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The Vibrational Spectra of Antimony Pentafluoride–Sulfur Dioxide (1/1)

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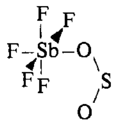
Complete solid state Raman and infrared spectra have been obtained for antimony pentafluoride–sulfur dioxide (1:1), and assignments have been made for the fundamental vibrations. In addition, depolarization data are reported for the liquid-phase Raman spectra. The SbO stretch in F_5SbOSO is assigned to a band at 266 cm^{-1}. This falls at lower energy than does SbN for the analogous acetonitrile complex of SbF_5. The three fundamental vibrations ascribed to the SO_2 moiety of F_5SbOSO are assigned to Raman bands at ~1320, ~1100, and ~539 cm^{-1}; these are shifted approximately −15, −45, and +15 cm^{-1} from the values found for the equivalent modes in free sulfur dioxide. Qualitatively, other sulfur dioxide complexes show the same kind of shift, regardless of their mode of bonding. The difference (Δ) between the two high-frequency bands, however, appears to be symptomatic: if $\Delta > 190$ cm^{-1}, the complex is oxygen bonded; if $\Delta < 190$ cm^{-1}, the complex is bonded through the sulfur (free sulfur dioxide liquid has $\Delta \sim 190$ cm^{-1}).

With the exception of F_5SbOSO all of the simple complexes of SO_2 for which x-ray structural data are available involve attachment at sulfur. The interaction of SO_2 with the strong acceptor SbF_5 leads instead to the formation of an Sb–O bond, **1**.[1] In contrast with the S-bonded compounds for which a number of infrared studies are available, there are no detailed vibrational data available for F_5SbOSO. The present infrared and Raman study of F_5SbOSO was undertaken with the idea that the S- and O-bonded forms might be distinguishable by vibrational spectroscopy. A spectroscopic criterion for the mode of attachment would be useful in the study of new SO_2 complexes, and would have particular value in the characterization of SO_2 interactions with surfaces.



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Experimental Section

Except as noted below all procedures were similar to those reported for $F_5SbNCCH_3$ and $F_5AsNCCH_3$.[2,3] As with these systems the hygroscopic nature of the F_5SbOSO complex required that all sample preparation and manipulation be carried out under high vacuum or in a drybox.

Infrared Spectra. For the low-temperature spectra, about 0.1 mmol of sulfur dioxide was frozen onto the sample plate at −196°C of the low-temperature cell, followed by a similar quantity of the Lewis acid, and then a final layer of excess SO_2 (~0.3 mmol). As the temperature rose to about −60 to −50°C, the white, crystalline complex appeared. After the reaction was complete, the excess sulfur dioxide was removed by distillation at −70 to −60°C. Before recooling in order to take the spectrum, the sample was first warmed to ca. −30°C and allowed to anneal. Although not totally satisfactory, room-temperature spectra in the medium infrared region were recorded for the powdered solid between two AgCl plates sealed by means of Kel-F grease. A small amount of decomposition occurred as noted by the presence of a weak band attributable to absorbed sulfur dioxide.

Raman Spectra. The solid complex of 1:1 stoichiometry and sulfur dioxide solutions of the complex were prepared and sealed off on high vacuum line. In a sealed tube under its own vapor pressure the F_5SbOSO samples melted between 68 and 72°C (lit. 57°C[4] and 66–72°C[1]). When completely fused, the liquid may be supercooled to ambient temperature and kept indefinitely without resolidification. Although no bands attributable to the parent compounds were observed in the spectra of the solid (Figure 1), Raman bands due to free SO_2 were found in the supercooled liquid and in the vapor above the liquid. All liquid-phase spectra were obtained at room temperature, while those on polycrystalline solids were determined at −107, −60, and −10° as well.

Except where noted, none of the fundamentals exhibit a marked temperature dependence. The infrared frequencies quoted in the tables are for −196 and 22°C; those for the Raman data are for 22°C. The values cited in the text are an average of the Raman and infrared data, unless stated otherwise.

Table I. Numbering and Approximate Description of the Fundamental Vibrations of F_5SbOSO

A′ class		A″ class	
ν_1	SO′ stretch	ν_{14}	SbF_4 stretch [E]
ν_2	SO stretch	ν_{15}	SbF_4 stretch [B_2]
ν_3	SbF_4 stretch [E][a]	ν_{16}[b]	F′–SbF_4 wag [E]
ν_4	SbF′ stretch [A_1]	ν_{17}	O–SbF_4 wag [E]
ν_5	SbF_4 stretch [A_1]	ν_{18}[b]	SbF_4 in-plane deformation [E]
ν_6	O′SO deformation	ν_{19}	SbF_4 out-of-plane deformation [B_2]
ν_7[b]	F′–SbF_4 wag [E]		
ν_8	SbF_4 out-of-plane deformation [A_1]	ν_{20}	SbO–SO′ torsion
		ν_{21}	FSb–OS torsion
ν_9	SbO stretch [A_1]		
ν_{10}	SbF_4 in-plane deformation [B_1]		
ν_{11}	O–SbF_4 wag [E]		
ν_{12}[b]	SbF_4 in-plane deformation [E]		
ν_{13}	SbOS deformation		

[a] The symbols in brackets refer to the symmetry class of the equivalent coordinate for $F_5SbNCCH_3$.[23] [b] Whether ν_7 and ν_{16} are the pair of F′–SbF_4 wags and ν_{12} and ν_{18} are the pair of SbF_4 in-plane deformations or vice versa is indeterminant. Hence the choice given above is arbitrary. (See ref 3.)

Results and Discussion

Selection Rules and Assignments. The crystal structure of F_5SbOSO[1] shows that this substance is molecular with octahedral coordination about the antimony atom and that the sulfur dioxide is bonded through one of the oxygens. The site symmetry is C_1; however, the molecular symmetry approximates C_s, the mirror plane lying along one of the two dihedral planes between the equatorial fluorine atoms. The selection rules based on C_s symmetry require 21 fundamentals, 13 A′ and 8 A″, all of which have both Raman and infrared activity. Nevertheless, the F_5SbO portion of the molecule closely approaches C_{4v} symmetry; hence one presumes to find a number of accidental degeneracies causing its spectra to bear a marked resemblance to those for the F_5SbN moiety in the analogous acetonitrile complex.[2,3] Table I gives the designation and approximate description of these 21 vibrations, along with the symmetry class for the corresponding $F_5SbNCCH_3$ fundamental. The assignments are given in Tables II and III.

The two SO stretches occur in the region between 1050 and 1350 cm^{-1}. The OSO′ deformation as well as the F_5SbO vibrations all lie below 700 cm^{-1}. Assignments for the SO_2 moiety follow directly from those of the free molecule.[5] Comparison with the data for the acetonitrile adduct[2,3] and other metal fluorides of ~C_{4v} symmetry shows a tentative but reasonable classification is possible for the vibrational modes of the F_5SbO moiety.[6] As with the acetonitrile adduct,[2,3] assignments for the deformation region are the most tenuous, and are therefore discussed in detail below.

The SbO stretch and the O–SbF_4 wags as well as the seven

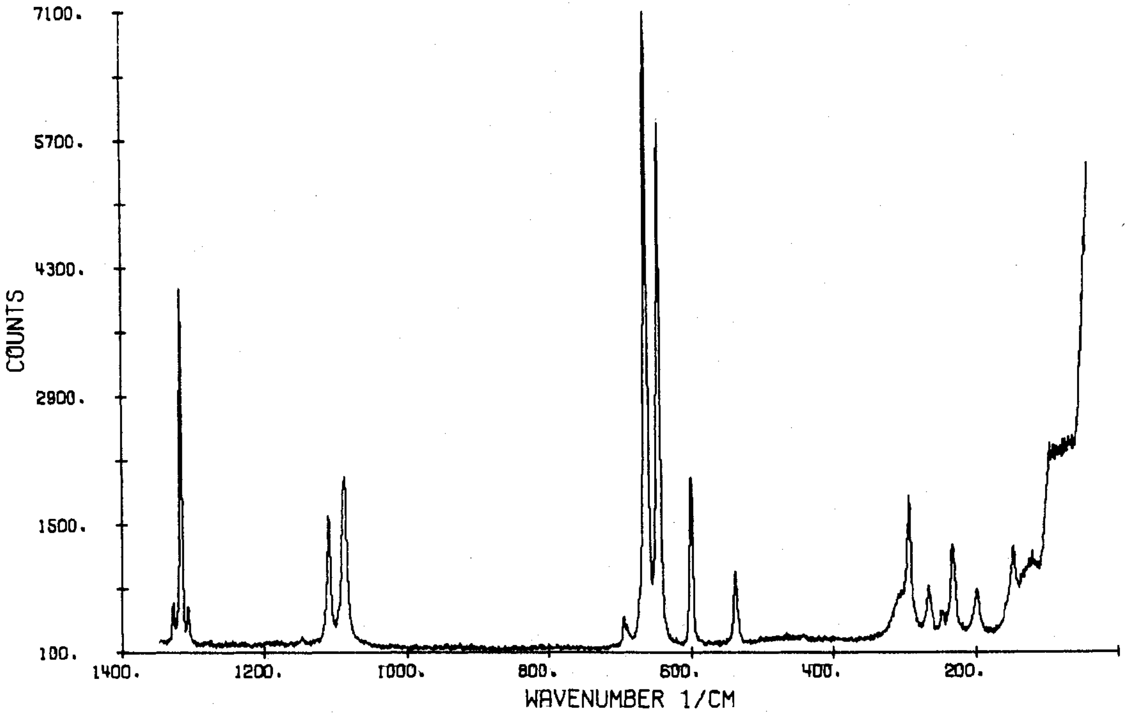


Figure 1. Raman spectrum of polycrystalline F_5SbOSO at 22°C (0–1400 cm^{-1}).

SbF deformations fall in the 350 to 140 cm^{-1} region of the spectrum. As in the case of $F_5SbNCCH_3$,[23] infrared data prove to be of little help; only a single, very broad feature ~260 cm^{-1} encompassing a number of fundamental vibrations appears in the spectrum. Also, the low symmetry of the F_5SbOSO molecule results in selection rules that allow all bands to appear in both the Raman and the infrared.

Most certain are the assignments of two definitely polarized features in the liquid-phase Raman spectra at 295 and ~270 cm^{-1}. Owing to its greater intensity and relative position, the former is ascribed to ν_8 (the SbF_4 out-of-plane equatorial deformation, A'). The analogous A_1 mode in $F_5SbNCCH_3$ occurs at ~290 cm^{-1}.[3] The latter may then be ν_9 (SbO stretch, A'), the only remaining fundamental corresponding to an A_1 mode for C_{4v} symmetry. Because the MN stretch for each of the X_5MNCCH_3 species occurs between ~280 and ~215 cm^{-1} and is of similar intensity,[3] this choice seems credible.

Owing to its position relative to ν_8 (295 cm^{-1}), the very weak shoulder seen at ~310 cm^{-1} at room temperature may well be analogous to the F'–SbF_4 wag (E) of the acetonitrile adduct.[3] Hence, this band is assigned as ν_7 or its asymmetric counterpart ν_{16}. The O–SbF_4 wags (ν_{11}, ν_{17}) should lie at a somewhat lower frequency than ν_9 (SbO stretch, A') which comes at ~270 cm^{-1}. Again comparing the corresponding mode for the acetonitrile complex (N–SbF_4 wag, E),[3] the band at 232 cm^{-1} is a viable choice.

Four bands are yet unassigned (248, 200, ~161, and 148 cm^{-1}), three of which are probably fundamentals. The shoulder at 161 cm^{-1} is exceedingly weak and may be a combination or overtone. One possible, but by no means unique, assignment of the three fundamentals is given in Table II. (Also see Figure 1.)

This 140–25 cm^{-1} region contains one deformation (ν_{13}, SbOS deformation, A'), the two torsional modes (ν_{20}, FSb–OS torsion, A'' and ν_{21}, SbO–SO' torsion, A''), as well as miscellaneous lattice vibrations. Nine bands are observed in the Raman spectrum of the polycrystalline solid, Figure 1, all of which exhibit moderate temperature dependence. Only the ~85 cm^{-1} band may be assigned with any certainty; its relative intensity and frequency imply that it is the SbOS deformation, ν_{13}. The related SbNC deformation is observed in the acetonitrile complexes between 85 and 105 cm^{-1}.[2,3]

Table II. Observed Infrared Frequencies[a] (cm^{-1}) for Solid F_5SbOSO

−196°C[b]	22°C[c]	Assignment
~216 sh, br (?)		(?)
~260 s, vbr[d]		
	450 mw	(?)
	491 m	(?)
502 mw		$\nu_9 + \nu_{10}; \nu_7 + \nu_{12}$
541 s	538 mw	ν_6
601 w	602 w	ν_{15}
614 w	614 w	$2\nu_7; 2\nu_{16}$
647 ms	659 s	ν_5
663 s		ν_4
~695 vs	695 vs	$\nu_3; \nu_{14}$
1101 s	1102 ms, br	ν_2
1278 w		$2\nu_5$(?)
1307 w		$\nu_4 + \nu_5; \nu_1(^{34}SO)$
1323 s	1327 s	ν_1
1331 mw		$\nu_3 + \nu_5$
1417 w	1408 w	(?)

[a] The following bands were observed on occasion and may be ascribed to hydrolysis products (including SbF_6^-, SbF_5OH^-) or to products of reactions with cell window materials: ~825, ~865, ~896, ~925, ~955, ~997, ~1020, ~1050, 1171, 1227, 1635, 2188, 2415, 2450, 2630, ~3150, ~3200, ~3270, and ~3295 cm^{-1}. These were observed in scans of one or more samples; position and intensities often varied from sample to sample. Bands due to unreacted SbF_5 were also observed for many of the samples in varying intensities at 514, 673, 677, 705, 727, and 754 cm^{-1}. [b] Polycrystalline sample prepared in the low-temperature infrared cell. [c] Powdered sample between AgCl plates. This spectrum includes all the bands observed by Miller's group.[1] The band always found at 1149 cm^{-1} with such samples may perhaps be ascribed to absorbed SO_2 arising from partial decomposition of the complex. The bands at 450 and 491 cm^{-1} may also have their origin in such a decomposition and may represent vibrations associated with bridging fluorides in the free acid. [d] This band is very broad and poorly resolved; it is likely that all seven bands between 230 and 310 cm^{-1} (ν_7, ν_{16}, ν_8, ν_9, ν_{10}, ν_{17}, ν_{11}) contribute to its intensity.

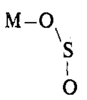
Structure Correlations. Important, from the standpoint of the possible application of vibrational spectroscopy to probe

Table III. Observed Raman Frequencies[a] (cm^{-1}) for F_5SbOSO at Room Temperature

Polycrystalline solid	Supercooled[b] liquid	Solution in liquid SO_2	Assignment
~85 br[e] (~16)[c]			ν_{13}
149 (11)	146 sh [0.9][d] (3)[c]	146 sh [–][d] (3)[c]	ν_{19} (?)
~161 sh (<3)			$2\nu_{13}$
199 (8)	200 [0.9] (5)	201 [~0.9] (4)	$\nu_{12}; \nu_{18}$ (?)
232 (16)	230 [0.80] (9)	233 [0.86] (5)	ν_{11}, ν_{17} (?)
248 (4.5)			ν_{10} (?)
266 (7)	~268 sh [0.6] (~6)	~275 sh [~0.5] (~4)	ν_9
295 (22)	295 [0.72] (14)	295 [<0.8] (10)	ν_8
~310 sh[e] (4)	~331 sh [<0.4] (2)		ν_7, ν_{16} (?)
539 (12)	539 [0.41] (7)	539 [<0.7] (4)	ν_6
600 (26)	600 [0.76] (9)	605 [~0.86] (5)	ν_{15}
645 (70)	650 [0.05] (100)	651 [0.02] (100)	ν_5
664 (100)	695 sh [0.2] (14)	684 [0.08] (15)	ν_4
691 (2)			ν_3
697 (3)			ν_{14}
1088 (19)	}1100 [0.28] (20)	1106 [~0.1] (24)	ν_2
1109 (13)			
1308 (4)			$\nu_4 + \nu_5; \nu_1(^{34}SO)$
1318 (40)	1325 [0.48] (22)	1325 [~0.5] (14)	ν_1
1328 (4)			$\nu_3 + \nu_5; \nu_2 + \nu_{11}$

[a] Eight other low-frequency, temperature-dependent bands, which are best ascribed to the two torsional coordinates, ν_{20} and ν_{21}, and to various lattice vibrations were observed for the solid at 27, 47, 57, 73, 95, ~101 (sh), 126, and 136 cm^{-1}. (See ref 6.) [b] Free sulfur dioxide (due to partial decomposition) dissolved in the supercooled liquid F_5SbOSO is probably responsible for a medium-intensity, polarized band always observed at 1149 cm^{-1} for such samples. [c] Numbers in parentheses are relative intensities (0–100). [d] Numbers in brackets for liquid phase data refer to depolarization ratios. (These are probably accurate to at least ±0.08 for data with two significant figures.) The theoretical value for a depolarized band is $\rho = 6/7 = 0.857$. [e] The two fundamentals at ~85 and ~310 cm^{-1} exhibit a conspicuous temperature dependence. Both increase in frequency as the temperature decreases; at −107°C their respective positions are 89 and 318 cm^{-1}. The latter is now distinctly separated from the medium intensity band at 295 cm^{-1}.

the manner in which sulfur dioxide is coordinated, are the changes detected in the sulfur dioxide vibrations upon complexation. To date, three distinct modes of bonding have been found for simple sulfur(IV) oxide complexes: (**1**) nonlinear bonding via an oxygen, as in F_5SbOSO;[1] (**2**) bonding via trigonal pyramidal coordination about the sulfur atom, as observed for $(CH_3)_3NSO_2$,[7] $MCl(CO)(SO_2)(P(C_6H_5)_3)_2$,[8] where M = Ir or Rh, and $Pt(P(C_6H_5)_3)_2CH_3I\text{-}SO_2$;[9] (**3**) bonding via trigonal planar coordination about the sulfur, as in $[Ru(NH_3)_4(SO_2)Cl]Cl$.[10] In every instance the SO



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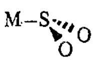

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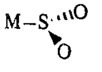

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stretches are at lower energy than those of free SO_2;[5] the deformation, on the other hand, always increases in frequency. Thus no one vibration is sufficiently diagnostic to classify a given adduct as having a particular kind of donor–acceptor bond.

There are, it appears, two characteristics which do set apart the S- and the O-bonded systems. For the latter, group theory predicts that all three modes be polarized since the two oxygen atoms are not related by a symmetry operation. In contrast, the S-bonded complexes will have one symmetric polarized and one asymmetric depolarized SO_2 stretch, because the two oxygens are now related by a plane of symmetry. The present data partially corroborate this idea (i.e., all three modes are polarized in F_5SbOSO); however, no precise polarization data are available from previous work on S-bonded molecules.

The other diagnostic pattern is the observed difference (Δ) in the two stretching frequencies. For liquid SO_2,[5] the value of Δ is about 190 cm^{-1}; after complex formation with SbF_5, this separation increases by about 30 cm^{-1} to 220 cm^{-1}. By contrast, the magnitude of this factor decreases for those adducts bound through the sulfur atom; Δ ranges from 125 cm^{-1} for $(CH_3)_2HNSO_2$ to 170 cm^{-1} for $(C_2H_5)_2(C_6H_5)NSO_2$,[11] and the transition metal–SO_2 complexes, for which structures are reported, have values in this same range[8-10] (see Figure 2).

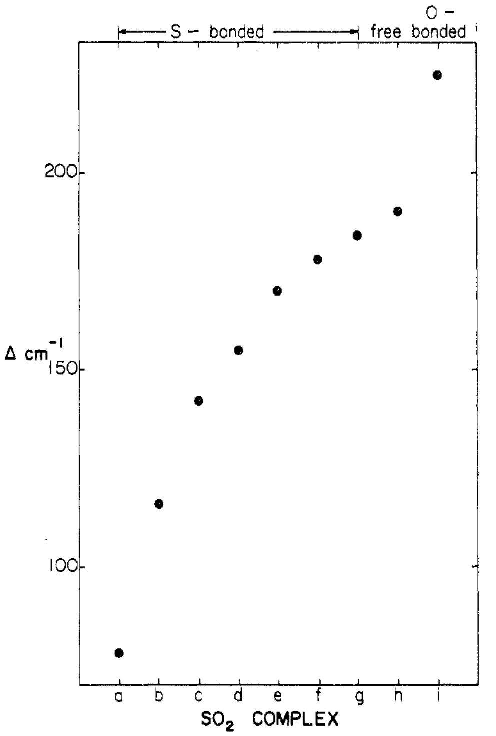

Figure 2. Difference between high- and low-frequency SO_2 stretches, Δ, for SO_2 complexes of known structure: (a) FSO_2^-; (b) $(CH_3)_3NSO_2$; (c) $[(\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$; (d) $RhCl(SO_2)(P(C_6H_5)_3)_2(CO)$; (e) $(C_2H_5)_2(C_6H_5)NSO_2$; (f) $Ru(NH_3)_4(SO_2)Cl$; (g) $Pt(P(C_6H_5)_3)_2(CH_3)ISO_2$; (h) SO_2(liq.); (i) F_5SbOSO. Compound c is unusual in that sulfur is four coordinate. The analogous organic sulfones listed by Bellamy (ref 14) have Δ values in the range 165 to 188 cm^{-1}. However, with highly electronegative substituents on sulfur high Δ values are the rule, e.g., 233 cm^{-1} for F_2SO_2 and 232 for Cl_2SO_2.

The large increase in Δ upon complex formation at oxygen is reasonable in view of the expected decrease in S–O bond order for the bridging Sb–O–S moiety, relative to the S–O bond order for the terminal oxygen. The purely kinematic influence of O attachment should be to decrease Δ for M–O–SO complexes, thus enhancing the influence of the primary force constant changes. The trends in off-diagonal force constants and their resulting influence on the value of Δ is less readily predicted. It does appear, however, that the increase in Δ upon O coordination is likely to be a general phenomenon and therefore a useful diagnostic feature for the mode of SO_2 coordination. These trends in Δ are not intended for application to compounds containing 4-coordinate sulfur such as sulfuryl halides or sultones.

Application of the above systematics to recent infrared data for adsorbed SO_2 implies that attachment to the surface generally occurs through sulfur.[12] One exception is the study by Deno et al. of SO_2 absorbed at elevated temperatures on Al_2O_3, where very large separation of the SO stretches is reported. In this case, however, the unusually high frequencies of the modes attributed to SO_2 do not fit well with previous observations on SO_2 complexes, so structural speculations are not justified. The Δ criterion also may be applied to the recently prepared compound $(C_6H_5)_3InSO_2$, for which Hsieh and Deacon favor an O-bonded structure $(C_6H_5)_3InOSO$.[13] The value of Δ calculated from their data, 199 cm^{-1}, agrees with the postulated In–O bond formation but in the absence of molecular weight data more complex structures cannot be excluded.

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Registry No. F_5SbOSO, 57031-35-3.

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Kinetics and Mechanism of the Oxidation of Uranium(IV) by Hypochlorous Acid in Aqueous Acidic Perchlorate Media

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The oxidation of uranium(IV) by hypochlorous acid has been studied in aqueous sodium perchlorate–perchloric acid solutions. The reaction $U^{4+} + 2HOCl = UO_2^{2+} + Cl_2(aq) + 2H^+$ proceeds appropriate to the rate law $-d[U(IV)]/dt = k_0[U^{4+}][HOCl][H^+]^{-1}$. At 25° and 3 *M* ionic strength, k_0 is 1.08 ± 0.07 sec^{-1}. Over the 1–25° temperature range, $\Delta H^{\ddagger}$ is 18.4 ± 0.1 kcal mol^{-1}, and $\Delta S^{\ddagger}$ is 3.1 ± 0.4 eu. The inverse hydrogen ion dependence of the rate law is explained by a rapid preequilibrium, in which a proton is lost from one of the reactants. A uranyl-like activated complex, $[H_2UO_2Cl^{3+}]^{\ddagger}$, is suggested, with one proton likely to be residing on each oxygen atom. Evidence is presented that the mechanism involves a two-electron transfer, with the intermediate chloride ion rapidly reacting with hypochlorous acid to form chlorine. The uranium(IV)–hypochlorous acid reaction plays an important role in the oxidation of uranium(IV) by aqueous chlorine solutions. The magnitude of this role was seriously underestimated by previous investigators.

Introduction

Both aqueous chlorine(0) and chlorine(I) are transient intermediates in the complex reactions of chlorine(III) with various metal ions such as vanadium(IV)[1] or uranium(IV).[2,3] The studies of many reactions of aqueous chlorine(0) are complicated by the accompanying chlorine(I) reactions, which arise from the equilibrium

$$Cl_2(aq) + H_2O = HOCl + H^+ + Cl^- \qquad (1)$$

At 25° and zero ionic strength,[4] the equilibrium constant for reaction 1 is 3.94×10^{-4} M^2 and its variation with ionic strength is reported elsewhere.[5] Dreyer and Gordon[6] studied the reactions of vanadium(IV) with aqueous chlorine(0) and chlorine(I) and determined the rate of the reaction with the aqueous Cl_2 species by correcting for that portion of the reaction due to chlorine(I).

The kinetics of the reaction[7,8]

$$U^{4+} + Cl_2(aq) + 2H_2O = UO_2^{2+} + 2Cl^- + 4H^+ \qquad (2)$$

and the kinetics of the analogous reactions with aqueous iodine(0)[8] and bromine(0)[9] all display a term in the rate law which is inverse second order in hydrogen ion. In a preliminary survey, Gordon and Feldman[2] found the reaction with chlorine(I)

$$U^{4+} + 2HOCl = UO_2^{2+} + Cl_2(aq) + 2H^+ \qquad (3)$$

to be much more rapid. Adegite and Ford-Smith[8] attempted to estimate the rate of uranium(IV)–chlorine(I) reaction by studying the dependence of the rate of the corresponding uranium(IV)–chlorine(0) reaction on the concentration of

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