 0.4^{13,20} \qquad (16)$$

$$FeSO_3^+ = Fe^{2+} + \cdot SO_3^- \quad Q_{17}{}^{21} \qquad (17)$$

$$FeOH^{2+} + \cdot SO_3^- \rightarrow Fe^{2+} + HSO_4^- \qquad (18)$$

$$FeSO_3^{2+} + \cdot SO_3^- + H_2O \rightleftarrows Fe(OH)_2SO_3 + SO_2 \qquad (19)$$

$$Fe(OH)_2SO_3 \rightarrow Fe^{2+} + SO_4^{2-} + H_2O \qquad (20)$$

$$FeSO_3^+ + H_2O = Fe^{2+} + HSO_4^{2-} + H^+ \quad Q_{21}{}^{21} \qquad (21)$$

$$Fe^{3+} + HSO_4^{2-} \rightarrow Fe^{2+} + HSO_4^- \qquad (22)$$

$$FeOH^{2+} + HSO_4^{2-} \rightleftarrows Fe(OH)_2SO_3 \qquad (23)$$

$$Fe(OH)_2SO_3 + SO_2 \rightarrow Fe^{2+} + S_2O_6^{2-} + H_2O \qquad (24)$$

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[17] In two of these experiments the conformity to a first-order rate description became poor at long times. In one experiment not reported here an absorbance increase occurred, rather than the expected decrease. Throughout the work described in this paper, unexpected absorbance increases occasionally occurred; these increases sometimes did and sometimes did not occur again upon repreparation of the solution. We did not try to learn all the reason(s) for the absorbance increases, but we did learn that addition of air is at least one way to cause an increase.

[18] We are grateful to Dr. T. W. Newton for suggesting these mechanisms.

[19] R. M. Milburn, *J. Amer. Chem. Soc.*, **79**, 537 (1957).

[20] Equations 8 and 11 are completely consistent with the proposed mechanism only to the extent that $[Fe^{3+}] = [Fe(III)]$. The effect of equilibrium 16 on this equality is small, but if $Q_{16}$ is near 0.4, the right side of each of these equations should be multiplied by the factor $1/(1 + 0.4[HSO_3^-]/[H^+])$. At $[HSO_3^-]/[H^+] = 1$ and $Q_{16} = 0.4$, this factor is 0.7 and so is significant. Examination of Tables II and III does indeed show $k(\text{obsd})/k(\text{calcd}) < 1$ in most of the experiments at high $[HSO_3^-]/[H^+]$.

[21] Reactions 17 and 21 are assumed to be at equilibrium in the absence of copper(II) but not in the presence of copper(II).

**Table III.** Observed and Calculated Rate Constants, Defined by Eq 11 and 13 (25.0°, 1.00 *M* Ionic Strength)

| $10^3$[S-(IV)]$_0$[a] | $10^3$[Fe-(III)]$_0$ | [$H^+$][b] | $10^3$ × [$Fe^{2+}$]$_0$ | [$HSO_3^-$]/[$H^+$][b] | $10^3$ × [$Cu^{2+}$] | $10^3k_{Cu}$,[c] $sec^{-1}$ | |
|---|---|---|---|---|---|---|---|
| | | | | | | Obsd | Calcd |
| 8.44 | 0.3 | 0.043 | 3.37 | 0.0982 | 4.32 | 8.4 | 7.5 |
| 46.4 | 0.3 | 0.430 | None | 0.00982 | 4.32 | 4.0[d] | 4.5 |
| 46.4 | 0.3 | 0.430 | 3.37 | 0.00982 | 4.32 | 0.60 | 0.75 |
| 8.44 | 0.3 | 0.043 | 3.37 | 0.0982 | 10.8 | 15 | 15 |
| 20.0 | 0.3 | 0.043 | None | 0.233 | 10.8 | 110 | 100 |
| 20.0 | 0.3 | 0.043 | 3.37 | 0.233 | 10.8 | 30 | 34 |
| 46.4 | 0.3 | 0.430 | 3.37 | 0.00982 | 10.8 | 1.9 | 1.5 |
| 0.844 | 0.3 | 0.043 | None | 0.00982 | 21.6 | 4.0[d] | 3.8 |
| 0.844 | 0.5 | 0.043 | 3.37 | 0.00982 | 21.6 | 1.8[d] | 2.1 |
| 0.844 | 0.5 | 0.430 | None | 0.00982 | 21.6 | 3.8[d] | 4.5 |
| 46.4 | 0.3 | 0.430 | 3.37 | 0.00982 | 21.6 | 2.3 | 2.2 |
| 0.844 | 0.5 | 0.043 | 3.37 | 0.00982 | 43.2 | 2.4[d] | 2.4 |
| 8.44 | 0.3 | 0.043 | 1.69 | 0.0982 | 43.2 | 33 | 28 |
| 8.44 | 0.5 | 0.043 | 3.37 | 0.0982 | 43.2 | 26 | 24 |
| 8.44 | 0.5 | 0.043 | 8.42 | 0.0982 | 43.2 | 15 | 17 |
| 17.2 | 0.5 | 0.043 | 3.37 | 0.20 | 43.2 | 45 | 49 |
| 34.4 | 0.5 | 0.043 | 3.37 | 0.40 | 43.2 | 94 | 100 |
| 46.4 | 0.3 | 0.43 | 3.37 | 0.00982 | 43.2 | 3.0 | 2.8 |
| 20.0 | 0.3 | 0.043 | 3.37 | 0.233 | 54.0 | 58 | 57 |
| 46.4 | 0.3 | 0.43 | None | 0.00982 | 63.6 | 4.3 | 4.3 |
| 30.6 | 0.3 | 0.030 | None | 0.60 | 108 | 120 | 120 |
| 30.6 | 0.5 | 0.030 | 3.37 | 0.60 | 108 | 100 | 110 |
| 0.844 | 0.5 | 0.043 | None | 0.00982 | 108 | 2.2[d] | 2.3 |
| 0.844 | 0.5 | 0.043 | 3.37 | 0.00982 | 108 | 1.6[d] | 2.1 |
| 3.44 | 0.5 | 0.043 | 3.37 | 0.0400 | 108 | 7.3 | 8.5 |
| 8.44 | 0.3 | 0.043 | 1.69 | 0.0982 | 108 | 25 | 22 |
| 8.44 | 0.5 | 0.043 | 3.37 | 0.0982 | 108 | 20 | 21 |
| 8.44 | 0.5 | 0.043 | 8.42 | 0.0982 | 108 | 16 | 18 |
| 17.2 | 0.3 | 0.043 | None | 0.20 | 108 | 54 | 47 |
| 34.4 | 0.3 | 0.043 | None | 0.40 | 108 | 110 | 94 |
| 34.4 | 0.5 | 0.043 | 3.37 | 0.40 | 108 | 86 | 85 |
| 2.54 | 0.5 | 0.086 | 3.37 | 0.00982 | 108 | 2.6 | 2.7 |
| 25.4 | 0.3 | 0.086 | None | 0.0982 | 108 | 31 | 31 |
| 25.4 | 0.5 | 0.086 | 3.37 | 0.0982 | 108 | 26 | 27 |
| 51.6 | 0.5 | 0.086 | 3.37 | 0.20 | 108 | 55 | 55 |
| 108 | 0.5 | 0.086 | 3.37 | 0.40 | 108 | 96 | 110 |
| 12.7 | 0.3 | 0.215 | 3.37 | 0.00982 | 108 | 3.3 | 3.3 |
| 46.4 | 0.3 | 0.430 | None | 0.00982 | 108 | 4.5 | 4.2 |
| 46.4 | 0.3 | 0.430 | 1.69 | 0.00982 | 108 | 4.0 | 3.8 |
| 46.4 | 0.3 | 0.430 | 3.37 | 0.00982 | 108 | 3.4 | 3.5 |
| 46.4 | 0.3 | 0.430 | 8.42 | 0.00982 | 108 | 2.7 | 2.8 |
| 46.4 | 0.3 | 0.430 | None | 0.00982 | 216 | 3.8 | 3.8 |
| 46.4 | 0.3 | 0.430 | 3.37 | 0.00982 | 216 | 3.2 | 3.5 |
| 0.2 | 4.8 | 0.043 | None | 0.002 | 4.32 | 6.55 | 12 |
| 0.2 | 4.8 | 0.043 | 3.37 | 0.002 | 4.32 | 2.18 | 2.1 |
| 0.2 | 4.8 | 0.043 | None | 0.002 | 8.64 | 8.37 | 12 |
| 0.2 | 4.8 | 0.043 | None | 0.002 | 13.0 | 14.4 | 12 |
| 0.2 | 4.8 | 0.043 | 1.69 | 0.002 | 43.2 | 8.25 | 7.9 |
| 0.2 | 4.8 | 0.043 | 6.74 | 0.002 | 43.2 | 4.55 | 5.4 |
| 0.3 | 9.7 | 0.086 | 3.37 | 0.001 | 43.2 | 1.18 | 5.1 |
| 0.3 | 19.7 | 0.086 | 3.37 | 0.001 | 43.2 | 6.79 | 10.4 |
| 0.2 | 4.8 | 0.043 | 3.37 | 0.002 | 108 | 5.01 | 6.0 |

[a] All concentration units are moles per liter. [b] Calculation of [$H^+$] and [$HSO_3^-$] was done using $Q_7$ = 0.043 *M*.[15] [c] The first 43 rate constants are $k'_{Cu}$, defined by eq 11; the last 9 rate constants are $k''_{Cu}$, defined by eq 13. [d] Rate constants were evaluated from the initial porton of the reaction.

Mechanism A can be excluded, along with any variations of mechanism A that involve two separate sulfur products as in step 19. These mechanisms predict formation of sulfate as the only sulfur product, not in accord with observation. Mechanism B is in accord with both the stoichiometric and kinetic observations and so remains as a credible mechanism. If mechanism B is correct, then $a/2$ (in eq 9) represents $k_{22}Q_{16}Q_{21}$, $b/2$ represents $k_{23}Q_{15}Q_{16}Q_{21}/Q_7$, and $c$ represents $k_{23}/k_{24}$.

It has been observed[3-12,14,22-24] that inert oxidants usually oxidize sulfur(IV) primarily or solely to sulfate and that labile oxidants usually produce an appreciable quantity of dithionate. Two proposals have been made to account for these observations. The proposals, well summarized in ref 12, focus on the properties of proposed intermediates consisting of reduced metal ion–sulfur(V) complexes. Mechanism B suggests another possibility, involving an intermediate consisting of an unreduced oxidant–sulfur(V) complex that leads to dithionate; this complex would not form if the oxidant were substitutionally inert. Still another possible mechanism for formation of dithionate is suggested by eq 19; dithionate formation could occur from an unreduced oxidant–sulfur(IV) complex reacting with intermediate sulfur(V). The observed rate law is not in accord with the idea that dithionate is primarily formed in this system as a product of reaction 19, but a similar pathway might be important in some other systems.

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The rate law given by eq 11 and 12, for reactions in the presence of copper(II) and excess sulfur(IV), is complicated. A part of the rate law is easily accounted for in terms of a reasonable mechanism, but the denominator term showing a $[Cu^{2+}]^2$ dependence in eq 12 is puzzling. This term definitely improves the fit between $k'_{Cu}$(calcd) and $k'_{Cu}$(obsd) at high $[Cu^{2+}]$, but we will neglect it in the following discussion. We suspect that the term is as likely to arise from changes in the reaction medium as from a mechanistic pathway; it is reasonable to expect that replacement of up to 0.6 $M$ $NaClO_4$ with up to 0.2 $M$ $Cu(ClO_4)_2$ can change activity coefficients considerably.

If the final denominator term in eq 12 is neglected, then the form of eq 12 is consistent with a mechanism A′, consisting of reactions 16, 17, 5, and 6, with reaction 17 no longer at equilibrium. The analogous mechanism B′ is also consistent with the form of eq 12. This mechanism consists of reactions 16 and 21, reaction 5 modified by addition of a reactant $H^+$, and reaction 6, with reaction 21 not at equilibrium. Because of the probable relationship between the catalyzed and uncatalyzed mechanisms ($Cu^{2+}$ and $HSO_3^-$ do not react in iron-free acidic perchlorate solutions) we think the stoichiometric evidence against mechanism A is evidence against A′ as well. The following discussion is based on the assumption that mechanisms B and B′ indeed describe the systems.

Mechanism B indicates inner-sphere complexation between iron(III) and sulfur(IV) before electron transfer. This complexation is not proven by the rate law, but we think it is probable because other oxidations by iron(III) typically occur by inner-sphere mechanisms,[25] as do reductions by sulfur(IV).[26] Metal ions that are reduced by sulfur(IV) by inner-sphere mechanisms include $HCrO_4^-$,[27] *trans*-$Co(en)_2SO_3OH_2^+$,[28] and $Fe(CN)_5(CNSO_3)^{5-}$.[29] It is also indicated in mechanism B that the sulfur(V) intermediate is hydrolyzed. Previous reports[30-32] of sulfur(V) radicals do not provide evidence that requires this proposal, but neither do they appear to provide evidence that conflicts with it. The rate of reaction 3 is not dependent on pH in the range 4-10,[30] a reasonable result if $\cdot SO_3^-$ is already hydrolyzed at pH 2.

**Derived Rate Constants.** If mechanism B′ is correct for the copper-catalyzed reaction, then $2m$ (in eq 12) $= k_{-21}/k_{21}k_5Q_{16}$ and $2n = 1/k_{21}Q_{16}$. If both mechanisms B and B′ are assumed, then various ratios of rate constants can be determined. The ratio $k_{-23}/k_{24} = c = 0.19$ is determined directly. The ratios $Q_{15}a/Q_7b = k_{22}/k_{23} = 1.1 \times 10^{-3}$, $n/m = k_5/k_{-21} = 0.15$, $na = k_{22}/k_{-21} = 3.7 \times 10^{-6}$, $(k_{23}/k_{22})(k_{22}/k_{-21}) = k_{23}/k_{-21} = 3.2 \times 10^{-3}$, $(k_{23}/k_{22})(k_5/k_{23}) = k_5/k_{22} = 4.2 \times 10^4$, and $(k_5/k_{-21})(k_{-21}/k_{23}) = k_5/k_{23} = 48$ can also be calculated from the relations between the empirical rate constants and the mechanisms. A lower limit for $k_{21}$ can be calculated from $n = 2.16 = 1/2k_{21}Q_{16}$ and from the upper limit $Q_{16} \leqslant 0.4$; $k_{21} \geqslant 0.58\ sec^{-1}$.

**Table IV.** Parameters Derived from the Empirical Rate Laws Assuming Mechanism B[a]

| | | | | | |
|---|---|---|---|---|---|
| $k_5$ | $2 \times 10^{12}$ | $k_{22}$ | $4 \times 10^7$ | $Q_{15}$ | $1.65 \times 10^{-3}$ [19] |
| $k_{21}$ | $\geqslant 0.58$ | $k_{23}$ | $3 \times 10^{10}$ | $Q_{16}$ | $\leqslant 0.4$[13] |
| $k_{-21}$ | $1 \times 10^{13}$ | $k_{-23}/k_{24}$ | 0.19 | $Q_{21}$ | $\geqslant 5 \times 10^{-14}$ |

[a] Units are molarity and seconds.

A value for $Q_{21}$ can be estimated from the value $\Delta G_R \approx$ 10 kcal/mol for formation of the sulfur(V) radical from $Fe^{3+}$ and $SO_3^{2-}$.[12] If the estimate is assumed to be valid for the reaction $Fe^{3+} + H_2O + SO_3^{2-} = Fe^{2+} + HSO_4^{2-} + H^+$, then $K_RQ_A = Q_{21}Q_{16}$, where $Q_A = [SO_3^{2-}][H^+]/[HSO_3^-] = 4.6 \times 10^{-7}$ $m$ in 1.00 $m$ $NaClO_4$.[15] If $Q_{16} \leqslant 0.4$, this relationship yields $Q_{21} \geqslant 5 \times 10^{-14}$ $M^2$, and thus, if $k_{21} \geqslant 0.58\ sec^{-1}$, $k_{-21}$ is estimated to be about $1 \times 10^{13}\ M^{-2}\ sec^{-1}$. Values for three additional rate constants can be calculated from this estimate for $k_{-21}$ and from the ratios given in the previous paragraph. The calculated values are $k_5 \cong 2 \times 10^{12}\ M^{-2}\ sec^{-1}$, $k_{22} \cong 4 \times 10^7\ M^{-1}\ sec^{-1}$, and $k_{23} \cong 3 \times 10^{10}\ M^{-1}\ sec^{-1}$, near the diffusion limit. The calculated[12] value for $\Delta G_R$ was based on the assumption that $\cdot SO_3$ is the intermediate sulfur(V) species. The hydrolyzed species may be more stable, yielding a smaller value for $\Delta G_R$ and smaller values for the rate constants. Nevertheless, a large magnitude for $k_{23}$ is probably not surprising; previously measured rates of reaction of sulfur(V) radicals are large. The second-order rate constants have been measured for sulfur(V) reaction with sulfur(V),[30] $O_2$,[30] $HO_2^-$,[31] and $O_2^-$,[31] and each is greater than $10^8\ M^{-1}\ sec^{-1}$.

The quantities derived above, based on the assumption of mechanism B, are presented in Table IV. An alternate form of mechanism B, using $FeOH^{2+}$ and $Fe(OH)_2^+$ in eq 22 and 23 (instead of $Fe^{3+}$, $FeOH^{2+}$, and hydrolyzed $\cdot SO_3^-$), is in accord with the form of the empirical rate law but is not satisfactory. The concentrations of $Fe(OH)_2^+$ are so small under the conditions of our study that $k_{23}$ in the alternate mechanism would have to be far greater than the diffusion-controlled limit in order to permit the observed values of the empirical rate constants.

**Excess Iron(III).** The rate constants measured for reaction mixtures containing excess iron(III) in the absence of copper(II) do not appear inconsistent with those reported by Karraker;[9] Karraker's experiments were done using much greater $H^+$ and Fe(III) concentrations than were used in the experiments reported here. Our data, and those of Karraker, indicate that the order with respect to $Fe^{2+}$ is less negative than −1 when Fe(III) is the reagent in excess. This observation is not in accord with mechanism B, because reaction 21 would remain at equilibrium under the conditions of our experiments, with $k_{22}/k_{-21} = 3.7 \times 10^{-6}$ and $k_{23}/k_{-21} = 3.2 \times 10^{-3}$. Moreover, the observation that eq 8-10 account for only about 10% of the rate in these experiments suggests that a pathway exists in excess iron(III) that is not included in mechanism B. A reaction between $Fe^{3+}$ and $FeSO_3^+$ is a reasonable suggestion for this pathway, although our data are not precise enough to test that suggestion. This reaction would compete more effectively with the $k_{-21}$ step in the presence of excess iron(III) and would also account for both the increased rate and the increased fraction of sulfate product formed in the presence of excess iron(III). Similarly, the effect of equilibrium 15 on reaction 23 can account for the increased fraction of sulfate product formed at high $[H^+]$.

The agreement between $k''_{Cu}$ values calculated from eq 14 (using data obtained from experiments with excess sulfur(IV)) and the $k''_{Cu}$ values observed in experiments with excess

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