

Contribution from the Department of Chemistry,
Texas Tech University, Lubbock, Texas 79409**Reduction of Hexachloroiridate(IV) Ion by Sulfur(IV) in Acidic Aqueous Solution^{1a,b}**ELDON L. STAPP^{1c} and DAVID W. CARLYLE*

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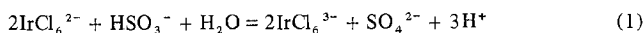
A stoichiometric and kinetic study of the reduction of IrCl_6^{2-} by HSO_3^- has been done. The reactions were observed in acetate buffer solutions at 25°. The products are IrCl_6^{3-} , SO_4^{2-} , and $\text{S}_2\text{O}_5^{2-}$. The observed rate law is $-d \ln [\text{IrCl}_6^{2-}]/dt = 0.024[\text{HSO}_3^-]/[\text{H}^+]$. A mechanism consistent with the data is proposed. The proposal is a one-electron transfer between IrCl_6^{2-} and SO_3^{2-} , followed by rapid reaction of intermediate S(V) with IrCl_6^{2-} to give SO_4^{2-} or by competing rapid dimerization of S(V) to give $\text{S}_2\text{O}_5^{2-}$.

Introduction

Sulfur(IV) is known to reduce metal ions by a variety of mechanisms and with variable stoichiometry.² Recent representative reports have suggested that electron transfer may occur within inner-sphere sulfite complexes (*trans*-Co(en)₂SO₃OH₂⁺ and CrO₂(SO₃)₂²⁻) or may occur by outer-sphere mechanisms (IrCl_6^{4-} ,⁵ Fe(1,10-phen)₃³⁺,⁶ and many others⁷). Still another report⁸ has described a mechanism involving electron transfer in the inner-sphere bridged ion Fe(CN)₅CNSO₃⁵⁻; electron transfer is believed to occur simultaneously to the iron in the bridged species and to the iron in a Fe(CN)₆³⁻ ion.⁸

We have been interested in the role of complexes formed between sulfur(IV) and oxidant metal ion,^{6,9,10} one of the objectives of this study was to characterize a system in which the complexation appeared unlikely. The second objective was to test the possible reactivity of $\text{S}_2\text{O}_5^{2-}$. The question of the reactivity of $\text{S}_2\text{O}_5^{2-}$ was raised in a recent study⁶ of the reduction of Fe(1,10-phen)₃³⁺ (or just FeL₃³⁺) by sulfur(IV). A rate law term second order in HSO_3^- was observed in the FeL₃³⁺ study; it was suggested⁶ that the term may arise from reduction of Fe(III) by $\text{S}_2\text{O}_5^{2-}$ or by reduction of a Fe^{III}-S^{IV} complex by S(IV).

The anionic, substitution-inert¹¹ IrCl_6^{2-} ion was chosen as a suitable oxidant because it appeared unlikely to engage in appreciable inner- or outer-sphere complexation with sulfur(IV). Thus, we anticipated that oxidation of sulfur(IV) by IrCl_6^{2-} would occur by an outer-sphere mechanism and that the presence or absence of a rate law term second order in HSO_3^- would be evidence for or against the reactivity of $\text{S}_2\text{O}_5^{2-}$. The net reactions that we have investigated are described by eq 1 and 2.



(1) Supported by the Robert A. Welch Foundation. (b) Based on the Masters thesis of E. L. S., Texas Tech University, Lubbock, Tex. (c) Robert A. Welch Fellow, 1972-1973.

(2) H. Russell, Jr., and D. M. Yost, "Systematic Inorganic Chemistry," Prentice-Hall, New York, N. Y., 1944, pp 358, 359.

(3) R. S. Murray and D. R. Stranks, *Inorg. Chem.*, **9**, 1472 (1970).

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

(5) A. Brown and W. C. E. Higginson, *Chem. Commun.*, 725 (1967).

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

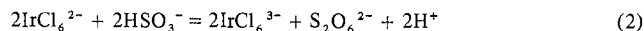
(7) J. Veprek-Siska, D. M. Wagnerova, and K. Eckschlager, *Collect. Czech. Chem. Commun.*, **31**, 1248 (1966).

(8) J. M. Lancaster and R. S. Murray, *J. Chem. Soc. A*, 2755 (1971).

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

(10) O. F. Zeck, Jr., and D. W. Carlyle, *Inorg. Chem.*, **13**, 34 (1974).

(11) C. S. Garner and I. A. Poulsen, *J. Amer. Chem. Soc.*, **84**, 2032 (1962).

**Experimental Section**

Reagents. Reagent grade Na₂IrCl₆ was used without further purification. A visible spectrum of an aqueous solution of IrCl_6^{2-} had a maximum at 488 nm with a molar absorptivity coefficient of 4050, in agreement with the results of Poulsen and Garner.¹¹ A fresh IrCl_6^{2-} solution was used for each experiment, although acidic solutions were spectrophotometrically shown to be stable for at least 7 days. Sodium hexachloroiridate(III) was made by reduction of Na₂IrCl₆ as described earlier.¹¹ The dried Na₃IrCl₆·2H₂O was stored in a desiccator. Just before each use, the solid salt was dissolved and analyzed spectrophotometrically.¹¹ Since dissolved oxygen interferes with the IrCl_6^{3-} spectrum,¹¹ the spectrophotometer cell was purged with nitrogen before the analysis. The concentration of iridium(III) was calculated from Beer's law using the literature value¹² of the molar absorptivity at 418 nm. Because IrCl_6^{3-} slowly hydrolyzes in water, the unused solutions were frozen at -10° and concentrations were checked before new experiments were done.

The preparations and analyses have been described previously for solutions of sodium chloride,¹⁰ copper(II) chloride,¹⁰ copper(I) chloride,¹⁰ iron(II) perchlorate,¹³ and aqueous SO₂.^{6,13} Sodium acetate was recrystallized from ethanol; aqueous solutions of sodium acetate were analyzed by titration of the acid displaced when aliquots were passed through Dowex 50W-X8 cation-exchange resin in the H⁺ form. Hydrochloric acid solutions were prepared by dilution of concentrated reagent grade acid; they were analyzed by titration with sodium hydroxide.

Doubly distilled water was used in all solutions. Nitrogen gas was treated as previously described.⁶

Rate Measurements. The slower reactions were allowed to occur in nitrogen-purged spectrophotometer cells in a recording spectrophotometer. The procedures were as described earlier,⁶ with monitoring wavelengths ranging from 488 to 525 nm. Most of the reactions were observed in a nitrogen-purged stopped-flow apparatus by methods that have also been described.^{6,13} The monitoring wavelength for the stopped-flow experiments was 488 nm.

The hydrogen ion concentration of each reaction mixture was calculated from the formal concentrations of aqueous sulfur dioxide, hydrochloric acid, and sodium acetate. The calculations were based on the values $Q_a = [\text{C}_2\text{H}_3\text{O}_2^-][\text{H}^+]/[\text{C}_2\text{H}_3\text{O}_2] = 3.09 \times 10^{-5} M^{14}$ and $Q_b = [\text{HSO}_3^-][\text{H}^+]/[\text{SO}_2] = 0.043 m^{15}$. The formal concentration of sodium acetate was fixed at 0.03 M in most of the experiments. The ionic strength of each solution was adjusted to 0.200 M with sodium chloride, and each reaction was thermostated at 25.0°.

Some reaction mixtures initially containing CuCl₂ or IrCl_6^{3-} were prepared for stopped-flow measurements. Each of these reagents was added to the IrCl_6^{2-} solution for mixing with the HSO_3^- solution.

Stoichiometry. Measurements of the reacting IrCl_6^{2-} :S(IV) ratios were made at 25.0° and 0.2 M ionic strength in the presence of 0.06 M acetate and in the absence of oxygen. The hydrogen ion concentrations were calculated as described above.

(12) J. C. Chang and C. S. Garner, *Inorg. Chem.*, **4**, 209 (1965).

(13) D. W. Carlyle, *Inorg. Chem.*, **10**, 761 (1971).

(14) This is the Q_a value in 0.200 M NaCl obtained by interpolation of data in H. S. Harned and F. C. Hickey, *J. Amer. Chem. Soc.*, **59**, 1284 (1937).

(15) M. Frydman, G. Nilsson, T. Rengemo, and L. Sillen, *Acta Chem. Scand.*, **12**, 878 (1958). This Q_b value was measured in 1.00 M perchlorate solution, but any error in the value of Q_b has little effect on the calculated $[\text{H}^+]$ since SO₂ was not a major species in our reaction mixtures.

Reaction mixtures with excess IrCl_6^{2-} were prepared with known initial concentrations of both reactants. The initial concentrations of IrCl_6^{2-} were obtained from spectrophotometric titrations with Fe^{2+} . These titrations were conducted in oxygen-free 10-cm spectrophotometer cells by making successive small additions of standardized iron(II) solutions. After completion of each reaction, the remaining IrCl_6^{2-} concentration was determined by spectrophotometric titration and $\Delta[\text{IrCl}_6^{2-}]/\Delta[\text{S(IV)}]$ was calculated. Reaction mixtures with excess sulfur(IV) were also prepared with known initial concentrations of both reactants. After completion of each reaction, an aliquot was withdrawn for sulfur(IV) analysis and $\Delta[\text{IrCl}_6^{2-}]/\Delta[\text{S(IV)}]$ was calculated.

Results

Stoichiometry. The results of our stoichiometric measurements, together with those obtained by Higginson and Brown,¹⁶ are shown in Table I. The values listed in the table do not appear to show systematic variations as $[\text{H}^+]$ is varied or as excess reagent is varied. Our values for $\Delta[\text{IrCl}_6^{2-}]/\Delta[\text{S(IV)}]$ are consistently lower than those reported earlier,¹⁶ and our estimate 1.6, obtained by comparing rate constants as described below, is between the earlier average of 1.84 and our average of 1.39 (with average deviation 0.10). Although the various measurements are not in quantitative agreement, they do provide qualitative evidence that net reactions 1 and 2 occur at comparable rates.

Rate Measurements. A series of experiments was done with excess sulfur(IV) and with $[\text{IrCl}_6^{2-}]_0 = 1.3 \times 10^{-4} M$. In each of these experiments the disappearance of IrCl_6^{2-} obeyed the first-order rate law indicated by eq I. The results

$$-\text{d} \ln [\text{IrCl}_6^{2-}]/\text{d}t = k' \quad (\text{I})$$

of the individual k' measurements are shown in Table II. The measured k' values listed in the table indicate that k' has a positive dependence on $[\text{HSO}_3^-]$ and an inverse dependence on $[\text{H}^+]$. A least-squares fit¹⁷ of the data at $0.71 \times 10^{-5} \leq [\text{H}^+] \leq 75 \times 10^{-5} M$ and $0.50 \times 10^{-3} \leq [\text{HSO}_3^-] \leq 6.4 \times 10^{-3} M$ to eq II gave a satisfactory result, with $k = 0.0241 \pm$

$$k' = k [\text{HSO}_3^-]/[\text{H}^+] \quad (\text{II})$$

0.0008 sec^{-1} , where 0.0008 is the calculated¹⁷ standard deviation. This value of k was used with eq II to obtain the k'_{calcd} values shown in Table II. We conclude that eq I and II describe the rates under the concentration conditions listed above. However, one experiment at $0.02 M \text{H}^+$, not listed in Table II, gave a rate constant greater than 6 times that calculated by eq II. In addition, each of the four experiments (two of them done in duplicate) listed in the table at $[\text{HSO}_3^-] \geq 11 \times 10^{-3} M$ gave k_{obsd} greater than k' calculated by eq II.

It does not appear that the high k_{obsd} values at high $[\text{HSO}_3^-]$ provide evidence for a pathway second order in $[\text{HSO}_3^-]$. The percentage deviation is not greater at $[\text{HSO}_3^-] = 24 \times 10^{-3} M$ than at $[\text{HSO}_3^-] = 11 \times 10^{-3} M$. An experimental error could not be found to account for the deviations. The duplications of the experiments at $[\text{HSO}_3^-] = 11 \times 10^{-3}$ and $24 \times 10^{-3} M$ were done several months later than the original experiments and gave results in good agreement with the originals. An experiment at $[\text{HSO}_3^-] = 6.00 \times 10^{-3} M$ was done along with the duplicates described above and gave a result in good agreement with eq II. Experiments at $[\text{HSO}_3^-] > 24 \times 10^{-3} M$ were not done. Experiments at high $[\text{HSO}_3^-]$ and low $[\text{H}^+]$ were too fast to yield precise k'_{obsd} values, and $[\text{H}^+]$

Table I. Results of Stoichiometric Measurements at 25° and 0.200 *M* Ionic Strength

| $10^3 \times$ $[\text{IrCl}_6^{2-}]_0,$ <i>M</i> | $10^3 \times$ $[\text{S(IV)}]_0,$ <i>M</i> | $-\log$ $[\text{H}^+]$ | $\Delta[\text{IrCl}_6^{2-}]/$ $\Delta[\text{S(IV)}]$ |
|--|--|---------------------------|---|
| 7.20 | 50.0 | 3.8 | 1.4 |
| 7.20 | 50.0 | 3.7 | 1.2 |
| 12.7 | 50.0 | 3.7 | 1.5 |
| 12.9 | 3.00 | 4.7 | 1.5 |
| 20.0 | 3.00 | 4.7 | 1.2 |
| 20.0 | 3.00 | 3.7 | 1.5 |
| 20.0 | 9.00 | 4.7 | 1.4 |
| 20.0 | 9.00 | 4.0 | 1.3, 1.5, 1.5 ^a |
| 22 | 22 | 6.5 | 1.81 ± 0.03^b |
| 22 | 22 | 4.4 | 1.87 ± 0.03^b |
| | | | 1.6 ± 0.5^c |

^a Three experiments. ^b Reported in ref 16. ^c Estimated from kinetic measurements, as described below.

would not be precisely known in experiments at high $[\text{H}^+]$ or high $([\text{HSO}_3^-] + [\text{H}^+])$.

The values of k'_{obsd} were not sensitive to the variations in conditions that we tested, as shown by Table II. The 10th and 20th experiments listed in the table were done at ionic strength 0.10, the 17th and 34th experiments were done at $[\text{NaC}_2\text{H}_3\text{O}_2] \neq 0.03 F$, and the 42nd experiment was done in the presence of a small concentration of dissolved oxygen, all without dramatic effect on k'_{obsd} , although dissolved oxygen did appear to slow the reaction by a factor of about 2.

Sixteen additional experiments, not listed in Table II, were done to look for possible retardation by IrCl_6^{3-} . Appreciable retardation was not found in these experiments at $[\text{IrCl}_6^{2-}]_0 = 8.9 \times 10^{-5} M$, $[\text{H}^+] = 7.3 \times 10^{-5}$ or $11.8 \times 10^{-5} M$, $[\text{NaC}_2\text{H}_3\text{O}_2] = 0.03 F$, $[\text{HSO}_3^-] = 0.0105$ or $0.024 M$, and $5 \times 10^{-5} \leq [\text{IrCl}_6^{3-}]_0 \leq 8 \times 10^{-3} M$.

Some experiments were done to measure the rate of reactions 1 and 2 in solutions containing excess IrCl_6^{2-} . The results obtained are less precise than those obtained with excess HSO_3^- because only small changes in large initial absorbances were observed (typically about 10% of 2). The results of these pseudo-first-order reactions are listed in Table III; the k''_{obsd} values are the observed rate constants and the k'_{calcd} values are calculated from eq II.

If eq II is valid in excess IrCl_6^{2-} , then the ratio k'/k'' is identical with the $\Delta[\text{IrCl}_6^{2-}]/\Delta[\text{S(IV)}]$ ratio. The parameter k' is defined by eq I, but k'' is defined as $-\text{d} \ln [\text{S(IV)}]/\text{d}t = k''$. Since $\text{d} \ln [\text{Ir(IV)}]/\text{d} \ln [\text{S(IV)}]$ is the stoichiometric ratio, it can be seen that the equivalent quotient k'/k'' is also the stoichiometric ratio. The average value 1.6 ± 0.5 appears reasonable and appears consistent with the assumption that eq I and II are valid under the conditions listed in Table III.

Copper(II) Effects. A few attempts were made to measure copper(II) catalysis of reactions 1 and 2. These attempts were not successful, because catalysis was slight and also because of apparent competition from the direct reaction between copper(II) and sulfur(IV). At $[\text{H}^+] = 1.2 \times 10^{-4} M$, $[\text{HSO}_3^-] = 6.0 \times 10^{-3} M$, $[\text{IrCl}_6^{2-}]_0 = 4 \times 10^{-4} M$, and $[\text{Cu(II)}]_0 = (3.5-21) \times 10^{-3} M$, the disappearance of IrCl_6^{2-} occurred by a process less than first order in IrCl_6^{2-} ; the order became closer to zero as $[\text{Cu(II)}]_0$ was increased. These observations are consistent with reduction of Cu(II) and Ir(IV) at similar rates, followed by regeneration of copper(II) in a fast $\text{Ir(IV)}-\text{Cu(I)}$ reaction. We did not test these ideas, except to verify that Cu(I)^{18} is oxidized rapidly by IrCl_6^{2-}

(16) A. Brown and W. C. E. Higginson, *J. Chem. Soc., Dalton Trans.*, 166 (1972).

(17) The calculation was done by computer, using a program based on Report LASL-2367 + Addenda, Los Alamos Scientific Laboratory, Los Alamos, N. M., 1959.

(18) The principal Cu(I) species in these aqueous chloride solutions are CuCl_2^- and CuCl_3^{2-} : P. J. Durrant and B. Durrant, "Introduction to Advanced Inorganic Chemistry," Wiley, New York, N. Y., 1970, p 1112.

Table II. Observed and Calculated Rate Constants for the Iridium(IV)-Sulfur(IV) Reaction at $1.3 \times 10^{-4} M$ IrCl_6^{2-} , 25.0°, and 0.200 *M* Ionic Strength^h

| $10^5[\text{H}^+], M$ | $10^3[\text{HSO}_3^-], M$ | $k'_{\text{obsd}}, \text{sec}^{-1}$ | $k'_{\text{calcd}}, \text{sec}^{-1}$ | $10^5[\text{H}^+], M$ | $10^3[\text{HSO}_3^-], M$ | $k'_{\text{obsd}}, \text{sec}^{-1}$ | $k'_{\text{calcd}}, \text{sec}^{-1}$ |
|-----------------------|---------------------------|-------------------------------------|--------------------------------------|-----------------------|---------------------------|-------------------------------------|--------------------------------------|
| 0.706 | 4.50 | 17.1 | 15.4 | 7.30 | 6.00 | 2.3 | 2.0 |
| 0.773 | 6.00 | 17.5 | 18.7 | 8.40 | 6.00 | 2.0 | 1.7 |
| 0.955 | 7.10 | 19.7 | 17.9 | 8.99 | 2.00 | 0.57 | 0.54 |
| 1.27 | 6.00 | 12.4 | 11.4 | 10.0 | 11.0 | 3.9 ^e | 2.7 ^c |
| 1.53 | 6.00 | 11.2 | 9.5 | 10.0 | 1.00 | 0.22 | 0.24 |
| 1.57 | 3.00 | 5.1 | 4.6 | 10.4 | 4.00 | 0.96 ^a | 0.93 |
| 1.64 | 6.00 | 10.1 ^a | 8.8 | 11.8 | 0.50 | 0.11 | 0.10 |
| 1.64 | 6.40 | 9.4 | 9.4 | 11.8 | 6.00 | 1.5 ^a | 1.2 |
| 1.80 | 4.50 | 6.6 | 6.0 | 11.9 | 1.00 | 0.19 | 0.20 |
| 2.20 | 0.50 | 0.65 ^b | 0.55 ^c | 11.9 | 2.00 | 0.43 | 0.41 |
| 2.47 | 1.25 | 1.5 | 1.2 | 11.9 | 6.00 | 1.55 ^a | 1.2 |
| 3.04 | 4.50 | 3.6 | 3.6 | 11.9 | 24.0 | 7.0 ^{a,e} | 4.9 ^c |
| 3.09 | 1.00 | 0.90 | 0.78 | 12.2 | 6.00 | 1.1 ^f | 1.2 ^c |
| 3.11 | 0.50 | 0.40 | 0.39 | 12.6 | 3.00 | 0.60 | 0.57 |
| 3.53 | 2.00 | 1.3 | 1.4 | 13.3 | 11.0 | 3.1 ^{a,e} | 2.0 ^c |
| 3.54 | 1.00 | 0.67 | 0.68 | 14.6 | 1.00 | 0.15 | 0.16 |
| 4.60 | 6.00 | 3.5 ^d | 3.1 | 14.6 | 2.00 | 0.38 | 0.33 |
| 4.88 | 6.00 | 3.2 | 3.0 | 30.6 | 5.96 | 0.48 | 0.47 |
| 6.00 | 4.50 | 1.9 | 1.8 | | | | |
| 6.30 | 9.80 | 2.6 ^b | 3.7 ^c | 74.7 | 0.99 | 0.035 | 0.032 |
| 7.20 | 21.1 | 9.6 ^e | 7.1 ^c | 74.7 | 0.99 | 0.017 ^g | 0.032 ^c |

^a Average of two experiments. ^b Ionic strength 0.1. ^c Calculated from eq II. ^d $[\text{NaC}_2\text{H}_3\text{O}_2] = 0.015 F$. ^e Not included in the least-squares calculation. ^f $[\text{NaC}_2\text{H}_3\text{O}_2] = 0.06 F$. ^g Atmospheric oxygen not removed from solution. ^h Experiments designated by notes *b*, *d*, *f*, and *g* were not included in the least-squares calculation.

under the conditions of our experiments. Assuming the IrCl_6^{2-} -Cu(I) reaction is first order in each reactant, we determined a lower limit of $1 \times 10^6 M^{-1} \text{sec}^{-1}$ at $[\text{H}^+] = 1.2 \times 10^{-4} M$.

Search for Radical Intermediates. Acrylic acid was polymerized in the presence of reacting Ir(IV)-S(IV) systems but was not polymerized in the presence of either of the reactants alone. A brief attempt to observe the esr spectrum of $\cdot\text{SO}_3^-$ in reacting Ir(IV)-S(IV) systems was unsuccessful. The lack of success is probably not meaningful, because the high reactivity of sulfur(V) radicals (see ref 9 and 10 and references therein) is expected to result in low radical concentration.

Discussion

The stoichiometry of the Ir(IV)-S(IV) reaction has already been discussed.¹⁶ Earlier work has revealed a positive correlation between dithionate production and the substitution lability of the oxidant.^{5,7} But Brown and Higginson have observed that substitution-inert IrCl_6^{2-} produces dithionate in conflict with the generalization, have pointed to a rich variety of possible mechanisms for oxidation of sulfur(IV), and have suggested that exceptions to the generalization should not be surprising.¹⁶

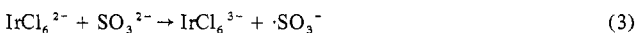
The forms of eq I and II are consistent with a rate-determining one-electron transfer between IrCl_6^{2-} and SO_3^{2-} ,¹⁹ followed by fast subsequent steps. If the rate-determining step is indeed reaction between IrCl_6^{2-} and SO_3^{2-} , then the second-order rate constant for this step can be estimated as $k'/Q_c = (2.41 \times 10^{-2})/(4.6 \times 10^{-7}) = 2 \times 10^4 M^{-1} \text{sec}^{-1}$, where $Q_c = [\text{H}^+][\text{SO}_3^{2-}]/[\text{HSO}_3^-]$,²⁰ this value can be compared with $4.2/(4.6 \times 10^{-7}) = 9 \times 10^6 M^{-1} \text{sec}^{-1}$ for the analogous rate term in the FeL_3^{3+} - HSO_3^- reaction.⁶

The empirical rate law does not provide evidence about the

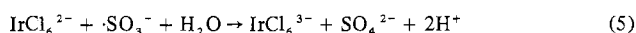
Table III. Rate Constants for the Iridium(IV)-Sulfur(IV) Reaction at Ionic Strength 0.2 *M*, $[\text{HSO}_3^-]_0 < 5 \times 10^{-6} M$, and 25°

| $10^5[\text{H}^+], M$ | $10^5 \times [\text{IrCl}_6^{2-}], M$ | $10^3 \times k'_{\text{obsd}}, \text{sec}^{-1}$ | $10^3 k'_{\text{calcd}}, \text{sec}^{-1}$ | $k'_{\text{calcd}}/k'_{\text{obsd}}$ |
|-----------------------|---------------------------------------|---|---|--------------------------------------|
| 11.8 | 4.22 | 5.0 | 8.61 | 1.7 |
| 3.50 | 5.46 | 17 | 37.6 | 2.2 |
| 26.8 | 6.25 | 5.0 | 5.62 | 1.1 |
| 3.50 | 16.1 | 52 | 111 | 2.1 |
| 26.8 | 16.7 | 13 | 15.0 | 1.1 |
| 11.8 | 23.7 | 45 | 48.3 | 1.1 |
| | | | | Av 1.6 ± 0.5 |

structure of the transition state or about steps occurring after the rate-determining step. Thus, even though IrCl_6^{2-} and SO_3^{2-} are each anions, the rate law is not inconsistent with complexation before electron transfer, perhaps in a chloride-bridged transition state somewhat analogous to $\text{Fe}(\text{CN})_5\text{-CNSO}_3^{5-}$.⁸ The rate law does not suggest the products of the rate-determining step; the products may be IrCl_6^{3-} and $\cdot\text{SO}_3^-$ or may be a IrS^{VIII} complex²¹ as shown in eq 3 and 4,



respectively. The evidence provided by the rate law, the stoichiometry, the substitution inertness of IrCl_6^{2-} , and the induced polymerization of acrylic acid is all most simply explained, however, by an outer-sphere rate-determining step, with the sulfur(V) intermediate being oxidized further by IrCl_6^{2-} or being dimerized to $\text{S}_2\text{O}_6^{2-}$ in competing reactions 5 and 6, respectively. Brown and Higginson proposed this



mechanism earlier,¹⁶ based on stoichiometric data alone.

The lack of rate dependence on IrCl_6^{3-} demonstrates that the rate-determining step is not reversible or does not produce IrCl_6^{3-} (possibly IrS^{VIII} instead). The reduced rate of

(19) In a recent study of the oxidation of ascorbic acid by IrCl_6^{2-} , M. C. Agrawal, K. C. Gupta, and S. P. Mushran, *Indian J. Chem.*, **10**, 642 (1972), have accounted for an inverse acid dependence by acid dissociation of a dominant species H_2IrCl_6 . However, we have made pH measurements to confirm that IrCl_6^{2-} has negligible base strength and is not protonated at pH 4.15. Acid dissociation of a species other than protonated IrCl_6^{2-} (probably HSO_3^-) is responsible for the inverse acid dependence in eq II.

(20) The Q_c value was measured¹⁵ in 1.00 *m* perchlorate and so probably introduces some error into the calculation.

(21) It has been shown that radicals can be coordinated to metal ions; a representative reference is A. Tkac, K. Vesely, and L. Omelka, *J. Phys. Chem.*, **75**, 2575 (1971). Speculation about $\cdot\text{SO}_3^-$ complexation with metal ions has been done in ref 5-7.

consumption of IrCl_6^{2-} in the presence of oxygen probably occurs because sulfur(V) intermediates are scavenged by oxygen instead of by IrCl_6^{2-} . The absence of strong catalysis by copper(II) suggests that sulfur(V) intermediates react very rapidly with IrCl_6^{2-} , however. The lack of rate dependence on buffer concentration confirms that the $[\text{H}^+]$ dependence shown in eq II should not be replaced by acetate or acetic acid dependences.

The fact that the data do not show much evidence that a term second order in HSO_3^- should be added to eq II shows that reduction by $\text{S}_2\text{O}_5^{2-}$ is not an important reaction under the conditions of this study. We present this fact as some evidence that the $[\text{HSO}_3^-]^2$ term in the reduction of the very similar FeL_3^{3+} ion⁶ does not arise from a reactive $\text{S}_2\text{O}_5^{2-}$ species. Even though the evidence is not conclusive, we think it is significant because of the many similarities be-

tween FeL_3^{3+} and IrCl_6^{2-} ; both oxidants are substitution-inert low-spin d^5 ions; they have one-electron reduction potentials of 1.06²² and 1.02²³ V, respectively. The different charges on the two ions probably at least partially account for the different behavior with respect to second-order bisulfate dependences.

We conclude that net reaction 1 probably occurs by a sequence of two outer-sphere electron transfers and that net reaction 2 occurs by outer-sphere electron transfer followed by combination of S(V) radicals.

Registry No. IrCl_6^{2-} , 16918-91-5; HSO_3^- , 15181-46-1.

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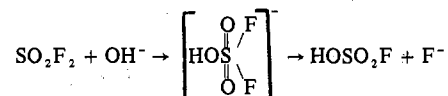
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Hydrolysis of Sulfuryl Fluoride

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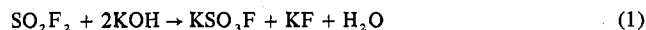
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Sulfuryl fluoride dissolves rapidly in water and may be quickly removed from solution by dynamic vacuum. The solubility of the gas has been measured at 0.0 and 23.3°. Hydrolysis of sulfuryl fluoride is slow in water but rapid in basic solutions, the net reaction being $\text{SO}_2\text{F}_2 + 2\text{OH}^- \rightarrow \text{SO}_3\text{F}^- + \text{F}^- + \text{H}_2\text{O}$. The rate law may be written as $-\text{d}[\text{SO}_2\text{F}_2]/\text{d}t = [\text{SO}_2\text{F}_2] \cdot \{k_w + k[\text{OH}^-]\}$. At pH values of 7.5 or greater, k_w is negligible when compared to $k[\text{OH}^-]$. Over the temperature range 0–25°, $k = 1.67 \times 10^{12} e^{-13,100/RT}$, when time is in seconds and concentrations are in moles per liter. The reaction is considered to be a nucleophilic displacement of fluorine in which the controlling process is

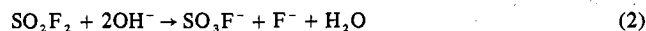


Sulfuryl fluoride reacts readily in aqueous solution with the nucleophiles NH_3 , $\text{C}_6\text{H}_5\text{O}^-$, and CN^- .

Previous studies of the hydrolysis of sulfuryl fluoride^{1–3} have shown that the reaction with water is much slower than with a basic solution and that the rate increases as the concentration of KOH is increased. The reaction with alcoholic KOH has been reported² to be



and with water containing hydroxide ion⁴ to be



If the resulting solution is allowed to stand, the fluorosulfate ion hydrolyzes to give sulfate and fluoride ions. However, studies by Ryss, Gribanova, and Drabkina^{5,6} and by Jones and Lockhart⁷ have shown that this reaction is very slow within the conditions of temperature and pH used in the

present research. Substantially none of the SO_3F^- ion reacted while the experiments now to be described were under way.

Results

Solubility of Sulfuryl Fluoride in Water. By working rapidly one can measure the solubility of sulfuryl fluoride in water before a substantial fraction of the solute has hydrolyzed. By use of experimental measurements given below and by assuming Henry's law to be obeyed, it can be calculated that 100 ml of water dissolves 52.9 cm³ (STP) of SO_2F_2 at 0.0° or 21.5 cm³ (STP) of SO_2F_2 at 23.3°. Trautz and Ehrmann³ have reported the solubility at 16.5° to be 0.4–0.5 cm³ of SO_2F_2 in 10 ml of water and Moissan and Lebeau¹ have reported 10 cm³ of gas per 100 ml of water at 9°. These values are too low.

When an aqueous solution of sulfuryl fluoride is held under the dynamic vacuum of a water aspirator, the dissolved gas is rapidly removed from solution. When a 10-ml sample of solution is under vacuum and subjected to vigorous shaking, the removal of sulfuryl fluoride is substantially complete within 20 sec.

Hydrolysis of Sulfuryl Fluoride. Upon standing at 25°, a solution of sulfuryl fluoride in water becomes increasingly acidic and the concentration of fluoride ion increases, because of the slow reaction

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