conductivity. For example ice has been doped with HF and KHP and AHP doped with $KHSO_4$. Doping the solution from which the crystal of KHA is growing with $KHSO_4$ should result in a number of hydrogen sulfate ions replacing dihydrogen arsenate ions in the lattice. A number of L defects should be built into the proton network since the hydrogen sulfate ion has one less proton and a corresponding increase in the conductivity realized. Such an effect has been found here and allows the calculation of the mobility of the L defect from the equation $\sigma = n_L e \mu_L$ provided we make the assumption that the L defects are not bound to the HSO_4 ions.[5] Using our dopant level for n_L and 1.6×10^{-19} C for e, we find $\mu_L = 2.40 \times 10^{-10}$ $cm^2\ V^{-1}\ sec^{-1}$. This is very much in agreement with the proton mobility in KHP where μ_L was found to be 6.0×10^{-10} $cm^2\ V^{-1}\ sec^{-1}$ at 25°. The low-temperature slopes of the pure and doped crystals differ slightly. The probable explanation is that in the pure crystal the overall energy of conduction requires formation and migration of L defects, whereas in the doped crystal they are already present. For the purpose of discussion we have separated these energy terms in Table I. Table I shows that the energy of formation of L defects is found to be greater for KHA (2.2 kcal/mol) than for KHP (0.6 kcal/mol). We cannot explain this difference.

Conclusion

We submit that from the conductivity data and the effect of doping on KHA and from comparisons with results obtained for KHP, protonic conduction is indicated in potassium dihydrogen arsenate.

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Spectroscopic Studies of Halosulfinate Ions

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In liquid sulfur dioxide solution, halide ions are specifically solvated so as to form halosulfinate ions. The halosulfinate ions also exist in other aprotic solvents and can be found in the well-known "solvates" which are isolated from liquid SO_2 solutions. The chloro-, bromo-, and iodosulfinate ions are highly colored due to an internal charge-transfer transition. Vibrational spectra of the XSO_2^- ions are consistent with the expected pyramidal (C_s) geometry. The results of an approximate normal-coordinate analysis as well as the relative intensities of the electronic transitions suggest the magnitude of the X^-–SO_2 interaction to be in the order $FSO_2^- > ClSO_2^- < BrSO_2^- < ISO_2^-$. It is apparent that the nature of the halide–sulfur dioxide interaction is obscured by solvation effects in solvents such as acetonitrile and dimethyl sulfoxide. The formation of halosulfinate ions probably plays a significant role in the chemistry of ionogenic halides in liquid SO_2.

Introduction

The existence of halosulfinate (XSO_2^-) ions in liquid sulfur dioxide solutions has been indicated by the work of several investigators[1-3] but there has been little systematic effort to demonstrate their existence or to define their structures. The ionogenic[4] character of the triarylchloromethanes in liquid SO_2 has been attributed to the formation of a complex between the chloride ion and the solvent molecules.[3] The presence of X^-–SO_2 complexes has been inferred from several unusually small rate constants for reaction in liquid SO_2.[5] Ultraviolet[3,6-8] and infrared[8] spectra of mixtures of halide ions and sulfur dioxide in various solvents have been interpreted in terms of $X^- \cdots SO_2$ complexes. The colors of solvates[1,2] of the type $MX \cdot nSO_2$ (n = 1–4) may be attributed to electronic transitions in complex anions, probably halosulfinates. The fluorosulfinate ion has been isolated and characterized;[9] the infrared spectrum of $KFSO_2$ has been interpreted in terms of the FSO_2^- ion of pyramidal (C_s) structure.[10] Recently, Woodhouse and Norris[11] and Salama, *et al.*,[12] have utilized ultraviolet spectroscopy to demonstrate the existence of Cl^-, Br^-, and I^- complexes with SO_2 in acetonitrile, dimethyl sulfoxide, and water. The formation constants reported in these studies strongly reflect the influence of the solvent on the stability of the halosulfinate ions.

This paper reports the results of a study of the halide ion–sulfur dioxide interaction in liquid sulfur dioxide

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using electronic, infrared, and Raman spectroscopy. Preliminary accounts were reported earlier.[13]

Experimental Section

Solvents.—Purification of "anhydrous grade" SO_2 (Matheson) was accomplished by a procedure similar to that described previously.[14] In order to ensure removal of SO_3, the procedure was modified to permit storage of liquid SO_2 over mercury at room temperature for at least 24 hr. Purification of 1,2-dichloroethane was carried out in the manner of Popov and Swenson[15] with CaH_2 substituted for P_2O_5 in the final drying step. It was then degassed by successive freeze–evacuate–melt cycles and stored in an evacuated flask attached to the vacuum system.

Solutes.—Reagent grade KI, RbI, CsI, and KF were dried by heating *in vacuo* at 200°. Halide salts of the types R_4NX and R_4PX ($R = CH_3$, n-C_3H_7, n-C_4H_9, n-C_6H_{13}) were used as halide ion sources since alkali metal halides generally exhibit very low solubility in liquid SO_2.[14] The ammonium halides were obtained from Eastman and the phosphonium halides, prepared by reaction of the phosphine and alkyl halide, were kindly provided by Professor C. E. Griffin of this department. These salts were recrystallized twice from ethyl acetate, benzene, methanol, or one of their binary mixtures; in some cases, addition of hexane was required to induce crystallization. Only carefully dried, deoxygenated, reagent grade solvents were used and all recrystallizations were carried out in a dry nitrogen atmosphere. Final solvent removal and drying was accomplished by heating *in vacuo*. The drying apparatus consisted of a tube fitted with a 30-mm spherical ground joint and a 6-mm stopcock; it was connected to the vacuum system through a trap at −196°. Optimum temperatures for drying without decomposition were obtained from the literature.[16] All salts were removed from the evacuated drying apparatus within an inert-atmosphere chamber and stored there until used.

Tetramethylammonium triiodide (99.9%) was kindly supplied by Professor A. I. Popov of Michigan State University and was used without further purification. Potassium fluorosulfinate was prepared by distillation of SO_2 onto a quantity of carefully dried KF in a glass tube. If the KF was not dried, decomposition products (FHF^- and $S_2O_5^{2-}$)[9] were detected in the $KFSO_2$. After 1 week at room temperature, the $KFSO_2$ was isolated by distillation of excess SO_2 through the vacuum system and stored in the inert-atmosphere chamber. Tetra-n-butylammonium perchlorate was prepared by reaction of $AgClO_4$ and $(n\text{-}C_4H_9)_4NI$ in anhydrous methanol. After filtration of the AgI, the solvent was removed by vacuum distillation.

Electronic Spectra.—Absorption spectra of liquid SO_2 solutions were obtained using a 1-mm silica cell mounted in a vacuum-jacketed dewar flask. The dewar and the required sampling apparatus were adapted for use with liquid SO_2 from the designs described elsewhere;[17] all stopcocks and joints were replaced with Delmar-Urry stopcocks and Fischer-Porter Teflon connectors. A thermistor, calibrated against SO_2 vapor pressure,[14] was used to monitor the temperature (±1°) of the solution in the silica cell.

Internal reflection techniques[18] were utilized to minimize absorption by the solvent. A trapezoidal sapphire internal reflection element (2 mm × 12 mm × 39 mm, 60° face angles), obtained from Wilks Scientific Corp., was mounted in a Teflon cell similar to that used for the infrared measurements.[13] Gaskets of Teflon film provided a vacuum-tight seal. During a measurement the cell was so oriented that the sample beam of the spectrometer was focused on the entrance aperture, entering normal to the surface of the element. Two plane, first surface mirrors were used to return the light from the exit aperture of the cell to the optical axis of the spectrometer. Provision for refocusing the beam would have, undoubtedly, improved the system but is not essential for its successful operation. To ensure reproducible alignment of the transfer optics, the mirrors and a cell mount were attached to an aluminum plate whose position is reproducibly determined by a set of pins in the sample compartment of the spectrometer. Spectra were recorded at room temperature against air in the reference compartment of a Cary Model 14 spectrophotometer. The slits were controlled so that resolution was always better than 10 Å.

Vibrational Spectra.—Raman spectra were observed using an instrument designed and built by Miller, *et al.*[19] This instrument utilizes a Spex Model 1400 double monochromator and a Spectra Physics Model 125 He–Ne laser. Sample cells were constructed from lengths of 8-mm Pyrex tubing by fusing flats to the ends. A solution makeup bulb is attached *via* a side arm and the entire unit is closed off with a Teflon Delmar-Urry valve. Although these cells were designed for use with solutions, the Raman spectra of crystals, grown from solution in the cell, were conveniently observed. All Raman spectra were observed at 20°.

Infrared spectra of the liquid SO_2 solutions and of several solid "solvates" were recorded with the Perkin-Elmer 621 spectrophotometer. A variable-path-length cell (Figure 1A) made from Teflon and fitted with Irtran 2 windows was used to obtain transmission spectra (above 700 cm^{-1}) of liquid SO_2 solutions at room temperature. A cell of similar design made from 316 stainless steel could not be used for this work since liquid SO_2 solutions of halides react with the metal. Apparatus illustrated in Figure 1B permitted makeup and transfer of solutions. Since very thin path lengths are required, heating of the capillary film by the infrared source is sufficient to cause continual bumping of the solution with the frequent result that little or nor sample is in the light beam. Removal of the higher

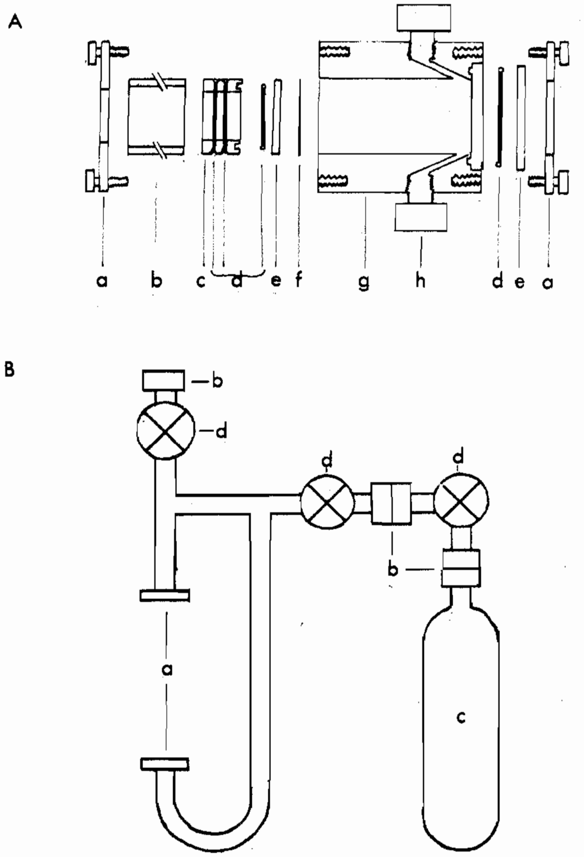

Figure 1.—Variable-path-length transmission cell. A. Exploded cross-sectional view: a, retaining rings; b, spacer (aluminum tube); c, seal (Teflon); d, "O" rings (ethylene–propylene); e, window; f, slit spacer (Teflon); g, body (Teflon); h, Cajon VCO coupling (Teflon). B. Solution-handling device (Pyrex): a, Cajon VCO coupling; b, Fischer-Porter Solve-Seal joint; c, solution bulb; d, Delmar-Urry Teflon valve.

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frequency radiation with filters was only partially successful in reducing the bumping.

Internal reflection methods were utilized in order to avoid these difficulties. Trapezoidal (2 mm × 20 mm × 52.2 mm, 45° face angles) internal reflection elements of germanium were obtained from Wilks Scientific Corp. and mounted in Teflon cells.[13] The spectral region was limited to the 700–4000-cm^{-1} transmission window of germanium. Connections to the glass solution bulbs (similar to that in Figure 1B) were made with Swagelok or Cajon VCO fittings made of Teflon. All spectra were observed using a 45° angle of incidence with a second germanium element in the reference beam. A set of transfer optics similar to that described by Barr and Flournoy[20] permitted location of the internal reflection cells in the sample compartment of a Perkin-Elmer 621 spectrophotometer. Concave mirrors prior to the sample cells were added to focus the beam at the center of the internal reflection element. After the unit was aligned and balanced, spectra were recorded using the standard-slit program; the spectra are of much better quality and higher resolution than those obtained with the earlier device.[13] Conventional mull techniques, using polyethylene, Irtran 2, or KRS-5 windows, were also employed for the study of selected solid samples; all samples were prepared in an inert atmosphere.

Procedures.—Exclusion of water and oxygen from solutions of halides in sulfur dioxide is essential to prevent the occurrence of complicating side reactions.[14] Sulfur dioxide was purified and manipulated in a grease-free vacuum system that utilized Delmar-Urry Teflon stopcocks, O-ring or Teflon-sleeved (Fischer-Porter) joints, and Cajon vacuum couplings. All O rings were made of ethylene–propylene copolymer elastomers. All solutions and solutes were handled either in the vacuum system or in an inert-atmosphere chamber containing helium equilibrated over sodium–potassium alloy. This chamber also contained the balance compartment of a Cahn Electrobalance to permit precise weighing of samples in an inert atmosphere. Large samples, in evacuated ampoules, were weighed on an analytical balance outside the chamber.

Electronic transmission spectra of liquid SO_2 solutions were obtained by the following procedure. Samples were weighed in the inert-atmosphere chamber and transferred to the solution flask in a helium atmosphere. After evacuation, the solution flask was cooled to −75° with a Dry Ice–2-propanol bath and the sample was introduced. Sulfur dioxide was distilled into the flask until the desired volume at −70° was obtained. After the resulting solution was thoroughly mixed, the flask was isolated from the vacuum line and the spectrum was recorded. Higher temperatures (−70 to −20°) were obtained by controlled addition of Dry Ice. The temperature was constant to within ±1° during all runs.

The more concentrated solutions of halides in liquid SO_2 that are required for Raman and internal reflection studies were made up by weight. The solution bulb was dried at 200°, evacuated, weighed, and taken into the inert-atmosphere chamber. A solid sample was placed in the solution bulb, whereupon it was closed off, removed from the inert-atmosphere chamber, evacuated, and weighed. Then a quantity of SO_2 was distilled into the bulb and it was closed off. The bulb was reweighed and then attached to the cell; the cell was evacuated and isolated from the vacuum system before the solution was transferred into it. All observations were made at room temperature under pressure.

The stoichiometry of the complex was examined in solutions of halide and SO_2 in 1,2-dichloroethane that were prepared so as to minimize exposure to the atmosphere and loss of SO_2. Two Fischer-Porter Teflon valves were attached to a standard volumetric flask to permit evacuation and introduction of solvent from the storage flask on the vacuum system. Quaternary ammonium halide solutions (near 10^{-3} M) were made up and SO_2 solutions of equal concentration were then prepared. A quantity of SO_2, determined by gas buret, was condensed into an evacuated flask using liquid N_2. Approximately 75% of the required solvent was introduced; the solution was allowed to return to room temperature and was made up to volume. After mixing of the halide and SO_2 solutions in the desired ratios, a portion was transferred in an oxygen-free, dry nitrogen atmosphere to a silica absorption cell that had been fitted with a Teflon valve. Ultraviolet spectra were recorded on the Cary 14 spectrophotometer within five minutes of mixing.

Precise determination of the halide to SO_2 rato in the residue remaining at room temperature when the SO_2 is evaporated from liquid SO_2–halide solutions could not be obtained by elemental analysis. Since solid tetraalkylammonium halides absorb SO_2 gas, it was decided to examine these products with known X^-:SO_2 ratios. A quantity of SO_2, determined by gas buret, was distilled into a small bulb (−196°) containing a known amount of salt; the bulb was closed off, and the product was allowed to attain room temperature. Infrared spectra of these products X^-:SO_2 = 10–0.25) were obtained by conventional mull techniques.

Results and Discussion

Halide Solvolysis.—Accounts of the early studies[1,2] of chemistry in liquid sulfur dioxide report that KBr and KI undergo solvolysis

$$4KBr + 4SO_2 \longrightarrow 2K_2SO_4 + S_2Br_2 + Br_2 \qquad (1)$$

$$2KI + 2SO_2 \longrightarrow K_2SO_4 + S + I_2 \qquad (2)$$

The rate of solvolysis is reported to increase rapidly with increasing dilution of the salt solution. Lichtin[3] has, however, reported that solutions of KI are quite stable if the sulfur dioxide is carefully purified. Observations in this laboratory support the latter report: neither KBr nor KI undergoes any detectable reaction with liquid SO_2 when in sealed tubes at room temperature for 1.5 years. The iodide solutions seem to undergo a photochemical reaction when exposed to ultraviolet light. These observations support Lichtin's conclusions that the reported "solvolysis" reaction is due to the presence of impurities (O_2) in the solvent and that this reaction is best described as an oxidation–reduction rather than a solvolysis reaction. Although solvolysis of Br^- and I^- may occur at high temperatures, it is of little importance under the conditions employed for these studies.

Internal Reflection.—The method of internal reflection spectroscopy has been discussed extensively in the literature; Harrick's monograph[18] is probably the most comprehensive treatment available. Dispersion effects can be minimized by use of an internal reflection element of high refractive index (germanium) at a high angle of incidence.[18,20] The weak-absorber approximation[18] is easily shown to be valid for the infrared spectra of these systems. Infrared band positions as determined by transmission (where possible) and by internal reflection (after correction for the wavelength dependence of effective thickness) were observed to be within experimental error (±5 cm^{-1}). No chemically significant differences in the infrared spectra as obtained by the two methods were observed. Although the weak-absorber approximation is valid in the ultraviolet spectrum for pure liquid SO_2, it is not valid for the most concentrated solutions. Thus, estimates of the molar absorptivities are only approximate and since polarizers were not available, only relative intensities, determined at approximately equal concentrations, will be utilized. It is only the large difference in the molar absorptivities of the solvent (~400 l. mol^{-1} cm^{-1}) and the solute (~10^4 l. mol^{-1} cm^{-1}) which permit any useful data to be obtained with this technique.

Electronic Spectra.—The electronic spectrum of gaseous sulfur dioxide in the near-ultraviolet region consists of two sets of bands:[21] a weaker set ($\epsilon_{\max} \simeq 0.2$) between 26 and 30 kK is assigned to a $^3B_1 \leftarrow {}^1A_1$ transition and a stronger set ($\epsilon_{\max} \simeq 400$) between 30

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[21] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. III, Van Nostrand, New York, N. Y., 1966, pp 511–513.

and 38 kK is assigned to a $^1B_1 \leftarrow {}^1A_1$ transition. As expected, these transitions are evident in the ultraviolet spectrum of the liquid: their presence precludes useful ultraviolet transmission spectroscopy in liquid SO_2 unless cells of 1-mm path-length or less are utilized. Even then, the cutoff (1% transmission) occurs below 30.0 kK. In the liquid at $-50°$, the singlet–triplet transition is centered at 27.8 kK with an absorption coefficient of 1.0 cm^{-1} or a molar absorptivity (ϵ_{max}) of 0.04 l. mol^{-1} cm^{-1} (Figure 2A). The singlet–singlet as well as the single–triplet transition can be observed in the liquid at room temperature by use of the sapphire internal reflection unit. After correction for the frequency dependence of the reflected intensity in the manner of Harrick,[18] the singlet–triplet transition occurs at 27.6 kK and the singlet–singlet transition occurs at 36.4 kK (Figure 2B). In the liquid at 25° the singlet–singlet transition is two to three orders of magnitude more intense than the singlet–triplet transition. No bands attributable to adsorbed SO_2 were observed in spectra of liquid SO_2, after removal of liquid SO_2 or with gaseous SO_2 (3 atm) in the cell.

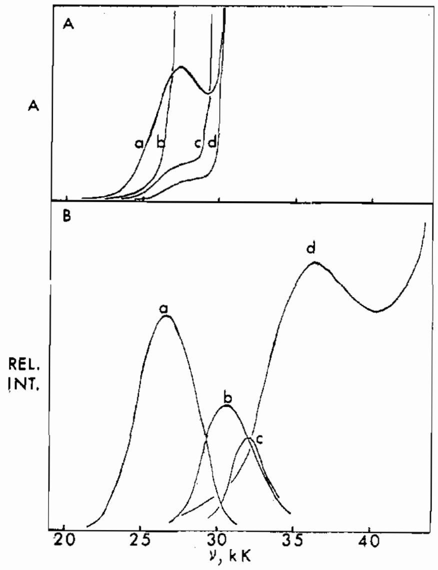

Figure 2.—Electronic spectra of X^- in liquid SO_2. A. Transmission spectrum at $-68°$: a, I^- ($\sim 10^{-4}$ *M*); b, Br^- ($\sim$0.01 *M*); c, Cl^- ($\sim$0.01 *M*); d, liquid SO_2 background. B. Internal reflection spectrum (sapphire element) of 0.1 *M* solutions at 25°: a, I^-; b, Br^-; c, Cl^-; d, solvent.

Dilute solutions of ionophoric iodides in liquid SO_2 possess a distinct yellow color due to the low-frequency portion of an absorption band centered near 27.5 kK (Figure 2A). The transmission spectrum of liquid SO_2 solutions of K^+, Rb^+, Cs^+, $(CH_3)_4N^+$, $(C_3H_7)_4N^+$, and $(C_6H_{13})_4N^+$ iodides in the concentration range (1–10) × 10^{-4} *M* are identical within experimental error; the molar absorptivity (ϵ_{max}) is independent of concentration and cation. The molar absorptivity, calculated by a least-squares analysis of Beer's law data, is 2.20 × 10^4 l. mol^{-1} cm^{-1} at $-70°$. The band maximum shifts to lower frequency with increasing temperature ($\Delta\nu_{max}/\Delta T$ = -7 cm^{-1} deg^{-1}). In addition, as the temperature increases ϵ_{max} decreases but the band broadens so that the oscillator strength ($f \simeq 4.6 \times 10^{-9}\epsilon_{max}\Delta\nu_{1/2}$)[22] remains constant at 0.45. All temperature-dependent parameters have been corrected for the change in solvent density;[14] it was assumed that the density of a dilute solution is closely approximated by that of the pure solvent. Significant characteristics of the spectrum of the iodide ion in liquid SO_2 are given in Table I. It is apparent that the transition giving rise to this band occurs in some species containing the iodide ion and that there is no marked change in this species at concentrations up to 10^{-3} *M*.

The large values of ϵ_{max} and *f* for the absorption band suggest that it is due to a strongly allowed charge-transfer type transition. It is unlikely that a perturbed SO_2 solvent transition is responsible for this extremely intense transition since the SO_2 band at 27.8 kK has been assigned to a singlet–triplet transition. From among the species which could give rise to this band, only three appear to be at all reasonable: I_3^-, a nonspecifically solvated I^-, and a specifically solvated complex ion of the type ISO_2^-.

The I_3^- ion, although a somewhat unlikely possibility, possesses an absorption spectrum[15] similar to that of I^- in liquid SO_2; it could be formed by an oxidation–reduction reaction with the SO_2. The transmission spectra of solutions of $(CH_3)_4NI_3$ at several concentrations ((1–10) × 10^{-4} *M*) in liquid SO_2 were obtained under conditions similar to those used for the iodide solutions. Significant characteristics of the I_3^- spectrum appear in Table I. The band maximum at 26.7 kK does not shift with temperature in the range -65 to $-20°$. The apparent molar absorptivity ($\epsilon_{max} \simeq 3.4 \times 10^4$ l. mol^{-1} cm^{-1}) changes with concentration, indicating that dissociation of the type indicated by eq 3 is occurring. It is apparent that the absorption spectra

$$I_3^- \text{ (soln)} \rightleftharpoons I_2 \text{ (soln)} + I^- \text{ (soln)} \qquad (3)$$

of I^- and I_3^- in liquid SO_2 differ in frequency, intensity, and concentration dependence. Since oxidation–reduction products are not detected upon evaporation of solvent from I^-–SO_2 solutions, both spectroscopic and chemical evidence rules out the presence of I_3^-.

Solutions of the iodide ion in a variety of solvents possess an intense ($\epsilon_{max} > 10^4$ l. mol^{-1} cm^{-1}) absorption band in the ultraviolet (40–50 kK) region of the spectrum. Such bands arise from a "charge transfer to solvent" (CTTS) transition.[23] A characteristic feature of CTTS transitions of the iodide ion is the linear relationship between the maximum absorption frequency and its temperature coefficient: $\nu_{max} = a(\Delta\nu_{max}/\Delta T) + b$. For ν_{max} = 27.5 kK, a temperature coefficient of -75 cm^{-1} deg^{-1} is predicted for the iodide CTTS transition. The observed temperature coefficient of the I^- band in liquid SO_2 is -7 cm^{-1} deg^{-1}, an order of magnitude smaller than predicted. Since the spectrum of the iodide ion in liquid SO_2 does not exhibit the temperature dependence characteristic of a CTTS transition, it can be concluded[23] that the I^-–SO_2 interaction is a specific one which results in the formation of a distinct complex. The simplest complex has the form $I^- \cdot SO_2$ or ISO_2^-.

To investigate the possibility of bromide and chloride complexes, transmission spectra (Figure 2A) of solutions of tetraalkylammonium chlorides and bromides in liquid SO_2 were obtained. No bands are observed but

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(22) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1968, p 124.

(23) M. J. Blandamer and M. F. Fox, *Chem. Rev.*, **70**, 59 (1970).

TABLE I

ELECTRONIC SPECTRA OF HALIDE–SULFUR DIOXIDE MIXTURES

	Solvent							
	Liquid sulfur dioxide					1,2-Dichloroethane		
	Transmission (−68°)			Internal reflection (25°)		Transmission (25°)		
Halide	ν_{max}, kK	$10^{-4}\epsilon_{max}$,[a] l. mol^{-1} cm^{-1}	$\Delta\nu_{max}/\Delta T$,[b] cm^{-1} deg^{-1}	ν_{max},[c] kK	Rel intens[d]	ν_{max}, kK	$10^{-3}\epsilon_{max}$,[e] l. mol^{-1} cm^{-1}	K[e,f]
I^-	27.6	2.20 ± 0.11	−7	26.7	1.0	26.3	5.0 ± 2.0	220 ± 20
				(∼40.0)			(22.0)	(18 ± 2)
						26.5[i]	9.9[i]	22[i]
								38,[h] 11[j]
Br^-	Solvent cutoff shifts to lower frequency		. . .	30.7	0.5	32.3	6.0 ± 2.0	600 ± 200
				(∼40.0)			(11.0)	(90 ± 30)
						32.2[i]	12.1[i]	99[i]
								160,[h] 11[j]
Cl^-	Solvent cutoff shifts to lower frequency		. . .	32.0	0.3	33.9	6.3 ± 2.0	2000 ± 600
							(6.5)	(2000 ± 600)
						34.0[i]	9.0[i]	360[i]
								372,[h] 25[j]
I_3^-	26.7	>3[g]	∼0	. . .	. . .	27.8[k]	25[k]	. . .

[a] Obtained from least-squares analysis of Beer–Lambert data. [b] Range: −68 to −10°. [c] Concentration range: 0.01–0.4 *M*; additional solid solvate bands in parentheses. [d] Determined with same cation at 0.1 *M*. [e] Values in parentheses determined using ϵ estimated from liquid SO_2 data. [f] Formation constant for 1:1 complex. [g] Concentration dependent. [h] Reference 11; acetonitrile solution. [i] Reference 12; acetonitrile solution. [j] Reference 11; DMSO solution. [k] Reference 15.

the ultraviolet cutoff of liquid SO_2 shifts to lower frequency and the solutions become yellow as the concentration is increased up to 0.1 *M*.

The electronic spectra of halide ions in liquid SO_2 solution and of some of the solid solvates were obtained, however, by internal reflection at room temperature. The very short effective path length is only partially compensated by multiple reflections so that rather concentrated solutions (0.01–0.3 *m* or 0.015–0.45 *M*) are required. Representative spectra are illustrated in Figure 2B and the observed band frequencies for the various halide solutions and for some of the solid solvates are given in Table I. All data have been adjusted for the frequency dependence of reflected intensity that is implied by the effective path length approximation.[18] The band in the iodide solutions occurs at somewhat lower frequency than observed by transmission in the more dilute solutions. Since internal reflection spectra were obtained at 25° while transmission spectra were observed only at low temperature, it is easily shown that this shift can be attributed entirely to temperature effects. Using the absorption frequency and temperature coefficient measured by transmission (27.6 kK at 203°K and −7 cm^{-1} deg^{-1}), a frequency of 26.8 kK is predicted at 298°K. Since the agreement between the frequency observed by internal reflection and that predicted from transmission data at lower concentration is so close, it is assumed that the absorbing species remains essentially the same at concentrations up to at least 0.4 *M*. Furthermore, it is probable that the band frequencies characteristic of bromide and chloride ions in liquid SO_2 are well represented by those observed under internal reflection conditions.

At the high concentrations required for internal reflection measurements, band intensity is neither independent of cation nor is it a linear function of concentration. The relative intensities of the bands of the halides (at equal concentrations and with the same cations) are, however, representative of the relative magnitudes of the molar absorptivities of the X^-–SO_2 complex. Relative intensities and molar absorptivities were estimated using the method of Harrick;[18] the values appear in Table I.

The spectrum of a solid solvate deposited on the sapphire element possesses the same high-intensity band as does the corresponding solution in liquid SO_2 (Table I). There are no bands which are characteristic of SO_2 or which might correspond to the higher frequency bands of trihalide ions.[15] A broad band which occurs near 40 kK and is independent of halide probably corresponds to the singlet–singlet transition in SO_2.

The formation of X^-–SO_2 complexes was also examined by observation of the ultraviolet absorption spectrum of mixtures of halide ion and sulfur dioxide in 1,2-dichloroethane. This solvent was chosen to minimize the effects of solvent complexation: acetonitrile and dimethyl sulfoxide are strong-donor solvents,[24] alcohols complex with SO_2,[25] and water not only reacts with SO_2 but is also a poor solvent in which to expect halide complexes with weak Lewis acids.[26] Tetra-*n*-propyl-, tetra-*n*-butyl-, and tetra-*n*-hexylammonium iodides, bromides, and chlorides were used as halide ion sources because of their high solubility. Since the uncertainty in the concentration of volatile SO_2 probably makes a more sophisticated analysis unjustified, Job's method of continuous variations was used to determine the stoichiometry of the complex. After the Job analysis indicated the formation of 1:1 complexes, the equilibrium in eq 4 was assumed. Formation constants (K) and molar absorptivities (ϵ_{max}) were estimated by solving pairs of simultaneous equations of the type indicated by eq 5 and averaging the results.

$$X^- + SO_2 \rightleftarrows (XSO_2)^- \qquad (4)$$

$$K = [XSO_2^-]/[X^-][SO_2] \qquad (5)$$

The calculated formation constants along with those recently reported by other authors[11,12] (also calculated from eq 5) are shown in Table I.

The frequencies of maximum absorption of the chloride and bromide complexes in 1,2-dichloroethane are somewhat higher than those observed in liquid SO_2 whereas that of the iodide complex is slightly less

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(24) V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions," Springer-Verlag, Vienna, 1968.

(25) P. A. D. deMaine, *J. Chem. Phys.*, **26**, 1036, 1042 (1957).

(26) A. I. Popov, *Halogen Chem.*, **1**, 225 (1967).

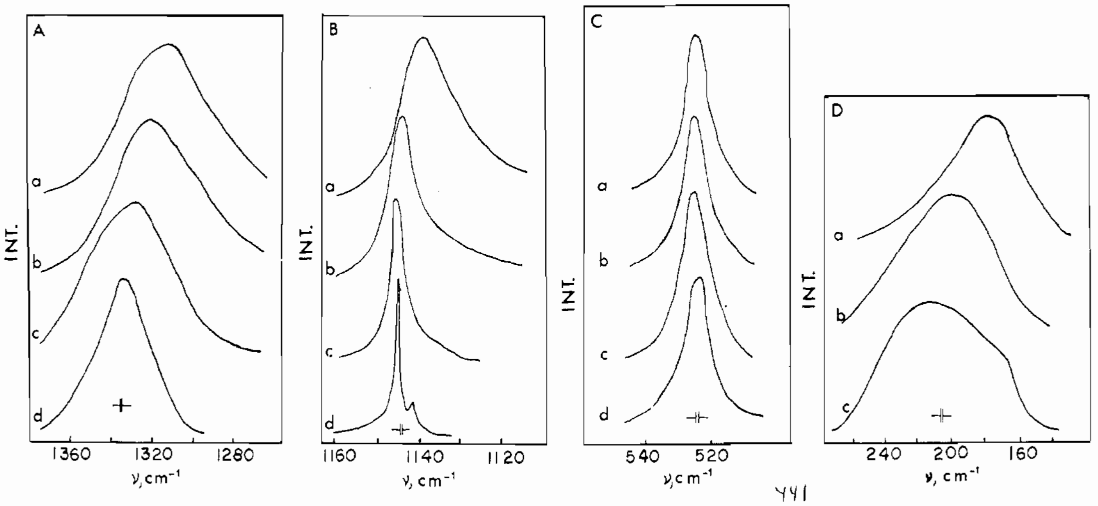

Figure 3.—Raman spectrum of 2.0 *M* X^- in liquid SO_2: A, S–O asymmetric stretching mode, ν_5; B, S–O symmetric stretching mode, ν_1; C, SO_2 bending mode, ν_3; D, S–X stretching mode, ν_2; a, KI; b, $(CH_3)_4NBr$; c, $(CH_3)_4NCl$; d, pure liquid SO_2.

than in liquid SO_2. These absorption frequencies are in reasonable agreement with those reported by other workers for acetonitrile solutions.[11,12] Since the frequency shifts are on the order of those expected from a change of solvent, the 1:1 complexes in 1,2-dichloroethane are probably good representations of the absorbing species in liquid SO_2. When both K and ϵ_{max} are determined by the 1,2-dichloroethane data, ϵ_{max} is the same within experimental error for all three halide complexes and the relative sizes of the formation constants are similar to those reported for acetonitrile solutions:[11,12] $K(XSO_2^-)/K(ISO_2^-) = 1$, 3, and 10 in 1,2-dichloroethane compared with 1, 4, and 10 in acetonitrile for I^-, Br^-, and Cl^-, respectively. The large uncertainty in K is attributed to uncertainty in the SO_2 concentrations. The lack of any significant dependence of ϵ_{max} upon halide is quite surprising in light of the results in liquid SO_2. Furthermore, the separation of K and ϵ_{max} is not particularly reliable.[27] For these reasons, the formation constants were also calculated with the ϵ_{max} from liquid SO_2 solutions, as well as with several other values in the range $(1–20) \times 10^3$ l. mol^{-1} cm^{-1}. The difference in the calculated formation constant for the chloride complex compared with those of bromide and iodide becomes larger as ϵ_{max} approaches the value observed in liquid SO_2. For ϵ_{max} equal to the values obtained from liquid SO_2 solution, the relative formation constants, $K(XSO_2^-)/K(ISO_2^-)$, are 1, 2.5, and 100 for I^-, Br^-, and Cl^-, respectively (see Table I). While the actual values of the formation constants are sensitive functions of ϵ_{max}, they are always in the order $K(ISO_2^-) < K(BrSO_2^-) < K(ClSO_2^-)$, implying that the stability of XSO_2^- in 1,2-dichloroethane solution increases from iodide to chloride. Except for the smaller values of ϵ_{max} ($<4 \times 10^3$), the fit for any one set of ϵ and K is as good as another.

Comparison of the values of K calculated from data obtained in the solvents dimethyl sulfoxide,[12] acetonitrile,[11,12] and 1,2-dichloroethane (Table I) reveals the influence of decreasing donor strength[24] of these solvents. Thus the equilibrium described by eq 4 is an oversimplification of the complexation reaction in these solvents. Formation constants calculated on the basis of this equilibrium indicate only the relative stabilities in that particular solvent. An equilibrium similar to that described by eq 6 is required for dilute solutions of the components. Neglect of the solvation

$$X^-\cdot(\text{solv})_n + SO_2\cdot(\text{solv})_m \rightleftharpoons XSO_2^-\cdot(\text{solv})_p^- + q(\text{solv}) \quad (6)$$

has been shown to result in considerable error in the values of both K and ϵ_{max};[27–29] these errors are particularly large if specific solvation occurs. Although specific solvation of X^- or XSO_2^- in either of these three solvents is unlikely, specific solvation, in the form of donor–acceptor complexes of the type $(CH_3)_2SO{\rightarrow}SO_2$ and $CH_3CN{\rightarrow}SO_2$, is quite probable. These interactions along with differences in the nonspecific solvation of X^- and XSO_2^- are probably sufficient to account for the observed trends in calculated values of the formation constants.

The differences in the transition energies of XSO_2^- in liquid SO_2 and in 1,2-dichloroethane also suggest that solvation of these species cannot be neglected. The changes in the transition frequencies $[\Delta\nu = \nu(SO_2) - \nu(EtCl_2)]$ are -1900 cm^{-1} (-5.5 kcal/mol), -1800 cm^{-1} (-5.1 kcal/mol), and $+500$ cm^{-1} ($+1.4$ kcal/mol) for Cl^-, Br^-, and I^-, respectively. These differences most probably arise from both stabilization of the ground state and destabilization of excited states, yet it is possible that they may be due entirely to ground-state interactions (nonspecific solvation). If this were the case, $ClSO_2^-$ and $BrSO_2^-$ would be stabilized and ISO_2^- destabilized in 1,2-dichloroethane compared with liquid SO_2. Thus, the magnitude of the differences in solvation energy may be approximately equal to the values of ΔG and ΔH (less than 5 kcal) determined for eq 4 in acetonitrile by others.[11,12] Correction of these values for a possible solvation effect would result in the following trend in the stability of the XSO_2^- ions: $ISO_2^- > BrSO_2^- > ClSO_2^-$. Although the magnitude of the difference in the stabilities of XSO_2^- in liquid SO_2 and/or in the crystal cannot be reliably estimated from available data, the results of vibrational spectroscopy offer additional evidence to support the validity of this latter trend.

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[27] R. Foster, "Organic Charge Transfer Complexes," Academic Press, New York, N. Y., 1969.

[28] S. Carter, J. N. Murrell, and E. J. Rosch, *J. Chem. Soc.*, 2048 (1965).

[29] S. Carter, *ibid.*, *A*, 404 (1968).

Vibrational Spectroscopy.—The Raman spectrum of pure liquid SO_2 was observed to be essentially the same as that reported by Anderson and Savoie.[30] The infrared spectrum of the liquid, above 700 cm^{-1}, was observed by transmission to possess the following bands: 1140 (vs), 1335 (vs), 1910 (w), 2300 (m), and 2480 (m) cm^{-1}. Only the bands at 1140 and 1355 cm^{-1} were observed by internal reflection; this can be attributed to the lower effective path length at these higher frequencies. As expected, the asymmetric S–O stretching mode at 1335 cm^{-1} is more intense than the symmetric mode at 1140 cm^{-1}. The higher frequency bands occur at frequencies similar to those reported for overtone and combination modes in the gas phase.[31]

Infrared spectra of the following X^-–SO_2 systems were obtained: iodides: Na^+, K^+, $(CH_3)_4N^+$, $(n\text{-}C_4H_9)_4N^+$, $(n\text{-}C_6H_{13})_4N^+$, $(n\text{-}C_4H_9)_3(CH_3)P^+$; bromides: $(CH_3)_4N^+$, $(n\text{-}C_4H_9)_4N^+$, $(n\text{-}C_4H_9)_4P^+$; chlorides: $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(n\text{-}C_4H_9)_4N^+$; fluorides: K^+. Raman spectra were obtained on a more limited scale: only the first three iodides and the first two bromides and chlorides in the above list were examined. At those frequencies where comparison was possible, the infrared bands were within ± 5 cm^{-1} of the Raman bands. The spectra are tabulated without specification of cation and without any of the cation vibrational modes since no cation effects were observed.

As the concentration of halide in liquid SO_2 is increased to approximately 2.0 *m*, the S–O stretching modes of the solvent become broader and increasingly asymmetric on the low-frequency side until a distinct shoulder develops. At equal concentrations, the degree of asymmetry increased in the order $Cl^- < Br^- < I^-$. The SO_2 bending mode, however, undergoes little change even at much higher concentration. At concentrations greater than 2.0 *m*, the spectrum in the S–O stretching region undergoes further change; the shoulder in the more dilute solutions becomes the dominant band. Another shoulder characteristic of the solid occurs when solid "solvate" is present. A low-frequency band, characteristic of the halide, becomes apparent in the Raman spectrum of these solutions. Other low-frequency Raman bands are present in nearly saturated solutions of bromide and iodide. The data are tabulated in Table II and the spectra are illustrated in Figures 3 and 4.

Removal of solvent from a quaternary ammonium halide solution by permitting SO_2 to distil off through the vacuum system leaves a highly viscous, yellow (orange) liquid. Vibrational spectra of these liquids, as observed by internal reflection and by transmission (suspension in Nujol), are identical with those of the concentrated solutions. Further removal of SO_2 by evacuation or by distillation into a cold trap results in the formation of crystalline solids. Prolonged evacuation or exposure to a trap immersed in liquid N_2 results in complete removal of the SO_2; *i.e.*, SO_2 cannot be detected in the infrared spectrum of the solid. Removal of SO_2 from solvates with the larger organic cations is more difficult than from salts with the small cation; for a given cation, the order of solid solvate stability is $I^- > Br^- > Cl^-$. Infrared spectra of the crystalline solvates as obtained by internal reflection

TABLE II

VIBRATIONAL SPECTRA OF HALOSULFINATE IONS[a]

		$\nu_1(A')$, $\nu_s(SO_2)$		$\nu_2(A')$, $\nu(SX)$		$\nu_3(A')$, $\delta_s(SO_2)$		$\nu_4(A')$, $\delta_s(XSO)$		$\nu_5(A'')$, $\nu_{as}(SO_2)$		$\nu_6(A'')$, $\delta_{as}(XSO)$	
		Ir	R	Ir	R	Ir	R	Ir	R	Ir	R	Ir	R
FSO_2^-	Cryst[b]	1100 vs	. . .	598 s	. . .	496 s	. . .	378 m	. . .	1170 vs	. . .	280 w	. . .
		1110 sh				520 sh		365 m		1200 sh			
	Cryst[c]	1101 vs	. . .	593 s	. . .	498 s	. . .	350 m	. . .	1180 vs	. . .		. . .
$ClSO_2^-$	SO_2 soln	1120 vs, b	1125 vs, p	. . .	214 m, p	526 m, b	528 m, p	. . .	172 w, p	1312 vs, b	1315 w, dp	. . .	103?
	Cryst	1120 vs	. . .	. . .	215	535 m	. . .	. . .	. . .	1290 vs	. . .	. . .	. . .
$BrSO_2^-$	SO_2 soln	1117 vs, b	1120 vs, p	. . .	203 m, p	530 m, b	528 m, p	. . .	115 vw, p	1308 vs, b	1312 w, dp	. . .	. . .
	Cryst	1109 s	. . .	. . .	201	530 m	. . .	. . .	. . .	1285 vs	. . .	. . .	. . .
		1080 m, sh[d]		. . .	. . .		. . .	. . .	. . .	1275 sh[d]	. . .	. . .	. . .
ISO_2^-	SO_2 soln	1112 s	1120 vs, p	. . .	184 m, p	530 m	528 m, p	. . .	~55?	1300 vs, b	1310 w, dp	. . .	. . .
										1280 sh	1284 w, dp		
	Cryst	1104 s	1115?	. . .	182 m	530 m	530 m	. . .	. . .	1275 vs	1277 w, dp	. . .	. . .
		1085 m, sh								1250 m[d]		. . .	. . .

[a] Cations indicated in text, frequencies in cm^{-1}, experimental error ± 5 cm^{-1}. [b] This work. [c] Reference 10. [d] Assigned to dimer.

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(30) A. Anderson and R. Savoie, *Can. J. Chem.*, **43**, 2271 (1965).

(31) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, Van Nostrand, New York, N. Y., 1945, p 225.

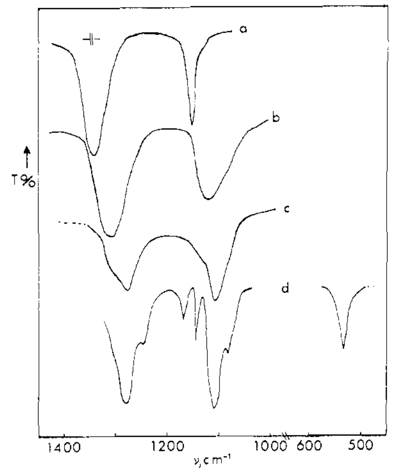


Figure 4.—Infrared spectrum of the I^-–SO_2 system: a, pure liquid SO_2 (internal reflection); b, 3.5 *M* $(C_6H_{13})_4NI$ in liquid SO_2 (internal reflection); c, $(C_6H_{13})_4N^+(ISO_2)^- + nSO_2$ (internal reflection of viscous liquid); d, crystalline $(C_6H_{13})_4{}^+N(ISO_2)^-$ (mull).

and by transmission (mull) are illustrated in Figure 4c, d. The spectrum in Figure 4d is that of a sample prepared by reaction of gaseous SO_2 with the solid iodide and is identical with that obtained from a sample recovered from SO_2 solution.

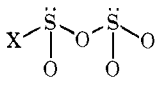
The spectra of the crystalline solids with $X^-:SO_2$ ratios greater than 1:1 indicate that they are probably mixtures: at low SO_2 content one SO_2 stretching mode is found near 1300 cm^{-1} and one near 1100 cm^{-1}; at high SO_2 content, two bands are found in each of these regions; one of each set is always more intense than the other (Figure 4d). The bands in Figure 4d at 1180 and 1140 cm^{-1} are due to the cation and to trapped SO_2, respectively. The low-frequency Raman bands characteristic of the halide are also present in the crystalline solids. At times other bands, probably due to lattice modes, were also observed in the low-frequency Raman spectrum but they were not reproducible.

Several attempts were made to examine mixtures of halide ions and SO_2 in "inert solvents" but these provided little additional information. Acetonitrile was used since it is the most inert of conveniently available solvents which are transparent in the S–O stretching region. Tetrabutylammonium halide salts were used as halide ion sources. Only four bands are present in the S–O stretching region: two bands due to free SO_2 and two bands due to complexed SO_2. The bands due to complexed SO_2 occur at the same frequencies (± 5 cm^{-1}) as those observed in the corresponding halide solution in liquid SO_2. Band frequencies for the iodide solutions correspond to those observed by Lippincott and Welsh.[8]

The infrared spectrum of $KFSO_2$ was obtained as a mull for comparison with the spectrum reported by Robinson, Lavery, and Weller.[10] The following bands were observed: 280 (vw), 365 (m, sh), 378 (m), 440 (vw), 496 (s), 520 (s, sh), 650 (w), 972 (m), 1100 (vs), 1170 (vs), 1200 (s, sh), 1235 (w, sh) cm^{-1}. The assignments by Robinson and coworkers are quite adequate for the major features if the doublets are assigned to crystal splitting. The bands at 440 and 650 cm^{-1} are probably due to disulfite[32] ($S_2O_5{}^{2-}$) while the band at 1235 cm^{-1} is best assigned to FHF^- because these bands become quite intense when the sample is exposed to air. It is reported that disulfite and bifluoride are formed when $FSO_2{}^-$ reacts with moisture in the air.[9]

All major features of the vibrational spectra are assigned to the same 1:1 X^-–SO_2 complexes which give rise to the electronic spectra discussed above. A consistent account of the data is obtained by regarding this complex as a halosulfinate ($XSO_2{}^-$) ion. By analogy with the fluorosulfinate ion,[10] the pseudoisoelectronic sulfite ion, the trimethylamine–sulfur dioxide adduct,[33] and the transition metal–sulfur dioxide complexes,[34] a pyramidal geometry with X–S bonding is expected in the halosulfinate ions. An $XSO_2{}^-$ ion, of C_s symmetry, has six fundamental vibrational modes, four of symmetry A′ and two of symmetry A″. All six modes are infrared and Raman active; the Raman spectrum should contain four polarized and two depolarized bands. An approximate description of these modes in terms of internal coordinates along with the frequency assignments is given in Table II. Frequency assignments are made by analogy with sulfur dioxide: the S–O symmetric and asymmetric stretching modes are expected near 1100 and 1300 cm^{-1}, respectively, and the SO_2 bending mode is expected near 525 cm^{-1}. All other bands occur near 200 cm^{-1} or below and were observed only by the Raman method. These bands are broad and the lower frequency ones are very weak. Only those bands which occur in both the solid solvates and in liquid SO_2 solution are assigned. The band of highest frequency (Figure 3D) is assigned to the X–S stretching mode since it is most intense and it is polarized. The symmetric and asymmetric S–X–O deformation modes are assigned to the remaining frequencies. The bands at 172 ($ClSO_2{}^-$), 115 ($BrSO_2{}^-$), and 55 cm^{-1} ($ISO_2{}^-$) are assigned to the symmetric deformation mode since they appear to be polarized. The proximity to another band or the very low intensities result in the uncertainty of the polarization of these bands. The asymmetric deformation is expected to be very weak in the Raman spectrum and is apparently observed only in the $ClSO_2{}^-$ spectrum as a very weak band near 100 cm^{-1}.

The infrared spectra of the solid solvates which have an $SO_2:X^-$ ratio near or greater than 1 possess two additional bands in the S–O stretching regions. The dependence upon SO_2 content suggests that these bands are not due to coupling with crystalline lattice modes. These bands may be attributed to the presence of a 2:1 SO_2–X^- complex although higher complexes cannot be entirely ruled out. Several structures which encompass the likely possibilities for this 2:1 complex are suggested by I–IV. Structure IV



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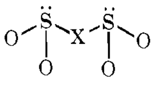

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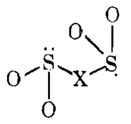

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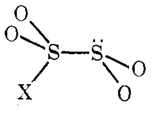

IV

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[32] A. W. Herlinger and T. V. Long, *Inorg. Chem.*, **8**, 2661 (1969).

[33] D. Vander Helm, J. D. Childs, and S. D. Christian, *Chem. Commun.*, 887 (1969).

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seems to be the most likely possibility because it has a structure similar to that of the isoelectronic $S_2O_5^{2-}$ ion.[32,35] Since sulfite ion dissolved in liquid SO_2 reacts according to eq 7,[36] the reaction of halosulfinate with

$$SO_3^{2-} + SO_2 \longrightarrow (O_3S\text{–}SO_2)^{2-} \qquad (7)$$

SO_2 to form the similar $(XO_2S\text{–}SO_2)^-$ seems likely. Although the data are insufficient to distinguish between the various options, the bands will be assigned tentatively to structure IV: 1085, 1100 (A′) and 1250, 1280 cm^{-1} (A″). The two higher frequencies in each set are coincident with the frequencies of the 1:1 complex.

When in solution, only the S–O stretching modes of the XSO_2^- ions appear at frequencies significantly different from those in the solids. Both in acetonitrile and in liquid SO_2, the bands occur near 1115 and 1300 cm^{-1}. These bands are assigned to nonspecifically solvated XSO_2^- ions. The vibrational spectra of the highly concentrated solutions are sufficiently similar to those of the dilute solutions to expect that XSO_2^- is the predominant species present. The marked low-frequency asymmetry of the S–O stretching bands in the latter solutions is attributed to the weak coordination of additional SO_2 molecules to XSO_2^-. This assignment suggests that the reported SO_2 solvates[1,2] of ionophoric halides are best described as halosulfinates.

Preliminary observations indicate that pseudohalides (SCN^- and N_3^-) also interact with SO_2. In contrast, the infrared spectrum of a saturated solution of tetra-*n*-butylammonium perchlorate in liquid SO_2 ($\sim$3 *m*) is merely a composite of the spectrum of the solvent and the solute. The solvent bands at 1140 and 1335 cm^{-1} are slightly broader than in the pure solvent but there is no evidence of lower frequency S–O stretching modes as in the halide solutions. The triply degenerate Cl–O stretching mode of perchlorate ion is observed at 1075 cm^{-1} with a shoulder at 1035 cm^{-1}. This splitting is larger than that expected from chlorine isotope effects[37] but somewhat smaller than that reported for coordinated ClO_4^-.[38,39] The absence of an infrared-active Cl–O symmetric stretching mode due to coordinated ClO_4^- (930–970 cm^{-1})[38,39] and the very slight solvent perturbation suggests that the splitting is due to some nonspecific interionic interactions. The absence of specific interaction between SO_2 and ClO_4^- is attributed to the weak basic character of ClO_4^-.

Normal-Coordinate Analysis.—Although modified somewhat by nonspecific solvation or by weak coordination to other SO_2 molecules, the important structural unit in these systems is the pyramidal XSO_2^- ion of C_s symmetry. A normal-coordinate analysis was applied to these ions to determine the contributions of particular internal coordinates to observed vibrational bands and to provide an estimate of the force constants. The characteristic-set method[40] was used to calculate the force constants of XSO_2^- to facilitate comparison with those reported for FSO_2^-.[10] Application of more sophisticated methods is probably unwarranted in the absence of accurate data on the bond distances and bond angles. Agreement between the results obtained by this method and those obtained by other methods is variable,[10,41–43] but the results seem to be sufficiently reliable to permit a semiquantitative comparison of XSO_2^- systems. Force constants determined by the characteristic-set method are generally comparable to those obtained by standard iterative methods but may be as much as 20% larger.

The characteristic set method assumes the form of the normal vibrations to be determined completely by the G matrix of the kinetic constants.[44] The characteristic set of coordinates is that for which the trace of the L matrix is a maximum; L is the transformation matrix relating the normal coordinates (Q) to a set of symmetry coordinates (S), $S \doteq LQ$. The computational method was that suggested by Herranz and Castaño[40] and will not be described further. Calculations were carried out using the IBM 360-44 digital computer system.

Symmetry coordinates corresponding to those used by Robinson and coworkers were used; they are indicated in Table II. Since frequencies corresponding to the asymmetric O–S–X bending mode of ISO_2^- and $BrSO_2^-$ were not observed, their values were estimated from reported thionyl bromide frequencies.[45]

$$\nu_{OSX}(XSO_2^-)/\nu_{SX}(XSO_2^-) \simeq \nu_{OSBr}(SOBr_2)/\nu_{SBr}(SOBr_2) \qquad (8)$$

The estimated values are $\nu_6(BrSO_2^-)$ = 63 cm^{-1} and $\nu_6(ISO_2^-)$ = 25 cm^{-1}. Values for the structural parameters used in the calculations are given in Table III.

TABLE III

STRUCTURAL PARAMETERS FOR XSO_2^-

	Distances, Å		Angles, deg	
	X–S	S–O	O–S–O	X–S–O
F	1.7	1.45	112	108
Cl	2.1	1.45	112	108
Br	2.3	1.45	114	110
I	2.5	1.45	116	110

The S–O bond lengths and the SO_2 bond angles were estimated from S–O stretching frequencies by use of the correlations of Gillespie and Robinson.[46] Covalent sulfur–halogen bond distances, covalent radii, and O–S–X bond angles were estimated from literature values;[47,48] the S–I bond distance was estimated from covalent radii and by comparison with P–I bond distances.[49] The bond angles are consistent with those reported for SO_2 complexes with trimethylamine[33] and with transition metals.[34]

The L matrices developed in the computation are strongly diagonal; off-diagonal elements are a factor of 5 smaller than the smallest diagonal element. Thus, the group vibrations represented by the symmetry coordinates, S_i, are a fair approximation of the normal coordinates. The force constants are tabulated in Table IV. The dependence of the S–X and S–O stretching

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Table IV

Force Constants for XSO_2^- (mdyn/Å)

Constant[a]	FSO_2^- [b]	FSO_2^-	$ClSO_2^-$	$BrSO_2^-$	ISO_2^-
f_r	9.18	9.42	10.61	11.00	11.14
f_R	2.93	3.22	1.23	2.47	3.10
f_α/Rr	0.44	0.46	0.23	0.27	0.28
f_β/rr	0.91	0.90	0.95	0.93	0.91
f_{Rr}	0.62	1.57	1.93	3.25	3.91
f_{rr}	0.46	1.63	1.07	1.88	2.13
$f_{r\beta}/r$	0.83	0.55	0.39	0.36	0.27
$f_{r\alpha}/(Rr)^{1/2}$	0.77	0.74	0.80	1.07	1.18
$f_{r\alpha}'/(Rr)^{1/2}$	−0.42	0.81	0.96	1.23	1.35
$f_{r\beta}/r$	−0.11	0.33	0.21	0.35	0.21
$f_{R\alpha}/(Rr)^{1/2}$	0.33	0.44	0.36	0.68	0.84
$f_{\alpha\alpha}/Rr$	0.08	0.15	0.18	0.25	0.27
$f_{\alpha\beta}/(Rr^3)^{1/2}$	0.11	−0.08	−0.08	−0.06	−0.07

[a] r = S–O stretch, R = S–X stretch, α = O–S–X bend, β = O–S–O bend. [b] Results of Robinson, et al.[10]

force constants upon the choice of values for the structural parameters is illustrated in Figure 5. It should be noted that the trends in the halogen dependence of these force constants are independent of the particular choice of parameters.

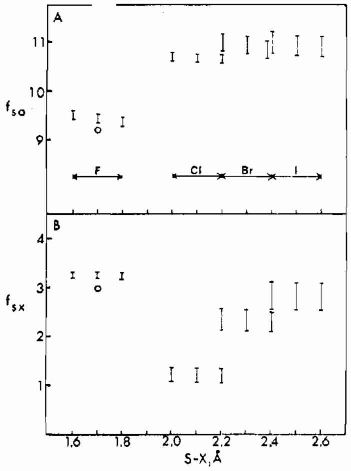

Figure 5.—Dependence of force constants (mdyn/ Å) upon structural parameters; 106° ≤ OSX ≤ 110°, 112° ≤ OSO ≤ 116° (circles indicate values from ref 10): A, dependence of S–O stretching force constant; B, dependence of S–X stretching force constant.

The S–O stretching force constants are in the range expected for oxyhalides of sulfur[46,50–51] (11.1, 9.7, and 7.8 mdyn/Å for F_2SO, Cl_2SO, and Br_2SO, respectively). The value for FSO_2^- is a little lower while the values for $ClSO_2^-$ and $BrSO_2^-$ are somewhat higher than those calculated for the corresponding oxyhalides. Comparisons of ISO_2^- parameters with those of other S–I bonded compounds are not possible since there are apparently very little data on the few compounds which have been reported.[47] The trend in the size of f_{SO}, as a function of halogen, $FSO_2^- < ClSO_2^- < BrSO_2^- < ISO_2^-$, is in the opposite direction to that of f_{SO} in other oxyhalides.

Values calculated for the S–X stretching force constants show a more surprising variation than do the S–O force constants. The values for f_{SF} and f_{SCl} are somewhat lower than those reported for the comparable sulfuryl[50] and thionyl[51,52] compounds. The values for f_{SCl} appear to be on the order of the force constants determined for metal chloride complexes[53,54] or for charge-transfer complexes.[55,56] Compared with f_{SBr} determined for thionyl bromide,[51,52] the S–Br stretching force constant of $BrSO_2^-$ is some 1.5–2.0 times as large. The calculated S–I stretching force constant of 3.1 mdyn/Å is quite large in comparison with the force constants estimated for bonds between I and other elements: $f_{BI}(BI_3)^{57}$ = 1.95 mdyn/Å, $f_{PI}(PI_3)^{58}$ = 1.21 mdyn/Å, $f_{AsI}(AsI_3)^{58}$ = 1.17 mdyn/Å, and $f_{GeI}(GeI_4)$ = 1.41 mdyn/Å. The large-size f_{SI} is particularly unusual since conventional S–I bonds are apparently so weak that they are very uncommon. Although the magnitudes of f_{SX} are of questionable significance, the trend in the values of f_{SX} is quite significant: $f_{SF} > f_{SCl} < f_{SBr} < f_{SI}$. This trend is not unexpected if the S–X stretching frequencies are compared with those observed for thionyl[45] or phosphorus halides[33]

$\nu(XSO_2^-)/\nu(X_2SO)$ = 0.65 (F) $\nu(XSO_2^-)/\nu(PX_3)$ = 0.57 (F)
= 0.46 (Cl) = 0.43 (Cl)
= 0.52 (Br) = 0.52 (Br)
= 0.57 (I)

This trend implies that the S–X bond order in the halosulfinates does not follow that observed in other sulfur halides or oxyhalides. The bending force constants are comparable to those reported for other sulfur oxyhalides. Several of the interaction force constants are very large, but the approximate nature of the computation suggests that they are of doubtful significance.

Description of Halosulfinate Ions.—The Lewis acid properties of sulfur dioxide are well established; numerous complexes with electron donors have been reported.[14] Similar donor–acceptor interactions between halide ions and SO_2, undoubtedly, give rise to the halosulfinate ions. The properties of the halosulfinate ions are conveniently described in terms of a model which involves donation of electron density into the lowest lying unoccupied molecular orbital of SO_2. Walsh[59] has described this orbital as an S–O antibonding π orbital of B_1 symmetry; this orbital undoubtedly contains some contribution from the sulfur d orbitals as well.[60] Thus, an increase of electron density by donation from the halide would result in a decrease in the S–O bond order and stretching force constant. Since the characteristic-set method yields a value of 10.7 mdyn/Å for f_{SO} in SO_2,[43] this prediction is qualitatively correct for FSO_2^- and $ClSO_2^-$. The higher values of f_{SO} and f_{SX} in $BrSO_2^-$ and ISO_2^- are likely due to an increase in the S–X bond order from Cl to I in halosulfinates due to increasing back-donation of electron density from SO_2 into empty orbitals on X. A similar back-donation has been widely utilized[61] to account for the stability of transition metal complexes with carbon monoxide, phosphines, olefins, and aromatics.

Although a complete molecular orbital treatment of

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these halosulfinate ions would provide a somewhat better basis for discussion, the available vibrational and electronic spectral data do indicate the trend in the S–X bond order to be S–F > S–Cl < S–Br < S–I. For a given cation, the difficulty of removal of SO_2 from the solid solvates also parallels this trend. Since the ionogenic character of halogen-containing solutes in liquid SO_2 is, undoubtedly, due to halosulfinate formation, this trend in stability suggests that iodides and bromides should be more ionized than chlorides. In support of this proposition, Lichtin[62] has indicated that triphenylbromomethane, unlike the corresponding chloride, is almost completely ionized in liquid SO_2. Studies investigating the validity of these suggestions with a variety of halogen-containing molecules are now under way.

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Selenium Pentafluoride Chloride, SeF_5Cl. Vibrational Spectrum, Force Constants, and Thermodynamic Properties

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The infrared spectrum of gaseous and the Raman spectrum of liquid SeF_5Cl are reported. The observed spectrum is consistent with symmetry C_{4v}. The structure of SeF_5Cl can be derived from an octahedron with one chlorine and five fluorine atoms occupying the six corners. A modified valence force field and thermodynamic properties in the range 0–2000°K were computed for SeF_5Cl.

Introduction

The existence of the novel selenium fluoride chloride, SeF_5Cl, has recently been discovered.[1] In this paper, we wish to report its vibrational spectrum, force constants, and thermodynamic properties.

Experimental Section

The preparation, purification, physical properties, and handling of SeF_5Cl are described elsewhere.[1] The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range of 4000–250 cm^{-1}. The instrument was calibrated by comparison with standard calibration points.[2] Stainless steel cells of 5- or 10-cm path length fitted with AgCl or AgBr windows were used as sample containers. The Raman spectrum of liquid SeF_5Cl was recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to $\sim -25°$, and a dc ammeter. Polarization measurements were carried out using a Model 310 polarization rotator from Spectra-Physics. Clear Kel-F tubes ($\sim$2-mm i.d.) were used as sample containers in the transverse viewing–transverse excitation technique.

Results and Discussion

Vibrational Spectrum.—Figures 1 and 2 show the infrared spectrum of gaseous SeF_5Cl and the Raman spectrum of liquid SeF_5Cl, respectively. The observed frequencies are listed in Table I.

Since SeF_5Cl can be considered as a monosubstituted derivative of octahedral SeF_6, it should belong to point group C_{4v}. The 11 normal modes of SeF_5Cl of symmetry C_{4v} can be classified as $4\ a_1 + 2\ b_1 + b_2 + 4\ e$. Of these, all 11 modes will be Raman active, whereas only the a_1 and e modes will be infrared active. Of the Raman lines, the four a_1 modes should be polarized, the rest being depolarized. The assignment of the observed bands to individual modes (Table I) is based on the following arguments. There are four clearly polarized Raman lines at 721, 656, 443, and 385 cm^{-1}. As predicted by theory, these have counterparts in the infrared spectrum. Hence, these four bands must belong to species a_1. The two higher frequency lines are within the range expected for stretching modes of mainly covalent Se–F bonds. They are assigned, respectively, to the SeF and the symmetric SeF_4 stretching vibrations on the basis of their relative Raman intensities.[3] Similarly, the SeCl stretching mode should be of higher Raman intensity than the SeF_4 umbrella deformation.[3] Therefore, the 443-cm^{-1} band is assigned to the SeF_4 deformation. This assignment is further supported by the fact that in the infrared spectra of both $SeF_4(OF)_2$ and SeF_5OF[4] very strong infrared bands were observed at about 430 cm^{-1}.

Of the remaining six depolarized Raman bands, the 745-, 424-, and 336-cm^{-1} lines have counterparts in the infrared region and, consequently, belong to species e. The very intense infrared band at 745 cm^{-1} obviously represents the antisymmetric SeF_4 stretching vibration. For $SeF_4(OF)_2$ and SeF_5OF, this mode was observed[4] at 743 and 750 cm^{-1}, respectively. By analogy with the known spectrum[3,5] of the SF_5Cl molecule, one might

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