useful reagent for the syntheses of hypochlorites,[47] the synthesis of $ClOIF_4O$ was accomplished according to

$$CsIF_4O_2 + ClOSO_2F \xrightarrow{-78\ °C} CsSO_3F + ClOIF_4O$$

The resulting $ClOIF_4O$ appears to be highly reactive, difficult to handle, and thermally unstable. Consequently, the compound could not be well characterized. The main evidence for its existence is the infrared spectrum of the gas, which is similar to that of $FOIF_4O$ except that the O—F stretch is replaced by a band at 763 cm^{-1}, characteristic of an O—Cl stretch,[47] and the I=O, IF, and I—O stretching modes are shifted to slightly lower frequencies. The compound decomposes to IF_5, and attempts to add it across the C=C double bond of C_2F_4 did not result in stable adducts.

Conclusion. Although the isolation of NF_4^+ salts of either IO_4^- or $IF_4O_2^-$ was not possible, solutions containing NF_4^+ and $HOIF_4O$ were found to decompose to produce $FOIF_4O$ in high yield. This is in marked contrast to the similar syntheses of $FOClO_3$ and $FOSO_2F$ where the corresponding $NF_4^+ClO_4^-$ [3] and $NF_4^+SO_3F^-$ [4] salts were shown to be the actual intermediates. $FOIF_4O$ is the first known example of an iodine hypofluorite and exists as cis and trans isomers. It is a stable compound and was thoroughly characterized. The analogous hypochlorite, $ClOIF_4O$, was also prepared for the first time but, as expected, is considerably less stable than $FOIF_4O$. The reaction of $CsIO_4$ with HF was found to be a convenient synthesis of $CsIF_4O_2$, which, by reaction with BiF_5 in HF, can readily be converted into $HOIF_4O$, thus providing easy access to tetrafluoroperiodates. The bonding in *trans*-$IF_4O_2^-$ was studied by vibrational spectroscopy, and the results of a normal-coordinate analysis are in excellent agreement with the trends previously established[37] for chlorine oxyfluorides.

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Registry No. *trans*-$CsIF_4O_2$, 77224-44-3; *cis*-$CsIF_4O_2$, 55188-51-7; *trans*-$HOIF_4O$, 25685-16-9; *cis*-$HOIF_4O$, 25685-15-8; *trans*-$FOIF_4O$, 72151-31-6; *cis*-$FOIF_4O$, 72123-55-8; $ClOIF_4O$, 77224-34-1; $CsIO_4$, 13478-04-1; HF, 7664-39-3; BrF_5, 7789-30-2; ClF_3, 7790-91-2; ClF_5, 13637-63-3; F_2, 7782-41-4; BiF_5, 7787-62-4; NF_4SbF_6, 16871-76-4; $ClSO_3F$, 13997-90-5; IF_5O, 16056-61-4.

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Oxidation by Aqueous Fluoroxysulfate: Catalysis by Silver(I)[1a]

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The oxidations of the ions Cr^{3+}, Co^{2+}, and VO^{2+} by the fluoroxysulfate ion, SO_4F^-, in aqueous solution are catalyzed by Ag^+. The rate-determining step for all three catalyzed reactions is the bimolecular oxidation of Ag^+ by SO_4F^-, which has a rate constant of $(1.3 \pm 0.2) \times 10^3$ M^{-1} s^{-1} at 17 °C. Activation parameters for this reaction are $\Delta H^* = 6.1 \pm 0.5$ kcal/mol and $\Delta S = -23 \pm 2$ cal/(mol deg). In the absence of Ag^+, Co^{2+} and VO^{2+} react very slowly with SO_4F^-, while Cr^{3+} does not react at all. Despite its high thermodynamic oxidizing power, the fluoroxysulfate ion acts as a very selective oxidant.

Introduction

The fluoroxysulfate ion, SO_4F^-, is the only known ionic hypofluorite.[2] It is also one of the most powerful of all aqueous oxidants, with a standard electrode potential of 2.46 V.[3] The rubidium and cesium fluoroxysulfates are rather easily made and are sufficiently stable that they can be conveniently stored prior to use. These salts are therefore very suitable substances with which to explore and take advantage of the chemical properties of a hypofluorite, which we may expect to act as a vigorous oxidizing and fluorinating agent.

In the course of our initial survey of the reaction chemistry of aqueous fluoroxysulfate,[2,4] we have observed that SO_4F^- readily oxidizes most reducing substrates. However, some reducing agents such as Cr^{3+} are not oxidized at all, while others such as Mn^{2+}, Ce^{3+}, Co^{2+}, and VO^{2+} react rather sluggishly. On the other hand, Ag^+ is very rapidly oxidized by SO_4F^-, and since higher oxidation states of silver are known to be powerful oxidants, it appeared to us that Ag^+ should catalyze oxidation by SO_4F^- and might thereby extend the application of the latter as an oxidizing agent. We have found that such catalysis does indeed take place, and we have undertaken to study the Ag^+-catalyzed reactions of SO_4F^- with Cr^{3+}, Co^{2+}, and VO^{2+}. For the sake of comparison, we have also examined the slow uncatalyzed reactions of SO_4F^- with Co^{2+} and VO^{2+}.

Experimental Section

Materials. Cesium fluoroxysulfate was prepared and purified by techniques described previously.[2,4] Solutions of $VO(ClO_4)_2$ in 1 M $HClO_4$ were prepared from commercial vanadyl sulfate by ion exchange. Stock solutions of lower acidity were obtained by partial neutralization of the acid with lithium carbonate. Zinc perchlorate was prepared by the reaction of Johnson-Matthey high-purity ZnO with $HClO_4$, followed by two recrystallizations. Other starting materials such as G. F. Smith $Zn(ClO_4)_2$, reagent grade ZnO, and reagent grade Zn metal resulted in $Zn(ClO_4)_2$ solutions containing impurities that rapidly reduced or decomposed fluoroxysulfate. The preparations of $Co(ClO_4)_2$, $Cr(ClO_4)_3$, and $LiClO_4$ have been described elsewhere.[5] Other materials were commercial products of reagent grade. Deionized water was distilled before use first from acid dichromate and then from alkaline permanganate.

Solutions of HSO_5^- in which the terminal peroxide oxygen was enriched in ^{18}O were prepared by allowing cesium fluoroxysulfate to decompose in a 1 M $HClO_4$ solution that was enriched in ^{18}O. The hydrogen peroxide formed was decomposed by addition of a stoichiometric amount of Ce(IV). The yield of peroxymonosulfate in 1 M $HClO_4$ was of the order of 40% of the fluoroxysulfate. This is considerably higher than the yield obtained at lower acidity.[4]

Analytical Procedures. Solutions of Co^{2+}, Co^{3+}, VO^{2+}, VO_2^+, and $HCrO_4^-$ were analyzed spectrophotometrically, with use of extinction

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coefficients from the literature.[6-9] Solutions of Cr^{3+} were oxidized to CrO_4^{2-} with alkaline H_2O_2 at 100 °C and were then analyzed spectrophotometrically, again with use of extinction coefficients from the literature.[10] Fluoroxysulfate concentrations were determined by reaction with iodide followed by titration with thiosulfate[2] or by reaction with ClO_2^- followed by spectrophotometric monitoring of the ClO_2 produced.[4] Peroxydisulfate was determined by titration with thiosulfate after reaction with 1 M KI for 15 min in an oxygen-free atmosphere.[11] In some cases, this technique was applied to mixtures of $S_2O_8^{2-}$ and Co^{3+} to give the sum of the oxidizing equivalents of the two species. The amount of $S_2O_8^{2-}$ was then determined by subtracting the spectrophotometrically determined Co^{3+} concentration. The sum of sulfate and bisulfate was determined by precipitation as $BaSO_4$, with use of a short room-temperature digestion to avoid hydrolyzing any SO_3F^- that might be present. Large amounts of Co^{2+} were first removed by cation exchange. Fluoride was determined by the technique of ion chromatography.[12]

Gas Evolution Experiments. These experiments were carried out in inverted Y-shaped vessels. Solid $CsSO_4F$ or a peroxymonosulfate solution was placed in one leg of the "Y", and the aqueous reaction medium was placed in the other. 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, with the use of a Consolidated Model 21-620 mass spectrometer.

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.[13]

Kinetic Procedures. Although the Ag^+-catalyzed reactions were fast enough to have benefited from the stopped-flow kinetic technique, we chose not to make use of this method because of the decomposition of fluoroxysulfate that would unavoidably take place during the setting up time. A fresh solution of SO_4F^- was prepared for each experiment by dissolving $CsSO_4F$ in water at 0 °C. Most kinetic runs were followed by spectrophotometric monitoring of the reaction product (Co^{3+}, VO_2^+, Cr(VI)), using a Zeiss PMQ-11 spectrophotometer equipped with a thermostated (±0.1 °C), rapid-mixing (<1 s) sample compartment. Twenty to thirty data points of absorbance vs. time were collected for each experiment, and these were fitted graphically to the expression $\ln (A(\infty) - A(t)) = -k't$ where $A(t)$ and $A(\infty)$ are respectively the absorbances of the product species at variable time and at infinity. Wavelengths used were 350 nm for $HCrO_4^-$, 313 and 340 nm for VO_2^+, and 280 nm for Co^{3+}.

In the few experiments that were carried out on the kinetics of decomposition of aqueous fluoroxysulfate, samples of the reaction mixture were periodically delivered into a weakly alkaline chlorite solution. The ClO_2 formed was determined by its optical absorption at 358 nm and was taken as a measure of the fluoroxysulfate concentration.[4] Rate constants were then obtained from plots of ln $[SO_4F^-]$ vs. time.

Except when noted otherwise, the logarithmic kinetic plots were linear for at least 60% of the reaction and usually for considerably longer.

Results and Discussion

Catalyzed Reactions. The kinetic and stoichiometric results of studies of the silver(I)-catalyzed oxidation of Cr^{3+}, VO^{2+}, and Co^{2+} appear in Table I. The speed of these reactions necessitated the use of very low Ag^+ concentrations. The average stoichiometric ratios $[Cr(VI)]_\infty/[SO_4F^-]_0$, $[VO_2^+]_\infty/[SO_4F^-]_0$, and $[Co^{3+}]_\infty/[SO_4F^-]_0$ are respectively 0.63 ± 0.05, 1.80 ± 0.1, and 1.66 ± 0.15. These values are respectively 6%, 10%, and 17% below the expected ratios for reactions 1–3. In general, the stoichiometries tend toward the theoretical values as the Ag^+ and reductant concentrations increase.

Table I. Silver-Catalyzed Oxidations by Fluoroxysulfate[a]

T, °C	$10^5 \times [Ag^+]_0$, M	$10^2 \times [\text{substrate}]_0$, M	$[\text{product}]_\infty/[SO_4F^-]_0$	$10^2 \times k'$,[b] s^{-1}	$10^2 \times k_{cor}'$,[c] s^{-1}	$10^{-2} \times k$,[d] $M^{-1}\ s^{-1}$
		Substrate Cr^{3+}; Product Cr(VI)[e]				
4.0	1.52	1.10	0.64	1.05	1.04	6.8
4.0	3.05	1.10	0.68	2.06	2.05	6.7
10.0	1.52	1.10	0.60	1.39	1.36	8.9
10.0	3.05	1.10	0.66	2.69	2.66	8.7
17.0	1.12	0.362	0.60	1.33	1.27	11.3
17.0	1.12	1.81	0.62	1.40	1.34	12.0
17.0	1.12	3.62	0.60	1.47	1.41	12.6
17.0	0.561	0.364	0.59	0.71	0.65	11.6
17.0	2.21	0.358	0.65	2.64	2.58	11.7
		Substrate VO^{2+}; Product VO_2^+[e]				
4.0	1.52	0.674	1.84	1.16	1.14	7.5
4.0	3.05	0.674	1.88	2.25	2.23	7.3
10.0	1.52	0.674	1.80	1.46	1.43	9.4
10.0	3.05	0.674	1.86	2.88	2.85	9.3
17.0	1.12	0.222	1.68	1.30	1.23	11.0
17.0	1.12	0.740	1.77	1.46	1.39	12.4
17.0	1.12	1.76	1.81	1.49	1.40	12.5
17.0	0.561	1.76	1.74	0.78	0.69	12.3
17.0	2.21	1.76	1.81	2.97	2.88	13.0
		Substrate Co^{2+}; Product Co^{3+}[f]				
4.0	1.27	9.57	1.66	0.99	0.95	7.5
4.0	2.54	9.57	1.76	1.95	1.91	7.5
10.0	1.27	9.57	1.77	1.31	1.23	9.7
10.0	2.54	9.57	1.80	2.53	2.55	10.0
17.0	1.12	1.42	1.49	1.75	1.67	14.9
17.0	1.12	4.73	1.58	1.62	1.48	13.2
17.0	1.12	9.52	1.67	1.64	1.48	13.2
17.0	0.561	9.52	1.59	0.93	0.77	13.7

[a] In 1.0 M $HClO_4$. Cations were added as the perchlorates, except for silver, which was added as the nitrate. [b] Slope of plot of $\ln (A_\infty - A)$ vs. time. [c] Obtained by correcting k' for the reaction of SO_4F^- in the absence of catalyst. This was accomplished by subtracting from k' a quantity equal to $-d \ln [SO_4F^-]/dt$ in the particular medium in the absence of $[Ag^+]$. For the cobalt and vanadium systems this correction was derived from the 1 M $HClO_4$ data in Tables III and IV, respectively. For the chromium system, the correction was based on the rate of decomposition of SO_4F^- in 1 M $HClO_4$ given in Table V, since this rate was not found to be significantly affected by the presence of small quantities of Cr^{3+} and Cr(VI). [d] $k = k_{cor}'/[Ag^+]$. [e] $[SO_4F^-]_0 = (3.6\text{–}3.7) \times 10^{-4}$ M. [f] $[SO_4F^-]_0 = 5.7 \times 10^{-4}$ M.

$$2Cr^{3+} + 3SO_4F^- + 8H_2O \rightarrow 2HCrO_4^- + 3HSO_4^- + 3HF + 8H^+ \quad (1)$$

$$2VO^{2+} + SO_4F^- + 2H_2O \rightarrow 2VO_2^+ + HSO_4^- + HF + 2H^+ \quad (2)$$

$$2Co^{2+} + SO_4F^- + 2H^+ \rightarrow 2Co^{3+} + HSO_4^- + HF \quad (3)$$

After correction for the small contribution from the uncatalyzed reactions (vide infra) and from the decomposition of aqueous SO_4F^-,[4] the pseudo-first-order rate constants k'_{cor} in all three systems appear to be directly dependent on the Ag^+ concentration and nearly independent of the concentration of reductant, in accordance with a rate law

$$-d[SO_4F^-]/dt = k[Ag^+][SO_4F^-]$$

where $k = k'_{cor}/[Ag^+]$. Values of the bimolecular rate constant k are given in the last column of Table I. Activation parameters derived from the temperature dependences of k are given in Table II.

Within experimental uncertainty the values of k and the corresponding activation parameters are the same for all three

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Table II. Activation Parameters for Reactions of SO_4F^-

substrate and medium[a]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol deg)	ref
ClO_2^-, $I = 1$ M	$7._3$	−14	4
Ag^+ (Cr^{3+}), 1 M $HClO_4$	$6._3$	−23	*b*
Ag^+ (VO^{2+}), 1 M $HClO_4$	$5._6$	−25	*b*
Ag^+ (Co^{2+}), 1 M $HClO_4$	$6._5$	−22	*b*
Co^{2+}, $I = 2$ M	$15._3$	−15	*c*
H_2O, 0.01 M $HClO_4$	$16._8$	−16	4
H_2O, 1 M $HClO_4$	$18._0$	−11	*d*
H_2O (Co^{2+}), $I = 2$ M	$18._0$	−11	*e*
H_2O (VO^{2+}), 0.9–1 M $HClO_4$	$16._9$	−15	*f*

[a] I = ionic strength. [b] Based on temperature dependence of k from Table I. [c] Based on temperature dependence of $k_{Co^{2+}}$ from Table III. [d] Based on temperature dependence of k_d from Table V. [e] Based on temperature dependence of k_d from Table III. [f] Based on temperature dependence of k' from Table IV, with use of experiments with $[VO^{2+}]_0 = 0.007 - 0.009$ M

systems, leading us to postulate that the rate-determining step for all three reactions is

$$SO_4F^- + Ag^+ \rightarrow SO_4^- + Ag^{2+} + HF$$

Both SO_4^- and Ag^{2+} may be effective in oxidizing the reducing substrate, and the SO_4^- may also produce more Ag^{2+} from Ag^+.[14] We cannot, however, rule out a possible two-electron rate-determining step to produce silver(III), for example

$$SO_4F^- + Ag^+ \rightarrow SO_4^{2-} + AgF^{2+}$$

The oxidation of chromium(III) presumably proceeds by way of one or more chromium species of intermediate oxidation state. These may be oxidized by the Ag^{2+} or by the SO_4^- but not directly by SO_4F^-, since their direct reaction with fluoroxysulfate would make the bimolecular rate constant for the chromium system larger than those for the other reductants.

The reaction schemes that we are proposing here are very similar to those proposed for the corresponding Ag^+-catalyzed oxidations by peroxydisulfate.[15] The most striking difference between the two systems is the nearly 10^6-fold greater rate of the reaction between SO_4F^- and Ag^+.

The rate constants for the oxidation of Cr^{3+}, VO^{2+}, and Co^{2+} by Ag^{2+} are known,[16] and they are large enough to maintain essentially steady-state concentrations of Ag^{2+} under our experimental conditions. We estimate that in our experiments the Ag^{2+} concentration is never more than 1% of the Ag^+ concentration. This condition should tend to minimize the oxidation of water by silver(III) formed in the equilibrium[17]

$$2Ag^{2+} \rightleftarrows Ag^+ + Ag^{3+}$$

Nevertheless, the oxidation of water by Ag^{3+} probably accounts for the observed deviations from the predicted stoichiometry. The fact that the deviations are greatest in the cobalt system implies that Co^{2+} reacts more slowly with SO_4^- than do the other reductants, while the decrease in the deviation as the Ag^+ increases confirms our suggestion that Ag^+ is itself acting as a scavenger of SO_4^-.

In an effort to determine possible catalysis of the SO_4F^-–VO^{2+} reaction by divalent copper or nickel, we examined the effect of 1.2×10^{-3} M $CuSO_4$ or $Ni(ClO_4)_2$ on the reaction of 6.8×10^{-4} M SO_4F^- with 0.0135 M $VO(ClO_4)_2$ in 0.94 M $HClO_4$ at 17 °C. Pseudo-first-order rate constants were found to be 6.1×10^{-4} s^{-1} in the absence of "catalyst", 5.7×10^{-4} s^{-1} in the presence of Cu^{2+}, and 7.6×10^{-4} s^{-1} in the presence of Ni^{2+}. We conclude, therefore, that under these conditions Cu^{2+} and Ni^{2+} show little or no catalytic activity.

Table III. Kinetics and Stoichiometry of the Uncatalyzed Reaction between Co^{2+} and SO_4F^- [a]

T, °C	$[Co(ClO_4)_2]_0$, M	$[HClO_4]$, M	$[Co^{3+}]_\infty/[SO_4F^-]_0$	$10^3 \times k'$,[b] s^{-1}	$10^3 \times k_d$,[c] s^{-1}	$10^3 \times k_{Co^{2+}}$,[d] M^{-1} s^{-1}
4.0	0.574	0.363	1.91	1.89	0.155	3.03
4.0	0.230	0.282	1.68	0.868		
4.0	0.097	0.242	1.39	0.433		
10.0	0.574	0.363	1.92	3.58	0.296[i]	5.74[i]
10.0	0.230	0.282	1.66	1.65		
10.0	0.230	0.574	1.70	1.52		
10.0	0.230	1.31	1.50	1.38		
10.0	0.0957	0.242	1.38	0.838		
10.0	0.0479	0.242	1.06	0.556		
17.0	0.574	0.363	1.94	7.00	0.701	11.05
17.0	0.230	0.282	1.71	3.38		
17.0[e]	0.0957	0.242	1.33	1.68		
17.0[f]	0.0479	0.242	1.00	1.21		
17.0[g]	0.0479	0.225	0.98	1.18		
17.0[h]	0.0957	1.00	1.20	1.60		
17.0[h]	0.0479	1.00	1.06	1.41		
17.0[h]	0.0144	1.00	0.60	0.805		
10.0[h]	0.0957	1.00	1.27	0.811		
4.0[h]	0.0957	1.00	1.25	0.41		

[a] $[SO_4F^-]_0 = (8–10) \times 10^{-4}$ M. Unless otherwise indicated, ionic strength was maintained at 2.0 M by addition of $LiClO_4$. [b] Slope of plot of ln ($A_\infty - A$) vs. time. [c] Intercept of plot of k' vs. $[Co^{2+}]_0$. [d] Slope of plot of k' vs. $[Co^{2+}]_0$. [e] $[SO_4F^-]_0 = 7.98 \times 10^{-4}$ M, $[S_2O_8^{2-}]_\infty = 2.6 \times 10^{-4}$ M. [f] $[SO_4F^-]_0 = 9.22 \times 10^{-4}$ M, $[S_2O_8^{2-}]_\infty = 2.3 \times 10^{-4}$ M. [g] Ionic strength maintained at 2.0 M by addition of $Zn(ClO_4)_2$. [h] No other electrolyte added. Ionic strength 1.0–1.3 M. [i] Excluding data for 0.57 and 1.3 M $HClO_4$.

Uncatalyzed Reaction of SO_4F^- with Co^{2+}. Kinetic and stoichiometric data for this relatively slow reaction are given in Table III. At the highest concentrations of Co^{2+} used, the reaction stoichiometry approaches that corresponding to reaction 3. In addition to the measurements of $[Co^{3+}]_\infty/[SO_4F^-]_0$ shown in Table III, the stoichiometry was confirmed by a measurement of the sulfate and bisulfate produced in the reaction of 0.0442 M SO_4F^- with 0.54 M $Co(ClO_4)_2$ in 0.34 M $HClO_4$ at ca. 25 °C. After reaction $[SO_4^{2-}] + [HSO_4^-]$ was found to be 0.0416 M.

At intermediate concentrations of Co^{2+}, another oxidized species is formed in addition to Co^{3+}. Within experimental error, this species appears to be entirely $S_2O_8^{2-}$. At very low Co^{2+} concentrations, O_2 is also formed. The source of this oxygen was determined by isotopic analysis of the gas produced in the room-temperature reaction of 0.018 M SO_4F^- (0.166 mmol) with 0.0155 M $Co(ClO_4)_2$ in 0.2 M $HClO_4$ made up in water whose oxygen was 1.56_5 atom % ^{18}O. The oxygen evolved (0.06 mmol after ca. 80% reaction) was 1.47_8 atom % ^{18}O, indicating that some 94% of it had come from the solvent (assuming the fluoroxysulfate oxygen to have the natural ^{18}O abundance of 0.20_3 atom %).

Under conditions such that O_2 formation is significant, production of bisulfate and HF is reduced, indicating that SO_3F^- is being formed. Thus the room-temperature reaction of 0.0196 M SO_4F^- with 0.03 M $Co(ClO_4)_2$ in 0.14 M $HClO_4$ produced $([HSO_4^-] + [SO_4^{2-}]) = ([HF] + [F^-]) = 0.012$ M.

The pseudo-first-order rate constants k' given in Table III show only a minor dependence on $[H^+]$. At each temperature, however, they show a linear dependence on $[Co^{2+}]$, with a positive intercept. Least-squares treatment of the data yields the values of the slopes and intercepts that are given in the last two columns. The intercepts are comparable in magnitude

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to the rate constants for the decomposition of SO_4F^- in a similar aqueous medium (see Table V). This suggests that the reaction of SO_4F^- with Co^{2+} consists of the superposition of a bimolecular reaction on the first-order SO_4F^- decomposition, leading to the rate law

$$-d[SO_4F^-]/dt = k_{Co^{2+}}[Co^{2+}][SO_4F^-] + k_d[SO_4F^-]$$

At the lowest Co^{2+} concentrations in Table III, the k_d pathway accounts for approximately 50% of the overall reaction. Attempts to work at still lower $[Co^{2+}]$ resulted in irreproducible kinetic and stoichiometric results. The results in Table III do not permit a definite answer to the question of whether or not Co^{2+} is actually oxidized by the k_d path. The activation parameters derived from the temperature dependence of k_d and $k_{Co^{2+}}$ are given in Table II.

A number of facts must be taken into account in devising a mechanism for the uncatalyzed reaction between SO_4F^- and Co^{2+}. The formation of $S_2O_8^{2-}$ implies the participation of SO_4^- radicals, and we suggest eq 4–6 for the bimolecular reaction path, where eq 6 becomes significant as the Co^{2+} concentration is reduced.

$$Co^{2+} + SO_4F^- \xrightarrow[H^+]{k_{Co^{2+}}} Co^{3+} + SO_4^- + HF \qquad (4)$$

$$Co^{2+} + SO_4^- \rightarrow Co^{3+} + SO_4^{2-} \qquad (5)$$

$$2SO_4^- \rightarrow S_2O_8^{2-} \qquad (6)$$

Turning to the first-order path, we note that significant quantities of oxygen are evolved when this path becomes important. This oxygen comes almost entirely from the solvent, in contrast to the oxygen produced in the decomposition of aqueous fluoroxysulfate, which comes half from the solvent and half from the SO_4F^-.[4] In addition to O_2, the decomposition of aqueous SO_4F^- produces H_2O_2 and HSO_5^-.[4] The H_2O_2, like the O_2, contains one oxygen from solvent and one from the SO_4F^-, while the HSO_5^- contains solvent-derived oxygen as the terminal oxygen atom in its peroxide moiety.[4]

Significant production of H_2O_2 from SO_4F^- cannot be taking place in the cobalt system, since any such H_2O_2 would be oxidized to O_2 that derived half its oxygen from the fluoroxysulfate. Hence the formation of H_2O_2 from SO_4F^- must somehow be inhibited in the cobalt system. We have also observed that peroxymonosulfate is rapidly oxidized to O_2 by a mixture of Co^{2+} and Co^{3+}, and we have found that the evolved O_2 has an isotopic composition approximating that of the terminal peroxide oxygen atoms. For example, when $O_3SOO^*H^-$ is prepared by the reaction of SO_4F^- with H_2O^* whose oxygen is 1.53 atom % ^{18}O and is then allowed to react with 0.001–0.2 M $Co(ClO_4)_2$ in 0.5 M $HClO_4$, the evolved O_2 contains 1.48 atom % ^{18}O. Thus the O_2 produced in the Co^{2+}–SO_4F^- system could come from decomposition of HSO_5^-.

We postulate that the initial steps in the first-order decomposition of aqueous SO_4F^- consist of the parallel reactions

$$SO_4F^- + H_2O^* \xrightarrow{k_a} O_3SOO^*H^- + HF$$

$$SO_4F^- + H_2O^* \xrightarrow{k_b} I \rightarrow SO_3F^- + HOO^*H$$

We further suggest that the cobalt species do not interfere with the k_a path, other than to decompose the $O_3SOO^*H^-$ to O^*_2, but that Co^{2+} scavenges the intermediate I and thereby prevents the formation of H_2O_2

$$2Co^{2+} + I \rightarrow SO_3F^- + 2Co^{3+}$$

The intermediate I must therefore be more reactive than SO_4F^- itself. We have no real clues as to its identity, but possibilities are the peroxy isomer of SO_4F^-, $O_2S(F)OO^-$, or an unsymmetrical isomer of hydrogen peroxide, H_2O–O.

Table IV. Kinetics and Stoichiometry of the Uncatalyzed Reaction between VO^{2+} and SO_4F^- [a]

T, °C	$[VO(ClO_4)_2]_0$, M	$[HClO_4]$, M	$[VO_2^+]/[SO_4F^-]_0$	$10^3k'$,[b] s^{-1}
29.5	0.106	0.97	1.62	3.9
29.5	0.0190	0.95	1.32	2.8
29.5	0.0090	0.91	1.16	2.3
29.5	0.00186	0.98	0.81	2.0
29.5	0.00105	0.98	0.70	1.8
29.5	0.0190	0.49	1.17	2.8
29.5	0.0190	0.088	1.66	3.9
29.5	0.0190	0.020	1.83	4.8
17.0	0.00237	1.0	0.98	0.66
17.0	0.00711	1.0	1.10	0.66
17.0	0.0178	1.0	1.37	0.89
10.0	0.00711	1.0	1.15	0.31
17.0[c]	0.0479	0.33	1.48	1.2[d]
17.0[c]	0.101	0.33	1.51	1.7
17.0[c]	0.201	0.31	1.53	1.6[e]
17.0[c]	0.403	0.32	1.60	4.2[e]

[a] $[SO_4F^-]_0 = (6.6–11.3) \times 10^{-4}$ M. Unless otherwise specified, $LiClO_4$ was added when required to make ionic strength approximately 1.0 M. [b] Slope of plot of $\ln (A_\infty - A)$ vs. time. [c] $Zn(ClO_4)_2$ added to make ionic strength 2.0 M. [d] Logarithmic plot only linear for 55% of reaction. Curvature at longer time was in the direction corresponding to larger k'. [e] Logarithmic plot only linear for 35–37% of reaction. Curvature at longer time was in the direction corresponding to larger k'.

Table V. Rate of Decomposition of SO_4F^- in Various Aqueous Media

T, °C	medium	10^4k_d, s^{-1}
4.0	1 M $HClO_4$	1.3
10.0	1 M $HClO_4$	2.6
17.0	1 M $HClO_4$	5.9
29.5	1 M $HClO_4$	22[a]
17.0	0.3 M $HClO_4$, 1.7 M $LiClO_4$	6.2

[a] Extrapolated value.

In our previous study[4] we postulated that in the absence of cobalt a substantial portion of the H_2O_2 is oxidized to O_2 by SO_4F^-. Hence the scavenging of the precursor of the H_2O_2 by Co^{2+} should result in a decrease in k_d. Such a decrease is not evident in our data, which may be telling us that the reaction system is considerably more complex than our simple scheme implies.

Uncatalyzed Reactions of VO^{2+} with SO_4F^-. This reaction is also relatively slow. Some kinetic and stoichiometric data appear in Table IV. The stoichiometric ratio $[VO_2^+]_\infty/[SO_4F^-]_0$ is quite variable; it increases with increasing $[VO^{2+}]_0$ and decreases with increasing acidity. The pseudo-first-order rate constant is somewhat larger than k_d for the decomposition of aqueous SO_4F^- (see Table V), but only at the very highest VO^{2+} concentrations is there a strong dependence of k' on $[VO^{2+}]$, and under these conditions the kinetic plots were rather poor.

Small amounts of $S_2O_8^{2-}$ and O_2 are produced in the course of the reaction. For example, the reaction of 0.01 M SO_4F^- with 0.03–0.06 M VO^{2+} in 1 M $HClO_4$ at 20 °C produced 0.0015–0.0016 M $S_2O_8^{2-}$. To determine the quantity of O_2 formed and its source, we allowed 0.011 M $CsSO_4F$ (0.16 mmol) to react with 0.022 M $VO(ClO_4)_2$ in 1 M $HClO_4$ at 24–25 °C, in water whose oxygen was 1.38_1 atom % ^{18}O. The resulting O_2 (0.0235 mmol) contained 0.76_2 atom % ^{18}O, which indicates that about half (47.5%) of this oxygen came from the solvent.[18]

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(18) The solvent in this experiment was partially enriched in ^{18}O. However, we have found that when normal HSO_5^- reacts with Co^{2+} in enriched water, the evolved oxygen is not significantly enriched in ^{18}O.

This reaction is undoubtedly complicated by the reactivity of VO^{2+} toward both HSO_5^- and H_2O_2. We have found the former reaction to proceed quite rapidly, with a bimolecular rate constant of 13 $M^{-1}\ s^{-1}$ at 24 °C in 1 M $HClO_4$. For initial VO^{2+} and HSO_5^- concentrations of 2.16×10^{-2} and 2.71×10^{-4} M, respectively, 5.09×10^{-4} M VO_2^+ is produced. We therefore conclude that any HSO_5^- formed from the fluoroxysulfate will rapidly and nearly quantitatively oxidize VO^{2+} to VO_2^+.

The reaction between VO^{2+} and H_2O_2 has been carefully studied by Brooks and Sicilio.[19] The reaction is complicated, but the rate is comparable to the reaction rates in Table IV. The reaction usually oxidizes less than 2 mol of VO^{2+}/mol of H_2O_2, and the stoichiometry varies considerably with experimental conditions. This variability may account for the variations in stoichiometry of the VO^{2+}–SO_4F^- reaction. Our isotopic results are consistent with the O_2 product deriving from oxidation of H_2O_2.

All in all, we do not have a very clear understanding of the VO^{2+}–SO_4F^- system. It does seem, however, that VO^{2+} is somewhat less reactive toward SO_4F^- than is Co^{2+}. It also differs from Co^{2+} in that it does not appear to scavenge the precursor of H_2O_2 formed in the decomposition of aqueous SO_4F^-. Since VO^{2+} is generally considered to be a much better reducing agent than Co^{2+}, these are rather remarkable conclusions.

General Observations

Perhaps the most surprising feature of the aqueous chemistry of fluoroxysulfate is the enormous selectivity that this oxidant displays in its reactions with reducing substrates. The fluoroxysulfate ion shows this selectivity despite its formidable thermodynamic oxidizing power.[3] The relative reactivities toward SO_4F^- of the reductants that have been studied to date stand in the order $ClO_2^- > Ag^+ >>> Co^{2+} > VO^{2+} > H_2O >>> Cr^{3+}$. It is clear that thermodynamic driving force is not a major factor in determining these reactivities, but at the present time we are not in a position to say what is.

The rapid oxidation of Ag^+ seems especially noteworthy, since it is thermodynamically the poorest reductant of all those studied. There appears to be very little in the way of an activation barrier to the oxidation of Ag^+. Even peroxydisulfate, which has barely enough thermodynamic oxidizing power to effect this oxidation, does so at a significant rate. We are not aware of any explanation that has been offered for this surprising redox lability of the Ag^+–Ag^{2+} couple.

From a practical standpoint, the use of Ag^+ as an oxidation catalyst considerably extends the range of oxidations that can be effected with the fluoroxysulfates and makes it seem likely that these salts will find significant application as chemical reagents.

At this time we can claim only the most rudimentary understanding of the uncatalyzed reactions between SO_4F^- and VO^{2+} or Co^{2+}. It appears that when the rate of reaction of fluoroxysulfate with a substrate is comparable to the rate of its reaction with water, the system can become extraordinarily complicated. This is undoubtedly due at least in part to the variety of products and intermediates that are formed in the course of the water reaction.

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Registry No. SO_4F^-, 73347-64-5; Cr^{3+}, 16065-83-1; Co^{2+}, 22541-53-3; VO^{2+}, 20644-97-7; Ag^+, 14701-21-4.

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Preparation of the $XeOTeF_5^+$, $FXeFXeOTeF_5^+$, $XeF_2{\cdot}BrOF_2^+$, and $XeOSO_2F^+$ Cations and Their Study by ^{129}Xe, ^{125}Te, and ^{19}F Pulse Fourier Transform NMR and Raman Spectroscopy[1]

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The reactions of $XeOTeF_5^+AsF_6^-$ with BrF_5 have been studied in solution by multinuclear NMR spectroscopy and shown to yield the new fluorine-bridged cations $FXeFXeOTeF_5^+$ and $XeF_2{\cdot}BrOF_2^+$. The latter has also been isolated at low temperature as its AsF_6^- salt and characterized in the solid state by Raman spectroscopy. The previously reported $XeOTF_5^+$ cation has been more fully characterized by Raman spectroscopy of its AsF_6^- and $Sb_2F_{11}^-$ salts and by multinuclear NMR spectroscopy and its solution structure unambiguously established. ^{129}Xe and ^{19}F NMR evidence has also been obtained for the $XeOSO_2F^+$ cation by dissolving $XeOTeF_5^+AsF_6^-$ in HSO_3F.

Introduction

The pentafluoroorthotellurate group, $OTeF_5$, is capable of stabilizing the +2, +4, and +6 oxidation states of xenon[3-7] and is highly electronegative.[8] Sladky[3-5] has prepared and characterized several xenon(II) derivatives containing the $OTeF_5$ group according to the sequence of reactions given by eq 1–3. Both $FXeOTeF_5$ and $Xe(OTeF_5)_2$ have been characterized by ^{19}F[3,4] and ^{129}Xe[9] NMR and Raman[3,4] spectroscopy. Previous evidence for the $XeOTeF_5^+$ cation was based on the Raman spectrum of its AsF_6^- salt.[5] Prior to this present study of ours, no $OTeF_5$ and analogues of the V-shaped $Xe_2F_3^+$ cation had been reported. Sladky[4] has shown that $XeOTeF_5^+AsF_6^-$ and XeF_2 react at 60 °C according to eq 4.

$$2HOTeF_5 + XeF_2 \rightarrow Xe(OTeF_5)_2 + 2HF \qquad (1)$$

$$Xe(OTeF_5)_2 + XeF_2 \rightarrow 2FXeOTeF_5 \qquad (2)$$

$$FXeOTeF_5 + AsF_5 \rightarrow XeOTeF_5^+AsF_6^- \qquad (3)$$

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