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Aqueous Fluoroxysulfate: Decomposition and Some Chemical Reactions[1a]

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Aqueous SO_4F^- decomposes to form O_2, H_2O_2, and HSO_5^-. At 15 °C in 0.01 M $HClO_4$ the first-order rate constant k = 3.6 × 10⁻⁴ s⁻¹, $\Delta H^* = 16.8 \pm 0.4$ kcal/mol, and $\Delta S^* = -15.7 \pm 1.5$ cal/(mol deg). The H_2O_2 and O_2 products both contain one oxygen atom from solvent and one from the fluoroxysulfate. The HSO_5^- product also contains an atom of solvent oxygen in its terminal peroxide position. A mechanism is proposed in which the rate-determining steps are the interaction of SO_4F^- with water to form HSO_5^- and H_2O_2. The H_2O_2 probably interacts further with SO_4F^- by means of a free-radical chain reaction to produce O_2. Fluorosulfate ion, SO_3F^-, appears to be formed only in the oxygen-transfer step that produces H_2O_2. Chlorite ion is rapidly oxidized to ClO_2 by SO_4F^- in accordance with the rate law $-d[SO_4F^-]/dt$ = $k_{ClO_2^-}[ClO_2^-][SO_4F^-]$. In acid solution at 14.7 °C, $k_{ClO_2^-} = 1.8 \times 10^4$ L/(mol s), $\Delta H^* = 7.3 \pm 0.6$ kcal/mol, and ΔS^* = -14 ± 2 cal/(mol deg). The oxidation of $Co(NH_3)_5ClO_2^{2+}$ by SO_4F^- produces ClO_2 and a mixture of $Co(NH_3)_5F^{2+}$ and $Co(NH_3)_5H_2O^{3+}$. The oxidation of Cr^{2+} by SO_4F^- produces 42–47% Cr^{3+} and 41–45% CrF^{2+}, the balance consisting of polynuclear Cr(III) species. The oxidation of I^- to I_2 by SO_4F^- consumes no acid and hence does not produce SO_3F^-. These rapid reactions may be interpreted in terms of mechanisms involving either 1- or 2-equiv oxidation in the rate-determining steps. Oxygen transfer does not appear to be significant, but fluorine transfer is obviously involved at least in the oxidation of Cr^{2+} and $Co(NH_3)_5ClO_2^{2+}$.

Introduction

The recent synthesis of the fluoroxysulfate ion, SO_4F^-,[2] adds it to a rather select list of substances that oxidize water at a rate that is convenient for detailed study. The fluoroxysulfate ion is formally a hypofluorite, and hence it may be regarded as a derivative of hypofluorous acid, HOF. Hypofluorous acid has been found to react by the transfer of either an oxygen atom or an OH^+ ion.[3–6] However, ¹⁹F NMR data[2,7] suggest that the fluorine atom in SO_4F^- is considerably less negative than that in HOF, and we might expect other modes of reaction, such as F atom or F^+ ion transfer, to compete with oxygen transfer in fluoroxysulfate reactions. Support for this idea will be found in the results of the present study.

It is our hope that, by elucidating some of the redox properties of this unusual species, we shall be able to improve our general understanding of the behavior of very strong oxidants and, in particular, that we may shed a little more light on the mechanisms by which water itself can be oxidized.

Experimental Section

Materials. Rubidium and cesium fluoroxysulfates were prepared as described previously by passing a 20% mixture of fluorine in nitrogen through 1.3–2 M solutions of the corresponding sulfates at temperatures between 0 and −5 °C.[2] The precipitates were filtered through porous Teflon filter disks (Chemplast) in a Teflon PFA apparatus (Savillex Co.). They were dried first by drawing dry argon through them for 1 h and then overnight in a vacuum desiccator. The product was stored in a desiccator at temperatures between −10 and +4 °C. Except when otherwise noted, the cesium salt was used in all experiments.

$Co(NH_3)_5(ClO_2)(NO_3)_2$ was synthesized by a procedure described previously.[8]

Xenon trioxide solutions in dilute $HClO_4$ or HNO_3 were prepared by hydrolysis of xenon hexafluoride[9,10] and were purified by methods

described elsewhere.[11] Peroxymonosulfate was obtained from Du Pont Co. as the commercial product "OXONE", which had the empirical formula $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. Other chemicals were commercial products of reagent grade. Distilled water was redistilled before use first from alkaline permanganate and then from acid dichromate solution.

Analytical Procedures. Fluoroxysulfate salts and solutions of xenon trioxide were analyzed iodometrically by reaction with iodide followed by titration with thiosulfate. Mixtures of H_2O_2 and HSO_5^- were also determined iodometrically in the following way: The total oxidizing power ($H_2O_2 + HSO_5^-$) was determined by carrying out the reaction with iodide in the presence of ammonium molybdate. The HSO_5^- alone was determined on a separate aliquot by reaction with 0.1 M KI at 0 °C in the absence of molybdate. (Correction was made for slow reaction of H_2O_2 under these conditions.) The H_2O_2 concentration was calculated as the difference between the two iodometric titers.

The fluoroxysulfate concentration of solutions containing other oxidizing species was determined by oxidation of ClO_2^- and spectrophotometric monitoring of the ClO_2 produced, using a Zeiss PMQ-11 spectrophotometer. A suitable aliquot of the fluoroxysulfate solution (1–2 μmol) was added with stirring to ca. 9 mL of a solution at 0 °C containing ca. 2.5×10^{-3} M $NaClO_2$ and ca. 2×10^{-5} M NaOH. The sodium chlorite solutions in dilute base are stable for long periods of time. The resulting solution was immediately transferred to a spectrophotometer cell, leaving no gas space, and the cell was tightly stoppered. The chlorine dioxide absorbance was measured at 358 nm, an absorption maximum with $\epsilon = 1242$ M⁻¹ cm⁻¹.[12] The absorbance was typically stable for ca. 10 min. If appreciable acid was present in the fluoroxysulfate sample, a slow increase in absorbance took place due to disproportionation of chlorous acid. Otherwise, a slow decrease in absorbance was observed, presumably due to volatility of the chlorine dioxide, and also possibly due to disproportionation of the chlorine dioxide in base. Xenon trioxide, peroxymonosulfate, and hydrogen peroxide at concentration levels similar to that of fluoroxysulfate do not interfere with this procedure. In a standardization procedure, 2.00-mL aliquots of a freshly prepared 6.1×10^{-4} M SO_4F^- solution in water at 0 °C were assayed by this method. The fluoroxysulfate concentration was taken as that given by an iodometric titration; any peroxymonosulfate present would make this value slightly high. The ratio of chlorine dioxide found to fluoroxysulfate added was 1.85 ± 0.01. The method was tested with different concentrations of fluoroxysulfate in both water and perchloric acid (up to 0.1 M); the same value of 1.85 was obtained. The ratio varied slightly for different fluoroxysulfate preparations but was constant for any given batch. High concentrations of hydrogen peroxide lower the ratio somewhat. A series of experiments were

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performed in which H_2O_2 was added to the chlorite quenching solution just prior to addition of an SO_4F^- solution. A 1% decrease in the ratio was found for $[H_2O_2] = 18[SO_4F^-]$, and a 3.5% decrease was found for $[H_2O_2] = 54[SO_4F^-]$. Fluoroxysulfate concentrations were calculated through the use of an empirical stoichiometry factor that corrected for these effects.

The $Co(NH_3)_5F^{2+}$ and $Co(NH_3)_5H_2O^{3+}$ formed in the reaction of $Co(NH_3)_5ClO_2^{2+}$ with excess SO_4F^- were separated by ion exchange and assayed spectrophotometrically. When excess $Co(NH_3)_5ClO_2^{2+}$ was used, the $Co(NH_3)_5F^{2+}$ was separated by ion exchange after the excess reductant had been converted to $Co(NH_3)_5H_2O^{3+}$ by reaction with bisulfite. (A small amount of $Co(NH_3)_5SO_4^+$ is also formed in the bisulfite reaction.) The amount of unreacted $Co(NH_3)_5ClO_2^{2+}$ was determined from its spectrophotometric absorbance at 358 nm ($\epsilon = 2320$ M^{-1} cm^{-1})[8] after flushing free ClO_2 from the solution with an air stream. The amount of ClO_2 formed in the reaction was determined from the decrease in absorbance brought about by the flushing.

The $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5F^{2+}$ formed in the reaction of Cr^{2+} with excess SO_4F^- were separated by ion exchange. The chromium content of each fraction was determined spectrophotometrically after oxidation to CrO_4^{2-} with alkaline hydrogen peroxide. The extinction coefficient of alkaline CrO_4^{2-} was taken to be 4815 M^{-1} cm^{-1} at 375 nm.[13]

Acid produced in the decomposition of fluoroxysulfate solutions was determined by potentiometric titration to a pH 8 end point. This resulted in titration of HF and HSO_4^-, but not HSO_5^- ($pK_a \sim 9.4$).[14a]

Gas Evolution Experiments. These experiments were usually carried out by placing each of the two reagents to be mixed (solid $CsSO_4F$ and aqueous reaction medium, H_2O_2 and Ce(IV), HSO_5^- and Na_2CO_3) in one leg of a vessel shaped like an inverted Y. After the vessel was evacuated and the solutions were outgassed, the contents of the two legs were mixed, and reaction was allowed to proceed to completion. The evolved gases were then removed with a Toepler pump, their total amount was measured manometrically, and their molecular and isotopic compositions were determined by mass spectrometry, using a Consolidated Model 21-620 mass spectrometer.

The oxygen of the H_2O_2 present in a mixture of H_2O_2 and HSO_5^- was released by oxidation with Ce(IV) after first destroying the HSO_5^- by potentiometric titration with I^-, using a shiny platinum electrode. The terminal oxygen in the HSO_5^- present in such a mixture was evolved from a separate portion by first destroying the H_2O_2 with excess chlorine, then flushing out the excess with nitrogen, and adding sodium carbonate in vacuo to bring the pH to ca. 9 and induce rapid bimolecular decomposition of the HSO_5^-.[14]

The oxygen isotopic composition of water samples was determined mass spectrometrically after conversion to O_2 by oxidation with alkaline hypobromite in the presence of cobalt oxide.[15]

Kinetic Procedures. The kinetic studies of the decomposition of aqueous fluoroxysulfate were carried out by the addition of solid $CsSO_4F$ or $RbSO_4F$ with vigorous stirring to 20–70-mL portions of an appropriate reaction mixture that had already reached equilibrium at the desired reaction temperature. Aliquots were taken at suitable intervals and assayed for fluoroxysulfate by the reaction with chlorite. Kinetic data were fitted by a least-squares procedure to the function $\ln [SO_4F^-] = kt + I$.

The kinetics of the rapid reaction between SO_4F^- and ClO_2^- were monitored on a Durrum stopped-flow apparatus. One syringe contained the freshly prepared fluoroxysulfate solution (in water or acid); the other syringe contained the chlorite (in dilute base to prevent disproportionation). The appearance of ClO_2 was monitored spectrophotometrically at 358 nm. The initial concentration of SO_4F^- in each kinetic experiment was calculated from the ClO_2 yield by making use of the stoichiometry factor $[ClO_2]_\infty/[SO_4F^-]_0$ determined in separate experiments. The values of this factor were approximately 1.85 in acid or neutral solution and 0.87 in 8×10^{-4} M NaOH.

Results

Decomposition of Fluoroxysulfate Solutions. Kinetic data for the decomposition of aqueous fluoroxysulfate are shown in Table I. Fairly good first-order kinetic plots were obtained

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Table I. Kinetics of Decomposition of Fluoroxysulfate Solutions[a]

medium	$10^3 \times$ $[SO_4F^-]_0$, M	additive	$10^3 \times$ [additive], M	$10^4 k$, s^{-1}
H_2O	1.23			3.2[b]
H_2O	1.11	XeO_3	0.23	2.85
H_2O	2.51	XeO_3	0.23	2.97
H_2O	1.92[c]	XeO_3	0.23	2.97
H_2O	2.04	XeO_3	0.69	3.03
H_2O	5.33	XeO_3	0.80	3.01
H_2O	8.57	XeO_3	63	3.28
H_2O	1.03	H_2O_2	1.08[d]	5.35
H_2O	1.68	H_2O_2	22.9	13.4
H_2O (4.6 °C)	1.61	XeO_3	0.23	0.945
H_2O (10.0 °C)	1.78	XeO_3	0.23	1.67
H_2O (19.9 °C)	2.43	XeO_3	0.23	4.77
10^{-3} M $HClO_4$	1.52	XeO_3	0.23	3.16
0.010 M $HClO_4$	1.91			3.91
0.010 M $HClO_4$	1.00			3.44[e]
0.010 M $HClO_4$	1.84	XeO_3	0.69	3.56
0.010 M $HClO_4$	4.69	XeO_3	0.80	3.80
0.013 M $HClO_4$	8.57	XeO_3	67.5	2.81
0.010 M $HClO_4$	13.4			3.64
0.010 M $HClO_4$	1.18	H_2O_2	1.08[f]	5.30
0.010 M $HClO_4$	1.19	H_2O_2 KHSO$_5$[h]	1.01[g] 1.00	4.75
0.010 M $HClO_4$	1.07	H_2O_2	20.5	15.2
0.010 M $HClO_4$	1.09	H_2O_2	69.9	37
0.010 M $HClO_4$	1.20	KHSO$_5$[h]	1.04	3.12
0.010 M $HClO_4$ (4.6 °C)	1.63	XeO_3	0.23	1.18
0.010 M $HClO_4$ (10.0 °C)	1.80	XeO_3	0.23	2.10
0.010 M $HClO_4$ (19.9 °C)	1.90	XeO_3	0.23	6.03
0.10 M $HClO_4$	1.47	XeO_3	0.23	3.62
0.10 M $HClO_4$ + 0.90 M $LiClO_4$	1.47	XeO_3	0.27	4.02

[a] $CsSO_4F$ used at 15.0 °C unless otherwise indicated. [b] After first 20 min, during which a considerably slower rate was observed ($k \approx 2.2 \times 10^{-4}$ s^{-1}). [c] $RbSO_4F$. [d] Final $[H_2O_2] = 6.8 \times 10^{-4}$ M. [e] Carried out in nitrogen stream. [f] Final $[H_2O_2] = 7.9 \times 10^{-4}$ M. [g] Final $[H_2O_2] = 9.15 \times 10^{-4}$ M. [h] Added $KHSO_5$ was always accompanied by half as much $KHSO_4$ and K_2SO_4.

in all but the first experiment in the table. Xenon trioxide was introduced in many experiments because it was found to eliminate the induction period observed in the absence of added acid and generally to increase the quality of the kinetic plots. Aside from this effect, xenon trioxide appears to have little influence on the measured reaction rate, except at very high XeO_3 concentrations. Addition of HSO_5^- appears to reduce the rate slightly, at least in 0.01 M acid, while addition of H_2O_2 increases the rate markedly. Addition of acid results in a modest but significant rate increase. Semiquantitative measurements show that in a bicarbonate solution k increases to about 2×10^{-3} s^{-1}, while in carbonate or strong base the reaction becomes too rapid for easy measurement. The temperature dependence of the rate corresponds to activation parameters of $\Delta H^\ddagger = 16.7 \pm 0.2$ kcal/mol and $\Delta S^\ddagger = -17.0 \pm 0.7$ cal/(mol deg) in water, and $\Delta H^\ddagger = 16.8 \pm 0.4$ kcal/mol and $\Delta S^\ddagger = -15.7 \pm 1.5$ cal/(mol deg) in 0.01 M $HClO_4$.

Table II shows the yields of peroxymonosulfate and hydrogen peroxide produced under a variety of conditions. These yields were somewhat irreproducible, especially those of H_2O_2, but some general observations may be made. Both yields are significantly reduced by the addition of acid, reduction in formation of HSO_5^- being particularly marked. On the other hand, little or no HSO_5^- and H_2O_2 are formed in bicarbonate or NaOH solutions.

In 0.01 M acid, the amount of HSO_5^- produced increases approximately linearly with the initial concentration of SO_4F^-. The production of H_2O_2 also increases with SO_4F^- concen-

Table II. Oxidizing Products Formed in the Decomposition of Fluoroxysulfate Solutions[a]

medium	$10^4 \times$ $[SO_4F^-]_0$, M	$10^4 \times$ $[HSO_5^-]_{formed}$, M	$10^4 \times$ $[H_2O_2]_{formed}$, M
H_2O	5.99	3.2	1.4
H_2O	9.63	4.4	2.6
H_2O	10.9	3.9	1.9
1.08×10^{-3} M H_2O_2	10.3	1.78	$(-4.0)^b$
H_2O	26.5	7.4	4.0
H_2O	65.4	17	16
H_2O	107^c	23.3	23.7
H_2O	116	22	17
H_2O	182	24	5
0.0029 M $HClO_4$	11.0	1.8	2.5
0.0029 M $HClO_4$	28.2	3.8	2.2
0.010 M $HClO_4$	6.32	0.76	0.63
0.010 M $HClO_4$	6.86	1.0, 1.2^d	1.6, 2.8^d
0.010 M $HClO_4$ + 1.67×10^{-4} M H_2O_2	6.86	0.89, 0.89^d	0.14, 0.19^d
0.010 M $HClO_4$ + 3.34×10^{-4} M H_2O_2	6.86	0.89, 0.89^d	0.23, 0.27^d
0.010 M $HClO_4$ + 1.83×10^{-4} M $KHSO_5^e$	6.86	0.96, 1.10^d	2.2, 2.9^d
0.010 M $HClO_4$	10.2	1.4	1.8
0.010 M $HClO_4$	10.9	1.3	1.0
0.010 M $HClO_4{}^f$	15.0	2.4	4.1
0.010 M $HClO_4$ + 1.08×10^{-3} M H_2O_2	11.8	1.11	$(-3.8)^b$
0.010 M $HClO_4$ + 1.04×10^{-3} M $KHSO_5^e$	12.0	1.3	3.8
0.010 M $HClO_4$ + 1.01×10^{-3} M H_2O_2 + 1.00×10^{-3} M $KHSO_5^e$	11.9	1.2	$(-2.7)^b$
0.010 M $HClO_4$	27.9	3.6	2.5
0.010 M $HClO_4$	49.6^g	4.6	2.3
0.010 M $HClO_4$	65.3	6.5	2.6
0.010 M $HClO_4$	98.3^h	12.8	15.2
0.010 M $HClO_4$	121	16	9.7
0.010 M $HClO_4$	166	12	1.2
0.010 M $HClO_4$	189		
0.050 M $NaHCO_3$	15.1	0.6	
0.010 M NaOH	21.0		0.4
0.009 M H_2SO_4	16.8	2.2	i

[a] At 15.0 °C unless otherwise noted. [b] H_2O_2 was consumed in reaction. [c] At 24 °C. Final solution was found to be 0.007 96 M in acid when titrated to a pH 8 end point. [d] Results of duplicate experiments. [e] Added $KHSO_5$ was always accompanied by half as much $KHSO_4$ and K_2SO_4. [f] Reaction carried out in a stream of nitrogen. [g] At 25 °C. Titration to a pH 8 end point indicated the production of 0.004 86 M additional acid. [h] At 25 °C. Titration to a pH 8 end point indicated the production of 0.008 15 M additional acid. [i] Not measured.

tration, but seemingly in a less-than-linear fashion, though the severe scatter of the data makes it difficult to draw a definite conclusion. The dependence of HSO_5^- and H_2O_2 production on SO_4F^- concentration in solutions containing no added acid is obscured by the fact that increasing SO_4F^- leads to an increasing average acidity for these solutions.

The amounts of HSO_5^- and H_2O_2 formed appear little affected by the initial presence of HSO_5^-, while the initial presence of H_2O_2 substantially suppresses the production of H_2O_2. Dilute sulfuric acid, which contains a mixture of HSO_4^- and SO_4^{2-}, does not affect the yield of HSO_5^-.

The results of the experiments in Table II in which acid evolution was measured are consistent with the production of 1 mol of relatively strong acid (HF or HSO_4^-) for each mole of HSO_5^- formed and another 2 mol of relatively strong acid for each mole of O_2 generated. (This assumes that the SO_4F^- oxidizing power that is not accounted for as HSO_5^- or H_2O_2 goes into the formation of O_2. Justification of this assumption is presented in the following section.)

Carrying out the reaction in a nitrogen stream appears to decrease the rate slightly and to increase somewhat the yields of H_2O_2 and HSO_5^-.

Gas Evolution. The gases evolved in the decomposition of aqueous SO_4F^- were measured and analyzed in a number of experiments at ca. 24 °C. Reaction of 0.099 mmol of $CsSO_4F$ in 15 mL of 0.011 M $HClO_4$ led to the production of 0.0355 mmol of O_2. Reaction of 0.103 mmol of $CsSO_4F$ in 12 mL of 0.010 M $HClO_4$ containing 0.025 mmol of XeO_3 produced 0.0215 mmol of Xe and 0.0826 mmol of O_2. Reaction of 0.0365 mmol of $CsSO_4F$ in 5.25 mL of solution containing 0.0536 mmol of XeO_3 and 0.0272 mmol of HSO_5^- (along with 0.014 mmol of HSO_4^- and 0.014 mmol of SO_4^{2-}) yielded

0.0178 mmol of Xe and 0.0552 mmol of O_2. The oxygen yield in the absence of XeO_3 is consistent with the data of Table II; i.e., 72% of the fluoroxysulfate oxidizing power ended up as a molecular oxygen, the balance going to form HSO_5^- and H_2O_2. To interpret the experiments with added XeO_3, we note that each mole of xenon evolved should be accompanied by 1.5 mol of O_2 from the XeO_3. Hence, in the second experiment described above, the maximum possible oxygen yield is 0.0837 mmol (0.5 × initial moles of SO_4F^- + 1.5 × moles of Xe evolved), and essentially all of this O_2 is found. In the third experiment, if we include the peroxide oxygen from HSO_5^- initially present, the maximum possible O_2 yield is 0.0585 mmol. The observed O_2 production, 0.0552 mmol, indicates that most of the added HSO_5^- has yielded its available oxygen as O_2.

Oxygen-18 Experiments. Experiments were carried out at 24–25 °C to determine the source of the oxygen atoms in the H_2O_2 and HSO_5^- that were formed and in the O_2 that was evolved. A solution 0.0067 M in $CsSO_4F$ and 0.011 M in $HClO_4$ was made up in water whose oxygen was 1.55_7 atom % in [18]O. After decomposition, the evolved oxygen was found to be 0.87_9 atom % [18]O. If we assume the oxygen in the unenriched SO_4F^- to be 0.200 atom % [18]O, we conclude that each molecule of O_2 contains 1.00_5 atoms of oxygen from the fluoroxysulfate. In another experiment, a solution 0.0486 M in $CsSO_4F$ and 0.010 M in $HClO_4$ was prepared in water whose oxygen was 1.55_8 atom % [18]O. The evolved oxygen was found to contain 0.88_6 atom % [18]O, corresponding to 0.98_5 atom of fluoroxysulfate oxygen per molecule of O_2. The solution remaining after this experiment was titrated potentiometrically with I^- to destroy HSO_5^-. It was then treated with excess Ce(IV) in vacuo to liberate oxygen from the H_2O_2. This

Table III. Kinetics of Reaction between ClO_2^- and SO_4F^- [a]

[H$^+$], M	$10^3 \times$ [Cl(III)]$_0$, M	$10^3 \times$ [ClO$_2^-$]$_0$,[b] M	k_1,[c] s^{-1}	$10^{-3} \times k_{ClO_2^-}$,[d] L/(mol s)
		$t = 14.7\,^\circ$C		
0.0285	4.83	1.41	23.6	17.3
0.0721	4.83	0.676	11.1	16.9
0.192	9.67	0.556	10.2	18.7
0.495	4.83	0.111	1.87	17.4
0.481	19.3	0.457	8.67	19.1
0.491	9.67	0.225	4.13	18.7
e	0.967	0.967		13.0
		$t = 8.6\,^\circ$C		
0.0286	4.83	1.53	18.8	12.7
0.0721	4.83	0.753	10.5	14.6
0.196	4.83	0.306	4.05	13.7
0.495	4.83	0.126	1.80	14.7
e	0.967	0.967		9.3
		$t = 2.4\,^\circ$C		
0.0283	4.83	1.68	13.9	8.6
0.0720	4.83	0.850	8.24	10.2
0.196	4.83	0.351	3.52	10.5
0.495	4.83	0.146	1.37	9.7
e	0.967	0.967		6.7

[a] Initial [SO$_4$F$^-$] = (1.64–2.34) × 10^{-4} M. [Cl(III)] = [HClO$_2$] + [ClO$_2^-$]. Ionic strength = 1.0 M, maintained with LiClO$_4$. [b] Calculated from NBS data for ΔH and ΔS of formation of HClO$_2$ and ClO$_2^-$, leading to the following values of the ionization constant of HClO$_2$: 0.0117 M at 14.7 °C, 0.0133 M at 8.6 °C, and 0.0154 M at 2.4 °C.[19] [c] In acid solution k_1 is the pseudo-first-order rate constant obtained by fitting the kinetic data to the relationship $-d[SO_4F^-]/dt = k_1[SO_4F^-]$. k_1 is the slope of a plot of ln $(A_\infty - A)$ vs. time, where A and A_∞ are optical absorbances at 358 nm. [d] In acid solution $k_{ClO_2^-}$ was calculated from the relationship $k_{ClO_2^-} = k_1/[ClO_2^-]_{av}$, where [ClO$_2^-$]$_{av}$ is the average concentration of ClO$_2^-$ present during the reaction. In alkaline solution $k_{ClO_2^-}$ was determined directly by fitting the kinetic data to the bimolecular rate equation $d[ClO_2]/dt = 0.87k_{ClO_2^-}[SO_4F^-][ClO_2^-] = 0.87k_{ClO_2^-}\{[SO_4F^-]_0 - [ClO_2]/0.87\}\{[ClO_2^-]_0 - [ClO_2]\}$. [e] [OH$^-$] = ca. 8 × 10^{-4} M.

oxygen was found to contain 0.90$_7$ atom % ^{18}O, corresponding to the incorporation of 0.95$_4$ atom of oxygen from SO$_4$F$^-$ into each molecule of H$_2$O$_2$.

In a further experiment a 0.049 M solution of CsSO$_4$F was prepared in water whose oxygen was 1.56$_9$ atom % ^{18}O and allowed to decompose. The H$_2$O$_2$ was destroyed with Cl$_2$, and the HSO$_5^-$ was permitted to decompose in vacuo in a carbonate–bicarbonate buffer. The evolved O$_2$ contained 1.50$_8$ atom % ^{18}O. The oxygen obtained from HSO$_5^-$ in this way has been shown to consist almost entirely of terminal peroxide oxygen atoms from the peroxymonosulfate.[14] Hence we may conclude that in the decomposition of SO$_4$F$^-$, the HSO$_5^-$ formed derives at least 96% of its terminal peroxide oxygen from the solvent.

Oxidation of ClO$_2^-$ by SO$_4$F$^-$. As noted in the Experimental Section, the stoichiometry of this reaction in acid or neutral solution containing a substantial excess of Cl(III) corresponds closely to the production of 1.85 mol of ClO$_2$ for each mole of SO$_4$F$^-$ initially present. The ClO$_2$ yield drops substantially in alkaline solution. Thus, the reaction of 9.7 × 10^{-4} M ClO$_2^-$

with 2.00 × 10^{-4} M SO$_4$F$^-$ in 8 × 10^{-4} M NaOH produces only 1.74 × 10^{-4} M ClO$_2$, or 0.87 mol of ClO$_2$ for each initially present mole of SO$_4$F$^-$. This decrease in yield may be due to the rapid reaction of SO$_4$F$^-$ with solvent in alkaline solution.

In acid solution the ClO$_2$ yield decreases when SO$_4$F$^-$ is present in stoichiometric excess. In 0.01 M HClO$_4$ at 0 °C the reaction of 7.7 × 10^{-4} M Cl(III) with 5.8 × 10^{-4} M SO$_4$F$^-$ yielded only 6.4 × 10^{-4} M ClO$_2$, while the reaction of 4.8 × 10^{-4} M Cl(III) with 6.9 × 10^{-4} M SO$_4$F$^-$ yielded only 3.7 × 10^{-4} M ClO$_2$. This reduction in ClO$_2$ formation may reflect production of ClO$_3^-$. However no indication was found for any direct oxidation of ClO$_2$ by SO$_4$F$^-$.

The kinetic results are given in Table III. When the data are corrected for the ionization constant of HClO$_2$, they fit the rate law $-d[SO_4F^-]/dt = k_{ClO_2^-}[SO_4F^-][ClO_2^-]$. Activation parameters derived from the temperature dependence of $k_{ClO_2^-}$ in acid are $\Delta H^\ddagger = 7.3 \pm 0.6$ kcal/mol and $\Delta S^\ddagger = -14 \pm 2$ cal/(mol deg).

Oxidation of Co(NH$_3$)$_5$ClO$_2^{2+}$ by SO$_4$F$^-$. This reaction is rapid, though significantly slower than the oxidation of free chlorite. Data on the reaction stoichiometry appear in Table IV. These data are not entirely consistent, inasmuch as the amount of ClO$_2$ found is only 70–80% of that which would be expected from the amount of Co(NH$_3$)$_5$ClO$_2^{2+}$ consumed per mole of SO$_4$F$^-$. (This assumes that the unidentified chlorine-containing species is ClO$_3^-$.) No evidence was found for formation of the complex Co(NH$_3$)$_5$ClO$_3^{2+}$.
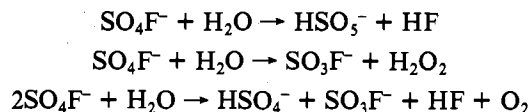
Oxidation of Cr(II) by SO$_4$F$^-$. The reaction of 0.0183 M Cr^{2+} with 0.0145 M SO$_4$F$^-$ was studied at 0 °C in 0.5 M HClO$_4$. Because of the speed of the reaction, two orders of mixing were employed. When oxidant was added to the Cr^{2+} solution, 47% of the Cr(III) product was present as Cr^{3+}, 44% as CrF^{2+}, and 9% as polynuclear species. When Cr^{2+} was added to a solution of the oxidant, the corresponding percentages were 43, 41, and 16%. Attempts to scavenge possible radical intermediates with Br$^-$ and Cl$^-$ were unsuccessful because of the rapid direct reaction between the halide ions and the fluoroxysulfate.

As we have observed previously,[2] fluoroxysulfate does not appear to oxidize Cr(III) in acid solution.

Oxidation of I$^-$ by SO$_4$F$^-$. The reaction of 0.0045 M CsSO$_4$F with 0.2 M KI in 0.020 M HClO$_4$ led to the formation of I$_3^-$ with no consumption of acid as determined by titration to a pH 8 end point. This indicates that fluorosulfate is not a significant product, the overall stoichiometry being 2H$^+$ + SO$_4$F$^-$ + 3I$^-$ → I$_3^-$ + HF + HSO$_4^-$.

Discussion

Decomposition of Aqueous Fluoroxysulfate. This is clearly a complex process, producing peroxymonosulfate, hydrogen peroxide, and oxygen. If we take into consideration the data on generation of O$_2$, H$^+$, HSO$_5^-$, and H$_2$O$_2$, we may formulate the overall stoichiometry in acid solution as a combination of the three reactions:

$$SO_4F^- + H_2O \rightarrow HSO_5^- + HF$$
$$SO_4F^- + H_2O \rightarrow SO_3F^- + H_2O_2$$
$$2SO_4F^- + H_2O \rightarrow HSO_4^- + SO_3F^- + HF + O_2$$

Table IV. Oxidation of Co(NH$_3$)$_5$ClO$_2^{2+}$ by SO$_4$F$^-$ [a]

| initial concn, 10^{-4} M			final concn, 10^{-4} M				Δ[RClO$_2^{2+}$]/[SO$_4$F$^-$]$_0$
RClO$_2^{2+}$	SO$_4$F$^-$	H$^+$	RClO$_2^{2+}$	RH$_2$O^{3+}	RF^{2+}	ClO$_2$	
4.01	1.22	100	2.07	b	b	1.14	1.59
3.97	2.42	100	0.815	b	b	1.06	1.31
69.4	36.2	100	18.9	b	b	b	1.39
232	71.9	500	141	b	35.8	b	1.27
232	294	500		165	62.6	b	

[a] At 0 °C. R = Co(NH$_3$)$_5$. [b] Not determined.

The production of peroxymonosulfate appears to be approximately proportional to the initial fluoroxysulfate concentration and independent of modest initially present amounts of HSO_5^-, HSO_4^-, and SO_4^{2-}. The ^{18}O experiment shows that the HSO_5^- produced contains a solvent oxygen atom as the terminal atom in its peroxy moiety. These facts can most easily be rationalized in terms of formation of the HSO_5^- by nucleophilic substitution of OH^- for F^-:

$$SO_4F^- + H_2O^* \rightarrow SO_4O^*H^- + HF$$
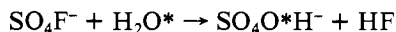
However, we are unable to explain the dependence of the HSO_5^- yield on pH, which manifests itself as a substantial increase in yield as the acidity is lowered below 0.01 M, followed by a precipitous drop in yield at pH values above 7.
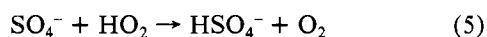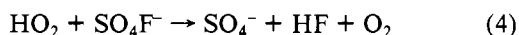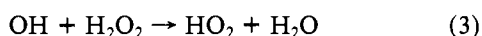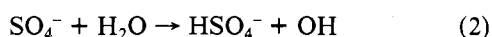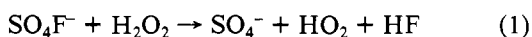
The oxygen-18 results indicate that both the H_2O_2 and the O_2 produced contain one oxygen atom from the solvent and one from the fluoroxysulfate. This, in conjunction with the measurements of H^+ evolution, would imply that the H_2O_2 is formed by transfer of oxygen from SO_4F^- to water

$$SO_4F^- + H_2O^* \rightarrow HOO^*H + SO_3F^-$$
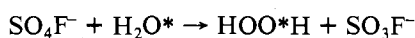
and that the O_2 results from subsequent oxidation of the H_2O_2

$$SO_4F^- + H_2O_2 \rightarrow HSO_4^- + HF + O_2$$
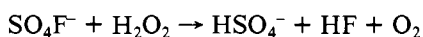
The latter conclusion is supported by the observation that the initial presence of H_2O_2 decreases the apparent amount of H_2O_2 formed in the reaction. However, if we consider the effect of 0.02–0.07 M H_2O_2 on the rate of disappearance of SO_4F^-, we conclude that the bimolecular reaction between SO_4F^- and H_2O_2 has a rate constant no greater than about 0.06 L/(mol s) at 15 °C. This direct reaction is thus too slow to consume a significant portion of the hydrogen peroxide formed in the decomposition of millimolar concentrations of SO_4F^-. We see, however, that 0.001 M H_2O_2 accelerates the decomposition of SO_4F^- to a significantly greater extent than would be extrapolated from the effect of the higher H_2O_2 concentrations. This is particularly evident in the absence of added acid. A possible explanation is that the consumption of H_2O_2 is not a bimolecular reaction with SO_4F^- at all but is taking place via a chain mechanism such as eq 1–5. This

$$SO_4F^- + H_2O_2 \rightarrow SO_4^- + HO_2 + HF \quad (1)$$

$$SO_4^- + H_2O \rightarrow HSO_4^- + OH \quad (2)$$

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \quad (3)$$

$$HO_2 + SO_4F^- \rightarrow SO_4^- + HF + O_2 \quad (4)$$

$$SO_4^- + HO_2 \rightarrow HSO_4^- + O_2 \quad (5)$$

is similar to the mechanism proposed to explain the reaction between $S_2O_8^{2-}$ and H_2O_2.[16] Such a mechanism is in qualitative agreement with our results, but unfortunately our data are not of sufficient quality to quantitatively confirm this or any other unique mechanism. As in the case of HSO_5^- formation, we do not understand the dependence of H_2O_2 yield on pH. One factor may be changes in rates resulting from ionization of HO_2 ($pK \sim 4.5$).

We had hoped that the role of XeO_3 in this system would be that of a scavenger of hydrogen peroxide and reducing radicals. Our own unpublished observations show that in dilute acid at 25 °C the reaction between 1.5×10^{-3} M H_2O_2 and 5×10^{-4} M XeO_3 is more than 90% complete in 30 s. We have observed little or no direct reaction between XeO_3 and HSO_5^-, but our gas evolution results indicate that at least

under some conditions the presence of XeO_3 will bring about the production of oxygen from HSO_5^- in a decomposing fluoroxysulfate solution. Moreover, in the gas evolution experiment with 0.002 M XeO_3 and 0.0086 M SO_4F^-, the ratio of evolved oxygen to evolved xenon was found to be 3.84, whereas the maximum ratio that could result from reaction of XeO_3 with an oxygen-liberating reductant is 3.00. It would appear that the action of XeO_3 in this system may be quite complex. If the XeO_3 is, in fact, scavenging H_2O_2 and reducing radicals, we might anticipate its presence to lead to a reduction in the rate of consumption of SO_4F^-. Although there is some evidence for such a reduction in rate, its magnitude seems less than we would expect, particularly in 0.01 M acid. It is quite possible that the reaction between XeO_3 and H_2O_2 itself produces intermediates that can react rapidly with SO_4F^-.

It is worth noting that fluoroxysulfate is the second reagent that we have found to be readily capable of transferring oxygen to water, the other being HOF.[5] Such oxygen transfer constitutes the only known way of preparing unsymmetrically labeled H_2O_2 and O_2 (i.e., HOO^*H and OO^*) other than as parts of a statistical mixture of molecules. Since SO_4F^- is considerably easier to synthesize than HOF, it should be a useful reagent for the preparation of such labeled species. Fluoroxysulfate may also find use as a means of preparing "end-labeled" peroxymonosulfate.

Oxidations by Fluoroxysulfate. Fluoroxysulfate reacts rapidly with free and coordinated ClO_2^-, with Cr^{2+}, and with I^-. Substantial oxygen transfer can probably be ruled out in all cases. Oxygen transfer to ClO_2^- should yield chlorate as a stable product; oxygen transfer to $Co(NH_3)_5ClO_2^{2+}$ would be expected to give $Co(NH_3)_5ClO_3^{2+}$; oxygen transfer to Cr^{2+} should form Cr(IV) and ultimately lead to the production of polynuclear Cr(III) species; oxygen transfer to I^-, by analogy with the transfer to H_2O, would be expected to yield SO_3F^- and consume acid:

$$2H^+ + SO_4F^- + 3I^- \rightarrow SO_3F^- + I_3^- + H_2O$$
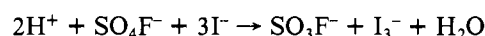
The fact that the oxidation of Cr^{2+} produces CrF^{2+} and the oxidation of $Co(NH_3)_5ClO_2^{2+}$ produces $Co(NH_3)_5F^{2+}$ suggests that these reactions involve either the transfer of an F atom in a free-radical process or the transfer of an F^+ ion in a 2-equiv oxidation. Only in the case of the oxidation of Cr^{2+} is it possible to make a definite distinction between these two mechanisms. Transfer of F^+ to Cr^{2+} would produce the chromium(IV) species CrF^{3+}. Chromium(IV) is labile to substitution, and we would expect it to lose the fluorine atom and react with Cr^{2+} to form polynuclear chromium(III) species. Hence, in this case a 1-equiv free-radical mechanism is indicated:
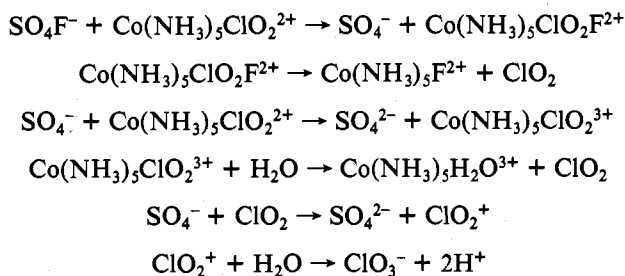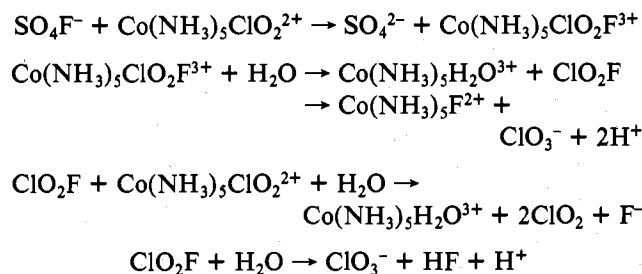
$$SO_4F^- + Cr^{2+} \rightarrow SO_4^- + CrF^{2+}$$

$$SO_4^- + Cr^{2+} \rightarrow SO_4^{2-} + Cr^{3+}$$
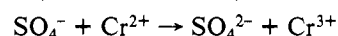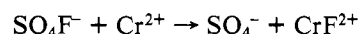
This scheme is analogous to that proposed for the oxidation of Cr^{2+} by $S_2O_8^{2-}$, the difference being that transfer of F from SO_4F^- takes the place of transfer of SO_4^- from $S_2O_8^{2-}$.[17]
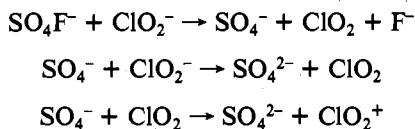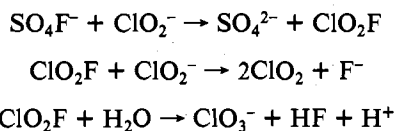
The reaction of $Co(NH_3)_5ClO_2^{2+}$ with SO_4F^- is obviously complex, and we do not have a full understanding of it at present. However, any mechanism that we propose for the reaction must take into account the fact that both 1- and 2-equiv oxidations of the ClO_2^- appear to occur. Either a 1- or a 2-equiv rate-determining step may be involved; for example, see Mechanisms I and II. The second of these mechanisms is somewhat similar to one that we have proposed for the oxidation of CrN_3^{2+} by molecular fluorine.[4]

(16) Tsao, M.-S.; Wilmarth, W. K. *Discuss. Faraday Soc.* **1960**, *29*, 137.

(17) Pennington, D. E.; Haim, A. *J. Am. Chem. Soc.* **1968**, *90*, 3700.

Mechanism I

$$SO_4F^- + Co(NH_3)_5ClO_2^{2+} \rightarrow SO_4^- + Co(NH_3)_5ClO_2F^{2+}$$

$$Co(NH_3)_5ClO_2F^{2+} \rightarrow Co(NH_3)_5F^{2+} + ClO_2$$

$$SO_4^- + Co(NH_3)_5ClO_2^{2+} \rightarrow SO_4^{2-} + Co(NH_3)_5ClO_2^{3+}$$

$$Co(NH_3)_5ClO_2^{3+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + ClO_2$$

$$SO_4^- + ClO_2 \rightarrow SO_4^{2-} + ClO_2^+$$

$$ClO_2^+ + H_2O \rightarrow ClO_3^- + 2H^+$$

Mechanism II

$$SO_4F^- + Co(NH_3)_5ClO_2^{2+} \rightarrow SO_4^{2-} + Co(NH_3)_5ClO_2F^{3+}$$

$$Co(NH_3)_5ClO_2F^{3+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + ClO_2F$$
$$\rightarrow Co(NH_3)_5F^{2+} +$$
$$ClO_3^- + 2H^+$$

$$ClO_2F + Co(NH_3)_5ClO_2^{2+} + H_2O \rightarrow$$
$$Co(NH_3)_5H_2O^{3+} + 2ClO_2 + F^-$$

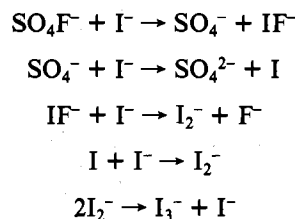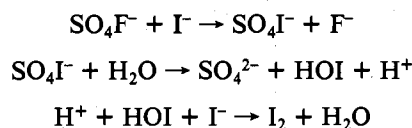$$ClO_2F + H_2O \rightarrow ClO_3^- + HF + H^+$$

A similar choice of mechanisms exists for the oxidation of free chlorite by fluoroxysulfate. In this case, however, the production of ClO_2 is nearly quantitative in acid solution unless an excess of SO_4F^- is present; i.e., the principal net reaction is probably $SO_4F^- + 2ClO_2^- \rightarrow SO_4^{2-} + F^- + 2ClO_2$. Mechanisms III and IV are possible. We should note that ClO_2F is a moderately stable molecule, and it should be possible to determine directly its reactivity toward H_2O, ClO_2^-, and $Co(NH_3)_5ClO_2^{2+}$.

Mechanism III

$$SO_4F^- + ClO_2^- \rightarrow SO_4^- + ClO_2 + F^-$$

$$SO_4^- + ClO_2^- \rightarrow SO_4^{2-} + ClO_2$$

$$SO_4^- + ClO_2 \rightarrow SO_4^{2-} + ClO_2^+$$

Mechanism IV

$$SO_4F^- + ClO_2^- \rightarrow SO_4^{2-} + ClO_2F$$

$$ClO_2F + ClO_2^- \rightarrow 2ClO_2 + F^-$$

$$ClO_2F + H_2O \rightarrow ClO_3^- + HF + H^+$$

It is interesting that the species that is reactive toward fluoroxysulfate is ClO_2^- rather than $HClO_2$. Apparently the increased electron density on the chlorite anion outweighs the electrostatic repulsion between it and SO_4F^-.

Finally, the same ambiguity as to mechanism remains for the oxidation of I^-, as indicated in Mechanisms V and VI. We

see that it is quite reasonable to postulate a 2-equiv oxidation of I^- without invoking oxygen transfer from the fluoroxysulfate. A similar uncertainty as to mechanism exists in the case of the reaction between I^- and $S_2O_8^{2-}$, in which there is evidence that both paths may be significant.[18]

Mechanism V

$$SO_4F^- + I^- \rightarrow SO_4^- + IF^-$$

$$SO_4^- + I^- \rightarrow SO_4^{2-} + I$$

$$IF^- + I^- \rightarrow I_2^- + F^-$$

$$I + I^- \rightarrow I_2^-$$

$$2I_2^- \rightarrow I_3^- + I^-$$

Mechanism VI

$$SO_4F^- + I^- \rightarrow SO_4I^- + F^-$$

$$SO_4I^- + H_2O \rightarrow SO_4^{2-} + HOI + H^+$$

$$H^+ + HOI + I^- \rightarrow I_2 + H_2O$$

General Observations. Although we have just begun to scratch the surface of the chemistry of fluoroxysulfate, our present results suggest that oxygen transfer may be a relatively uncommon mechanism for fluoroxysulfate oxidations. This may reflect the stability of products containing the SO_4 tetrahedron with respect to SO_3F^-, the formation of which requires extensive intramolecular rearrangement. It may also reflect the relatively positive character of the fluorine in fluoroxysulfate that we noted in our Introduction. Of interest in this regard would be studies of the reactions of SO_4F^- with such 2-equiv reductants as sulfite and bromate and, in particular, determination of whether or not the reactions involve transfer of fluoroxysulfate oxygen.

In this paper we have examined the reducing substrates ClO_2^-, Cr^{2+}, and I^- that are very rapidly oxidized by fluoroxysulfate, and we have noted others such as ClO_2 and $Cr(III)$ that are not oxidized at all. Although our information at present is much too limited to justify any sweeping conclusions, it may well be that any reductant that reacts very rapidly with fluoroxysulfate must be an unusually good acceptor for an F atom or F^+ ion.

(18) Wilmarth, W. K.; Haim, A. In "Peroxide Reaction Mechanisms"; Edwards, J. O., Ed.; Interscience: New York, 1962; pp 191-194.
(19) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumm, R. H. *Natl. Bur. Stand. (U.S.), Tech. Note* **1968**, *No. 270-3*, 25, 28.