

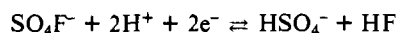
Oxidation of Aqueous Ru(bpy)<sub>3</sub><sup>2+</sup> by the Fluoroxysulfate Ion, SO<sub>4</sub>F<sup>-1</sup>Richard L. Cook,<sup>†</sup> Mary Woods,<sup>‡</sup> James C. Sullivan,\* and Evan H. Appelman\*

Received December 28, 1988

Stopped-flow spectrophotometry has been used to study the oxidation of the substitution-inert Ru(II) complex ion Ru(bpy)<sub>3</sub><sup>2+</sup> by the fluoroxysulfate ion, SO<sub>4</sub>F<sup>-</sup>. The reaction follows a bimolecular rate law and has 1:1 stoichiometry. At 13.3 °C, corrected to infinite dilution,  $k_2^0 = 1346 \pm 19 \text{ M}^{-1} \text{ s}^{-1}$ . Over the temperature range 2–24 °C,  $\Delta H^\ddagger = 37.1 \pm 1.1 \text{ kJ/mol}$  and  $\Delta S^\ddagger = -55 \pm 4 \text{ J/(mol K)}$ . The rate and stoichiometry are independent of whether the Ru complex is present as a chloride or a perchlorate salt, and the rate does not show a dependence on acidity. The oxidation of coordinated ligands is probably involved. The reaction is among the fastest reactions of SO<sub>4</sub>F<sup>-</sup>.

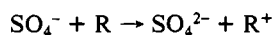
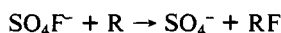
## Introduction

The fluoroxysulfate ion is an ionic hypofluorite with the formula SO<sub>4</sub>F<sup>-</sup>. It is usually prepared in the form of its cesium salt, which is soluble in water to the extent of about 0.5 M at room temperature.<sup>2</sup> The aqueous solutions decompose with a half-time of about 24 min at 20 °C.<sup>3</sup> The half-reaction



has a standard electrode potential of 2.47 V,<sup>4</sup> setting the fluoroxysulfate ion among the thermodynamically most powerful oxidants that can be handled in water. Nevertheless, previous studies have shown the ion to be quite selective in its reactions with aqueous reductants.<sup>3,5</sup> With some reductants, such as Ag<sup>+</sup> and ClO<sub>2</sub><sup>-</sup>, it reacts extremely rapidly, with bimolecular rate constants in excess of 1000 M<sup>-1</sup> s<sup>-1</sup>; with others, such as Co<sup>2+</sup> and VO<sup>2+</sup>, it only reacts very slowly, with rate constants less than 0.1 M<sup>-1</sup> s<sup>-1</sup>, while with still others, such as Cr<sup>3+</sup> in strong acid, it does not appear to react at all.

The detailed mechanism by which oxidations with fluoroxysulfate take place is not clear. Thompson and Appelman<sup>3</sup> have suggested a one-electron fluorine atom transfer process:



They adduced in evidence the observation that the oxidation of Cr<sup>2+</sup> by fluoroxysulfate produces an approximately equimolar mixture of hexaaquochromium(III) and fluorochromium(III). Such a mechanism, however, need not apply to reactions with other reductants. In this paper we report an investigation of the kinetics of reaction of fluoroxysulfate with the substitution-inert complex Ru(bpy)<sub>3</sub><sup>2+</sup> (bpy = 2,2'-bipyridine).

## Experimental Section

**Materials.** Cesium fluoroxysulfate (98%) was prepared by fluorination of an aqueous solution of cesium sulfate<sup>6</sup> and isolated as described previously.<sup>7</sup> Ru(bpy)<sub>3</sub>Cl<sub>2</sub> was obtained from G. F. Smith Chemical Co. To prepare a solution or Ru(bpy)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>, a solution of the chloride was first converted to the hydroxide by passage through an anion-exchange column in the hydroxide form, and the hydroxide solution was then neutralized potentiometrically with perchloric acid. Distilled water was redistilled first from alkaline permanganate and then from acidic dichromate. Other materials were commercial products of reagent grade.

**Analytical Procedures.** Fluoroxysulfate solutions were analyzed iodometrically as described previously.<sup>7</sup> Ru(bpy)<sub>3</sub><sup>2+</sup> solutions were analyzed spectrophotometrically, by using either a Perkin-Elmer 330 or a Cary 14 spectrophotometer. The extinction coefficient of Ru(bpy)<sub>3</sub><sup>2+</sup> was taken to be 14 200 M<sup>-1</sup> cm<sup>-1</sup> at 452 nm.<sup>8</sup> The qualitative analysis of evolved gases was carried out with a Finnigan 400 quadrupole mass spectrometer.

**Kinetic Measurements.** Stopped-flow spectrophotometric measurements of reaction kinetics and processing of the spectrophotometric data to obtain optical densities were carried out in the manner previously described.<sup>7</sup> The optical densities were fitted to a three-parameter first-

Table I. Stoichiometry of the Reaction of Ru(bpy)<sub>3</sub><sup>2+</sup> with SO<sub>4</sub>F<sup>-a</sup>

init concn, M			init concn, M		
10 <sup>6</sup> [Ru-(bpy) <sub>3</sub> <sup>2+</sup> ] <sub>0</sub>	10 <sup>6</sup> [SO <sub>4</sub> F] <sub>0</sub>	R <sup>b</sup>	10 <sup>6</sup> [Ru-(bpy) <sub>3</sub> <sup>2+</sup> ] <sub>0</sub>	10 <sup>6</sup> [SO <sub>4</sub> F] <sub>0</sub>	R <sup>b</sup>
Ru(bpy) <sub>3</sub> Cl <sub>2</sub>					
114	57	1.10	58	40.5	0.97
110	92	0.96	188	143.5	1.03
59	20.6	1.01			
Ru(bpy) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>					
39.3	35.2	0.99	71	52.6	1.01
40.2	22.3	1.03			

<sup>a</sup>No added electrolyte. <sup>b</sup>R = Δ[Ru(bpy)<sub>3</sub><sup>2+</sup>]/[SO<sub>4</sub>F]<sub>0</sub>.

order rate equation, with use of a nonlinear least-squares program.

A serious experimental difficulty in these studies was the instability of the oxidant solutions. These solutions were made up at the ice point and brought to temperature in the spectrophotometer immediately before use. Nevertheless, significant decomposition took place during the time it took to carry out a series of measurements, particularly at the highest temperatures. The solution of oxidant was analyzed iodometrically at the beginning and end of the series, and an attempt was made to interpolate the concentration of SO<sub>4</sub>F<sup>-</sup> at the time of each "shot". This correction was less than satisfactory, however, because of the buildup of peroxymonosulfate and hydrogen peroxide as byproducts of the decomposition.<sup>3</sup> These compounds react to a greater or lesser extent with iodide but appear to be unreactive toward Ru(bpy)<sub>3</sub><sup>2+</sup> over a period of many minutes. Therefore, in our experiments at the highest temperatures only the first one or two shots were usually used in the analysis.

Other sources of error were formation of gas bubbles and CsClO<sub>4</sub> precipitate in the light path. These usually manifested themselves as obvious irregularities in the signal during the reaction, and signals displaying such irregularities were discarded. Under some conditions, the reaction solutions were supersaturated in Ru(bpy)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>, and precipitation of this salt also took place. In perchlorate solutions, the initial Ru(bpy)<sub>3</sub><sup>2+</sup> concentration was always deduced empirically from the initial optical density calculated from the first-order least-squares fit of the data.

## Results

**Qualitative Observations and Stoichiometry.** Mixing of an Ru(bpy)<sub>3</sub><sup>2+</sup> solution with excess fluoroxysulfate on the benchtop led to an instantaneous discharge of the typical color of the Ru(II) complex. The product had the characteristic spectrum of a solution of Ru(bpy)<sub>3</sub><sup>3+</sup> (as determined by the oxidation of Ru(bpy)<sub>3</sub><sup>2+</sup> with

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<sup>†</sup> Student research participant from Andrews University, Berrien Springs, MI, sponsored in part by the Argonne Division of Educational Programs.

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**Table II.** Kinetics of the Reaction of Ru(bpy)<sub>3</sub><sup>2+</sup> with SO<sub>4</sub>F<sup>-</sup> in Water<sup>a</sup>

10 <sup>3</sup> [SO <sub>4</sub> F <sup>-</sup> ] <sub>0</sub> , M	k <sub>1</sub> (μ), <sup>b</sup> s <sup>-1</sup>	k <sub>1</sub> <sup>o</sup> , <sup>c</sup> s <sup>-1</sup>	k <sub>2</sub> <sup>o</sup> , <sup>d</sup> M <sup>-1</sup> s <sup>-1</sup>
2.5 °C			
1.09	0.57	0.67	637
2.70	1.36	1.71	645
4.56	2.44	3.27	725
7.48	4.04	5.82	782
16.7	7.03	11.8	709
			mean: <sup>e</sup> 699 ± 49
13.3 °C			
2.00	2.08	2.56	1312
3.94	4.02	5.32	1365
7.38	6.81	9.85	1342
12.1	10.3	16.3	1347
			mean: <sup>e</sup> 1346 ± 19
13.6 °C <sup>f</sup>			
1.53	1.65	1.99	1338
2.71	2.99	3.80	1426
4.93	5.25	7.15	1462
9.21	8.80	13.2	1444
			mean: <sup>e</sup> 1418 ± 52
23.6 °C			
1.51	2.92	3.52	2401 <sup>g</sup>
2.41	4.25	5.35	2261
4.03	7.24	9.66	2421
5.82	10.1	14.1	2441 <sup>h</sup>
			mean: 2374 ± 74

<sup>a</sup> [Ru(bpy)<sub>3</sub><sup>2+</sup>]<sub>0</sub> = (8.7–8.8) × 10<sup>-5</sup> M. Unless otherwise specified, Ru(bpy)<sub>3</sub>Cl<sub>2</sub> was used as the source of Ru(bpy)<sub>3</sub><sup>2+</sup>. Except as noted, entries are representative data from sets of three to five runs taken from the same stock solutions (see text). <sup>b</sup> k<sub>1</sub>(μ) = -d ln [Ru(bpy)<sub>3</sub><sup>2+</sup>]/dt. <sup>c</sup> k<sub>1</sub>(μ) corrected to infinite dilution by means of eq 1 (see text). <sup>d</sup> k<sub>2</sub><sup>o</sup> = k<sub>1</sub><sup>o</sup>/[SO<sub>4</sub>F<sup>-</sup>]<sub>av</sub>. <sup>e</sup> Based on a larger data set (see text). The uncertainty is twice the standard deviation of the mean. <sup>f</sup> Ru(bpy)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> used as the source of Ru(bpy)<sub>3</sub><sup>2+</sup>. <sup>g</sup> From a set of only two runs. <sup>h</sup> A single run.

PbO<sub>2</sub>), but this spectrum appeared to be overlaid by a very broad absorption, which faded in the course of a few minutes. Even with this additional absorption, the product solution was much less intensely absorbing than the original Ru(bpy)<sub>3</sub><sup>2+</sup> solution.

Reaction stoichiometries were determined by measuring spectrophotometrically the amount of Ru(bpy)<sub>3</sub><sup>2+</sup> consumed in a reaction with an insufficiency of fluoroxysulfate. The results are summarized in Table I, and they indicate that for both Ru(bpy)<sub>3</sub>Cl<sub>2</sub> and Ru(bpy)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> the stoichiometry ratio was close to unity.

Five milliliters of 0.0022 M Ru(bpy)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> was mixed with 1.6 mg (1 μmol) of CsSO<sub>4</sub>F on a vacuum line, and the evolved gases were examined by mass spectrometry. Carbon dioxide was the only significant gaseous product seen.

**Kinetic Results.** Table II summarizes the kinetic results in dilute aqueous solution, while Table III summarizes the effect of various concentrations of perchloric acid and sodium perchlorate on the rate at 13.6–13.7 °C. Entries are representative runs taken from the same stock solutions. Within each group the initial Ru(bpy)<sub>3</sub><sup>2+</sup> concentration was constant, but because of the instability of the fluoroxysulfate stock solution, the initial SO<sub>4</sub>F<sup>-</sup> concentration varied somewhat.

Since in dilute solution the varying initial concentrations of fluoroxysulfate cause substantial variations in ionic strength, the pseudo-first-order rate constants were corrected to infinite dilution by means of the relation

$$\log k_1(\mu) = \log k_1^o + 2z_a z_b A \mu^{1/2} / (1 + \mu^{1/2}) \quad (1)$$

in which k<sub>1</sub>(μ) is the pseudo-first-order rate constant observed at ionic strength μ, k<sub>1</sub><sup>o</sup> is the rate constant at infinite dilution, z<sub>a</sub> and z<sub>b</sub> are the charges on the two reactant species, and A is the Debye-Hückel limiting constant. The validity of the use of eq 1 may be judged from the relative constancy of the bimolecular

**Table III.** Reaction of Ru(bpy)<sub>3</sub><sup>2+</sup> with SO<sub>4</sub>F<sup>-</sup> in Electrolyte Solutions<sup>a</sup>

10 <sup>3</sup> [SO <sub>4</sub> F <sup>-</sup> ] <sub>0</sub> , M	k <sub>2</sub> (μ), M <sup>-1</sup> s <sup>-1</sup>	
	obsd <sup>b</sup>	calcd <sup>c</sup>
0.1 M HClO <sub>4</sub>		
1.31	575	
2.38	548	
5.05	484	
9.67	469	
mean: <sup>d</sup> 518 ± 52		505
0.05 M HClO <sub>4</sub>		
2.04	616	
3.87	617	
7.65	609	
mean: <sup>d</sup> 615 ± 4		647
0.05 M NaClO <sub>4</sub>		
1.03	672	
2.49	660	
4.61	672	
9.41	644 <sup>e</sup>	
mean: <sup>d</sup> 658 ± 18		647
Infinite Dilution		
1435 ± 36 <sup>f</sup>		1423

<sup>a</sup> At 13.6–13.7 °C, with Ru(bpy)<sub>3</sub>Cl<sub>2</sub> as the source of Ru(bpy)<sub>3</sub><sup>2+</sup>. [Ru(bpy)<sub>3</sub><sup>2+</sup>]<sub>0</sub> = (8.5–8.7) × 10<sup>-5</sup> M. Except as noted, entries are representative data from sets of three to five runs taken from the same stock solutions (see text). <sup>b</sup> k<sub>2</sub>(μ) = (-d ln [Ru(bpy)<sub>3</sub><sup>2+</sup>]/dt)/[SO<sub>4</sub>F<sup>-</sup>]<sub>av</sub>. <sup>c</sup> Calculated from eq 1 (see text) by using the four mean values of k<sub>2</sub><sup>o</sup> from Table II. <sup>d</sup> Based on a larger data set (see text). The uncertainty is twice the standard deviation of the mean. <sup>e</sup> From a set of only two runs. <sup>f</sup> Value obtained at 13.65 °C from a least-squares fit of the temperature dependence of mean k<sub>2</sub><sup>o</sup> values in Table II. The uncertainty is twice the calculated standard deviation.

rate constants, k<sub>2</sub><sup>o</sup>, which are calculated from k<sub>1</sub><sup>o</sup> by means of the relation

$$k_2^o = k_1^o / [\text{SO}_4\text{F}^-]_{\text{av}}$$

where

$$[\text{SO}_4\text{F}^-]_{\text{av}} = [\text{SO}_4\text{F}^-]_0 - [\text{Ru}(\text{bpy})_3^{2+}]_0 / 2$$

Values of k<sub>2</sub><sup>o</sup> are tabulated in the last column of Table II.

The bimolecular rate constants k<sub>2</sub>(μ) in the second column of Table III are simply the observed pseudo-first-order rate constants divided by [SO<sub>4</sub>F<sup>-</sup>]<sub>av</sub>. Equation 1 may also be used to attempt to correlate these bimolecular rate constants with electrolyte concentration. A linear plot of log k<sub>2</sub>(μ) versus μ<sup>1/2</sup>/(1 + μ<sup>1/2</sup>) should have an intercept of log k<sub>2</sub><sup>o</sup> (i.e. k<sub>2</sub>(μ) at infinite dilution) and a slope equal to 2A<sub>z<sub>a</sub>z<sub>b</sub></sub> = -2.00. The observed least-squares slope is, in fact, -1.87 ± 0.11, and the values of k<sub>2</sub>(μ) calculated from the least-squares fit are given in the last column of Table III. The agreement is better than we might expect at such high electrolyte concentrations, and it is probably at least partly fortuitous.

Activation parameters were calculated from a least-squares analysis of the variation of ln k<sub>2</sub><sup>o</sup>/T with 1/T, with use of the mean constants given in Table II. The results are ΔH<sup>‡</sup> = 37.1 ± 1.1 kJ/mol and ΔS<sup>‡</sup> = -55 ± 4 J/(mol K), where uncertainties are standard deviations.

## Discussion

Perhaps the most puzzling aspect of the reaction of fluoroxysulfate with Ru(bpy)<sub>3</sub><sup>2+</sup> is its stoichiometry. Since the ultimate sulfur-containing product is almost certainly a sulfate species, corresponding to a two-electron reduction of fluoroxysulfate, there would appear to be missing oxidizing power. Our observation of carbon dioxide as a gaseous reaction product suggests that this oxidizing power has gone into oxidative degradation of ligands coordinated to the ruthenium. The susceptibility of coordinated bipyridine to such degradation has been established in a previous study by Ghosh et al.<sup>8</sup> Unfortunately our results do not permit us to formulate a reaction mechanism, or even to identify positively

Table IV. Reactions of the Fluoroxy sulfate Ion

reductant	$k_2$ , <sup>a</sup> M <sup>-1</sup> s <sup>-1</sup>	$\Delta H^\ddagger$ , <sup>b</sup> kJ/mol	$\Delta S^\ddagger$ , <sup>b</sup> J/(mol K)	ref
ClO <sub>2</sub> <sup>-c</sup>	$2.4 \times 10^4$	30.5	-59	3
Ru(bpy) <sub>3</sub> <sup>2+d</sup>	$2.6 \times 10^3$	37	-55	f
Ag <sup>+c</sup>	$2.0 \times 10^3$	25.5	-96	5
Pu <sup>3+c</sup>	$1.9 \times 10^2$	31	-98	7
Co <sup>2+e</sup>	$2.0 \times 10^{-2}$	64	-63	5

<sup>a</sup> For the rate law  $-d[\text{SO}_4\text{F}^-]/dt = k_2[\text{SO}_4\text{F}^-][\text{reductant}]$ , calculated at 25 °C from activation parameters. <sup>b</sup> From the temperature dependence between 0 and 25 °C. <sup>c</sup> At 1 M ionic strength. <sup>d</sup> At infinite dilution. <sup>e</sup> At 2 M ionic strength. <sup>f</sup> This work.

the rate-determining step, which could involve attack either on the ruthenium center or on the ligand. From the fact that Ru(bpy)<sub>3</sub>Cl<sub>2</sub> and Ru(bpy)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> exhibit both the same stoichiometry and the same reaction rate, it would appear that low concentrations of chloride cannot compete with the initial rate-determining step, whatever it may be.

Comparing the reaction of Ru(bpy)<sub>3</sub><sup>2+</sup> with SO<sub>4</sub>F<sup>-</sup> with its

reaction with other oxidants, we note that the one-electron oxidant cerium(IV) reacts more rapidly ( $k_2 = 9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  in sulfuric acid<sup>9</sup> and  $>10^5 \text{ M}^{-1} \text{ s}^{-1}$  in perchloric acid<sup>10</sup>), while the formally two-electron oxidant thallium(III) reacts considerably more slowly ( $k_2 = 0.2 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>9</sup> Both of these reactions are assumed to involve outer-sphere electron transfer, and the thallium oxidation is thought to proceed by a sequence of two one-electron steps. Unfortunately, for neither of these oxidants has the reaction stoichiometry been determined.

Table IV summarizes the kinetic information that is presently available regarding fluoroxy sulfate reactions. These reactions span an impressive range of 10<sup>6</sup> in rates, with the Ru(bpy)<sub>3</sub><sup>2+</sup> reaction being among the fastest. It is not clear, however, just what factors are responsible for this large range, and it is evident that a great deal of further work will be required to clarify the situation.

Registry No. Ru(bpy)<sub>3</sub><sup>2+</sup>, 15158-62-0; SO<sub>4</sub>F<sup>-</sup>, 73347-64-5.

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## Luminescence Study of Complexation of Europium and Dicarboxylic Acids

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Received January 23, 1989

Luminescence lifetime measurements of Eu(III) have been used to study the hydration of Eu(III) when complexed by alkanedicarboxylate ligands. In its mono(malonate) complex, Eu(III) was found to have 2.3 fewer water molecules than the uncomplexed hydrated cation. In the formation of its 1:1 complexes with succinate, glutarate, and adipate, Eu(III) lost 1.5 molecules of water. When these dicarboxylate ligands reacted with the EuNTA complex to form the 1:1:1 ternary species, the malonate anion replaced 2.2, the succinate 1.5, and the glutarate and adipate 1.0 water molecules (all these values have ca.  $\pm 0.5$  uncertainty). These data are discussed in terms of the effect on chelation of increased alkyl chain length.

### Introduction

The thermodynamics of complexation of the lanthanides by dicarboxylate ligands (L = malonate, succinate, glutarate, or adipate) have been analyzed for insight into the nature of the complexes.<sup>1</sup> The data were consistent with bidentate chelation for all of the 1:1 complexes. However, it was pointed out that the values of the stability constants for the formation of the 1:1 complexes with succinate, glutarate, and adipate anions reflected less stabilization than expected from the basicity of the chelating ligands. In a subsequent paper,<sup>2</sup> the thermodynamics of the formation of ternary complexes of Gd(III) with nitrilotriacetic acid (NTA) and the same dicarboxylic acids were reported. Bidentate chelation was assigned to the malonate complexation, while the values for the succinate, glutarate, and adipate complexes were more consistent with monodentate structure of these dicarboxylate ligands in the ternary species.

In an attempt to investigate more directly the presence of chelate structure in these complexes, we have studied the europium complexes by luminescence lifetime measurements. It has been shown that changes in the luminescence lifetime of Eu(III) upon complexation in solution are proportional to the number of water molecules in the coordination sphere of the complexed Eu(III) and are relatively unaffected by the interaction of Eu(III) with many ligands.<sup>3</sup>

Table I. Calibration Data for Eu(III) Solids with H<sub>2</sub>O Hydration ( $k$  in ms<sup>-1</sup>)

anion (ref)	$n(\text{H}_2\text{O})^a$	$k_{\text{obs}}$	
		this work	ref 3
dipicolinate (4)	0	$0.73 \pm 0.03$	0.77
nicotinate (5)	2	$2.40 \pm 0.03$	2.49
oxalate (6)	3	$3.58 \pm 0.07$	3.55
thiodiacetate (7)	4	$4.42 \pm 0.08$	5.35
sulfate	4	$4.80 \pm 0.01$	4.79
chloride	6	$8.25 \pm 0.05$	8.25
bromate (8)	9	$8.83 \pm 0.03$	8.69

<sup>a</sup> Number of H<sub>2</sub>O molecules in the primary coordination sphere of Eu(III).

### Experimental Section

**Reagents.** A europium perchlorate stock solution was prepared by dissolving the oxide in perchloric acid and was standardized by complexometric titration with xylenol orange as the indicator.

The reagent grade malonic (Aldrich), succinic (J. T. Baker), glutaric (Aldrich), adipic (Mallinckrodt), and nitrilotriacetic (Aldrich) acids were used as received. The stock solutions were checked for purity and standardized by titration with standard base.

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