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Complex Formation between Sulfur Dioxide and Halide Ions in Acetonitrile Solution[1]

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An ultraviolet spectrophotometric study has shown the formation of 1:1 complexes, $SO_2 \cdot X^-$, between tetraethylammonium halides and sulfur dioxide in acetonitrile solution. With chloride, bromide, and iodide, strong, presumably charge-transfer, absorption maxima occur at 294, 321, and 378 nm, respectively. A linear correlation between absorption frequency and halide ionization potential is observed. Formation constants and $\Delta H°$ and $\Delta S°$ values have been obtained for the three heavier halides, from measurements at 15, 25, and 35°. $K(25°)$ values are 361 ± 6 (Cl^-), 99 ± 1 (Br^-), and 21.4 ± 0.4 (I^-).

Introduction

Although the interaction between sulfur dioxide and halide ions has been extensively studied, both in aqueous and nonaqueous systems, the state of knowledge in this area remains incomplete. A suggestion of an interaction in solution, especially for iodide ion, was first given at the beginning of the century in work by Walden and others.[3-5] Much of the early work, however, was concerned primarily with the characterization of various solvates isolable from liquid sulfur dioxide solutions of halide salts, again iodides in particular, as well as thiocyanates.[3,4,6-9] Mole ratios of sulfur dioxide to salt have ranged generally from 1 to 4, although higher values have also been reported. Later, mono- and disolvates of tetramethylammonium chloride and bromide were obtained by Jander and Mesech.[10] And relatively recently Seel and coworkers[11] have reported the formation of particularly stable monosolvates of fluoride salts, substances regarded as "true" fluorosulfites, the SO_2F^- anion maintaining its identity in liquid sulfur dioxide and other solutions. The present state of information regarding these solvates has been summarized by Waddington.[12]

A number of spectroscopic studies have been made of complex formation in these systems, primarily in aqueous solution. Witekowa, *et al.*,[13] and Jander and Türk[14] used ultraviolet spectra to obtain evidence and equilibrium data for the 1:1 sulfur dioxide–iodide ion complex. Witekowa, *et al.*,[13d,e] have further presented qualitative evidence for the corresponding bromide and chloride complexes. Lichtin also has obtained qualitative[15] as well as quantitative[16] data for complexation with all three aqueous halide ions. Working in acetonitrile solution, Lippincott and Welsh[17] have obtained infrared as well as ultraviolet data for complexing with iodide ion, emphasizing the charge-transfer nature of the interaction. These workers were unable, however, to find infrared evidence for chloride or bromide complexes in the solutions.

Halide–sulfur dioxide complex formation has been assumed in the interpretation of halide ion catalysis, studied in this laboratory,[18] of the otherwise very slow[19] radiosulfur exchange reactions between liquid sulfur dioxide and thionyl chloride or bromide. However, the need for more specific equilibrium data than those at present available, to supplement the kinetics results, has seemed desirable. The present ultraviolet spectral investigation of complex formation in acetonitrile solution between sulfur dioxide and tetraethylammonium halides represents an effort to meet this need.

Experimental Section

Materials.—Acetonitrile (Matheson Coleman and Bell, bp 80.5–82.5°) was doubly distilled from phosphorus pentoxide and once from oven-dried potassium carbonate. The purified material showed a uv cutoff at about 210 nm. Tetraethylammonium perchlorate was made by mixing appropriate amounts of tetraethylammonium hydroxide (Matheson Coleman and Bell, 25% aqueous) with perchloric acid (B & A, 70%, reagent), the product crystallizing from solution. Tetraethylammonium chloride, tetramethylammonium chloride, and tetraethylammonium bromide were Eastman White Label. Tetraethylammonium iodide was prepared by refluxing ethyl iodide and triethylamine in ether for about 2 hr, the product crystallizing on cooling. All these salts were recrystallized from "super-dry"[20]

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ethanol. Tetraethylammonium fluoride (Eastman, White Label) was purified by repeated recrystallization from acetonitrile and was isolated and analyzed as the monosolvate $(C_2H_5)_4NF \cdot CH_3CN$. All salts were dried over phosphorus pentoxide in a desiccator or exposed in a drybox. Halide analyses of the salts corresponded closely (99% or better) to those expected for the pure, anhydrous compounds. Sulfur dioxide (Matheson, anhydrous, or American Potash and Chemical, "Charg-A-Can") was dried before use by passage through Drierite or phosphorus pentoxide.

Uv-Visible Spectral Measurements.—Absorption spectra in the ultraviolet and visible regions were recorded with a Beckman DK2 spectrophotometer. One-centimeter Teflon- or glass-stoppered silica cells were normally used. In the examination of the spectrum of solutions of the solvate $(CH_3)_4NCl \cdot SO_2$, 0.1- and 0.01-cm cells were also used in order to extend the accessible concentration range. The cell holder was thermostated to $\pm 0.5°$ at 15, 25, and 35°.

Acetonitrile was the solvent in all the experiments. The halide and perchlorate salts employed were, except as otherwise noted, the tetraethylammonium compounds, chosen for solubility reasons. For the Job-plot measurements, absorbances were determined at the complex peaks with constant total concentrations of sulfur dioxide and halide salt and varying mole ratios between the two. For the Benesi–Hildebrand calculations, absorbances (over a range of wavelengths spanning the complex peaks) were determined for constant and relatively low sulfur dioxide concentration ($\sim 2 \times 10^{-4}$ M) and higher, varying halide concentration ($\sim 3 \times 10^{-3}$ to $\sim 4 \times 10^{-2}$ M). Experimental solutions were prepared by taking appropriate aliquots of previously prepared stock solutions in acetonitrile.

Sulfur dioxide concentrations in acetonitrile were determined on the basis of absorbance at its band maximum (282 nm), exploratory experiments having demonstrated the validity of Beer's law at least up to 4×10^{-3} M and having given a molar extinction coefficient at 282 nm of 471 M^{-1} cm^{-1} (25°). This determination rested initially on a standard gravimetric sulfate determination. The concentration of the sulfur dioxide stock solution was checked before and again after the preparation of each final batch of experimental mixed solutions (*e.g.*, for a given Benesi–Hildebrand calculation). The two values either checked well or showed at the most minor differences. In the latter case an average concentration was taken. Halide stock solutions were prepared by weighing the pure salts, all transfers being made in the drybox.

In the cases of the chloride and bromide complexes, it was necessary to take into account a small contribution to the observed absorbances by uncomplexed sulfur dioxide. In the iodide complex a small contribution was made by free iodide absorbance. Extinction coefficients for these substances were determined as needed, and corrections for their absorbances were made by the use of the Ketelaar modification of the Benesi–Hildebrand treatment of the data (see below).

Early in the work it was found that at least the iodide complex solution was not photochemically stable in ordinary light, the solution darkening irreversibly over a several hours period and the absorbance peak shifting toward shorter wavelength. Exploratory experiments suggested the probable occurrence of triiodide formation, a phenomenon previously mentioned in spectrophotometric studies involving iodine solutions.[21] In view of this difficulty, the final solutions were, in all cases, mixed rapidly and placed in the spectrophotometer just prior to measurement. This procedure, requiring only a fraction of 1 min, sufficed to reduce the photochemical effects to an insignificant level. The solutions were found stable over the period of observation in the dark cell compartment or in the spectral beam, a fact demonstrated by reruns of spectral scans on a given solution.

Since, in general, the experiments were not conducted at constant ionic strength, trials were performed to demonstrate the lack of significance of this factor. In one test, a typical solution, containing $\sim 2 \times 10^{-4}$ M SO_2 and $\sim 5 \times 10^{-3}$ M $(C_2H_5)_4NI$, was examined with added amounts of tetraethylammonium perchlorate from zero to 0.243 M. It was found that the absorbances at the complex peak remained constant within a 5% range and that no trend was evident with changing ionic strength. Since these observations suggested ionic strength, as such, not to influence our results, the body of the experiments were done with no added perchlorate.

Calculations.—The treatment used to obtain complex formation data from the uv spectra was essentially that of Benesi and Hildebrand,[22] as modified by Ketelaar, *et al.*[23] For the experimental concentrations employed $[X^-] \gg [SO_2]$ and both a 1:1 complex, $SO_2 \cdot X^-$, and the validity of Beer's law for the complex absorbance being assumed, this treatment involves the equation

$$[SO_2]l/\Delta\alpha = 1/\Delta\epsilon + 1/\Delta\epsilon K[X^-] \qquad (1)$$

Here K is the halide ion–sulfur dioxide complex formation constant ($SO_2 + X^- \rightleftarrows SO_2 \cdot X^-$) and $\Delta\alpha$ is the increase in observed absorbance over that expected for any SO_2 and/or X^- concentrations put into the solutions; similarly $\Delta\epsilon$ is the excess by which the molar extinction coefficient of the complex exceeds the sum of those for SO_2 and X^-; l is the cell path length (cm), and $[SO_2]$ and $[X^-]$ are initial measured molar concentrations. If complex formation is in accord with the above assumptions, a plot of $[SO_2]l/\Delta\alpha$ *vs.* $1/[X^-]$ should yield a straight line of slope $1/\Delta\epsilon K$ and intercept $1/\Delta\epsilon$. Thus the quantities K and $\Delta\epsilon$ (and hence $\epsilon_{\text{complex}}$) were determined over a range of wavelengths at each of three temperatures, the data being fitted by least squares. Since the $\Delta\epsilon$ values appeared independent of temperature, average values (corresponding to the $\epsilon_{\text{complex}}$ values given in Table I) were then used in second least-squares fittings to obtain refined K values, the plots now being forced through intercepts corresponding to the average $\Delta\epsilon$ values. K values and thermodynamic quantities in the table correspond to the refined calculations. The measured K values at the three temperatures were finally used to calculate complex formation enthalpies and entropies, *via* linear least-squares computations based on the equation

$$R \ln K = -\Delta H°/T + \Delta S° \qquad (2)$$

Preparation of $(CH_3)_4NCl \cdot SO_2$.—Following Jander and Mesech,[10] the monosolvate of tetramethylammonium chloride was prepared by evaporation of a liquid sulfur dioxide solution. Sulfur dioxide was condensed at Dry Ice–acetone temperature into a trap containing the dry salt, a clear, colorless solution being formed. The solution was evaporated first at room temperature (through a mercury bubbler to ensure maintenance of 1 atm of sulfur dioxide over the salt). After evolution of gas had ceased, a soapy appearing solid remained. This material was heated to 40°, whereupon more gas came off. (Jander and Mesech gave 35 and 88° as the respective decomposition temperatures of $(CH_3)_4NCl \cdot 2SO_2$ and $(CH_3)_4NCl \cdot SO_2$.) When gas evolution finally again ceased, the contents of the trap, a brittle solid, were transferred to the drybox and kept tightly stoppered until used. *Anal.* Calcd for $(CH_3)_4NCl \cdot SO_2$: Cl, 20.41; S(IV), 18.46. Found: Cl, 20.55; S(IV), 17.82.

Infrared Observations.—Infrared spectra were taken with either a Perkin-Elmer Model 21 or a Beckman IR-11 spectrophotometer.

For the observation of an acetonitrile solution of a potassium iodide–sulfur dioxide mixture, dry sulfur dioxide was passed through a saturated solution of the salt containing excess salt. The ir spectra both of this solution and of sulfur dioxide alone in the solvent were examined in sodium chloride solution cells in the spectrophotometer.

For the examination of the solid solvate $(CH_3)_4NCl \cdot SO_2$, fine

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TABLE I

OPTICAL AND FORMATION EQUILIBRIA DATA FOR 1:1 SULFUR DIOXIDE–TETRAETHYLAMMONIUM HALIDE COMPLEXES IN ACETONITRILE

			K,[b,c] M^{-1}		$-\Delta H^\circ$,[c]	
λ, nm	$10^{-3}\epsilon$,[a] cm^{-1} M^{-1}	15°	25°	35°	kcal mol^{-1}	ΔS°,[c] eu
			$SO_2 \cdot Cl^-$ Data			
280	5.74 ± 0.04	419 ± 7	372 ± 8	329 ± 5	2.12 ± 0.07	4.7 ± 0.2
285	7.39 ± 0.03	428 ± 4	377 ± 5	331 ± 4	2.27 ± 0.07	4.2 ± 0.2
290	8.58 ± 0.06	426 ± 4	367 ± 4	321 ± 4	2.48 ± 0.04	3.4 ± 0.1
295	8.98 ± 0.08	413 ± 7	355 ± 4	312 ± 5	2.49 ± 0.05	3.3 ± 0.2
300	8.30 ± 0.03	418 ± 8	357 ± 4	318 ± 3	2.42 ± 0.16	3.6 ± 0.5
305	6.76 ± 0.02	437 ± 10	370 ± 5	332 ± 2	2.44 ± 0.25	3.6 ± 0.8
310	5.13 ± 0.07	383 ± 12	329 ± 8	305 ± 6	2.01 ± 0.35	4.8 ± 1.2
	Av[d]	418 ± 7	361 ± 6	321 ± 4	2.32 ± 0.07	3.9 ± 0.2
			λ_{max} 294;[e] ϵ_{max} 9000; $f = 0.17$			
			$SO_2 \cdot Br^-$ Data			
305	8.10 ± 0.12	130 ± 2	104 ± 2	87 ± 1	3.59 ± 0.19	−2.8 ± 0.6
310	9.95 ± 0.10	125 ± 2	101 ± 1	85 ± 1	3.37 ± 0.12	−2.1 ± 0.4
315	11.36 ± 0.13	121 ± 2	99 ± 1	84 ± 1	3.18 ± 0.08	−1.5 ± 0.3
320	12.11 ± 0.17	116 ± 2	96 ± 2	82 ± 1	3.07 ± 0.02	−1.2 ± 0.1
325	11.76 ± 0.19	114 ± 2	95 ± 2	81 ± 1	2.94 ± 0.11	−0.8 ± 0.4
330	10.36 ± 0.28	114 ± 4	96 ± 3	84 ± 2	2.69 ± 0.15	0.1 ± 0.5
335	8.20 ± 0.28	121 ± 5	102 ± 4	89 ± 3	2.70 ± 0.19	0.2 ± 0.6
	Av[d]	120 ± 2	99 ± 1	85 ± 1	3.08 ± 0.13	−1.2 ± 0.4
			λ_{max} 321; ϵ_{max} 12,100; $f = 0.23$			
			$SO_2 \cdot I^-$ Data			
350	5.16 ± 0.53	24.5 ± 2.5	20.2 ± 2.1	16.9 ± 1.7	3.26 ± 0.02	−5.0 ± 0.1
360	7.50 ± 0.26	25.3 ± 0.9	21.4 ± 0.7	18.3 ± 0.6	2.86 ± 0.02	−3.5 ± 0.1
370	9.34 ± 0.11	25.8 ± 0.3	22.0 ± 0.3	18.9 ± 0.2	2.75 ± 0.04	−3.1 ± 0.1
380	9.91 ± 0.07	25.5 ± 0.2	22.0 ± 0.2	19.0 ± 0.2	2.61 ± 0.07	−2.6 ± 0.2
390	8.71 ± 0.19	26.3 ± 0.6	22.8 ± 0.5	20.0 ± 0.5	2.38 ± 0.004	−1.8 ± 0.01
400	7.26 ± 0.15	23.8 ± 0.5	21.2 ± 0.4	18.9 ± 0.4	2.04 ± 0.04	−0.8 ± 0.1
410	5.13 ± 0.13	22.4 ± 0.6	20.3 ± 0.5	18.4 ± 0.5	1.75 ± 0.02	−0.1 ± 0.05
	Av[d]	24.8 ± 0.5	21.4 ± 0.4	18.6 ± 0.4	2.52 ± 0.19	−2.4 ± 0.6
			λ_{max} 378; ϵ_{max} 9,900; $f = 0.20$			

[a] Averages of values from Benesi–Hildebrand calculations at 15, 25, and 35°. Errors shown are experimental standard deviations of the three calculated values. [b] $K = [SO_2 \cdot X^-]/[SO_2][X^-]$. From Benesi–Hildebrand calculations, ϵ assumed equal averages shown, independent of temperature. [c] Errors shown are standard deviations from least-squares treatment. [d] Errors shown for averages are experimental standard deviations calculated from observed individual values. [e] For SO_2: λ_{max} 282 nm; ϵ_{max} 471 cm^{-1} M^{-1}.

mulls in Nujol were prepared (in the drybox) of this material and of dry tetramethylammonium chloride. For the range 4000–650 cm^{-1}, the mulls were placed between sodium chloride windows. For the range 740–340 cm^{-1}, cesium bromide windows were used.

Results

The uv–visible absorption spectra of mixtures of sulfur dioxide and tetraethylammonium chloride, bromide, or iodide in acetonitrile solution showed strong bands at 294, 321, and 378 nm, respectively. These occurred toward longer wavelengths relative to the halide ion absorptions and were much stronger than the sulfur dioxide band at 282 nm. On the assumption that these bands correspond to the halide–sulfur dioxide complex formation, the stoichiometries of the complexes were investigated by Job's method of continuous variation.[24] The results clearly indicate maximum absorbances in all three cases at 1:1 halide:sulfur dioxide mole ratios. Hence, we infer the corresponding complex stoichiometries. Furthermore (although the iodide experiment, done early in the work before the problem was appreciated, showed some triiodide contamination) the results for the chloride and bromide complexes (Figure 1) also show absorbances within 1–2% of those expected on the basis of the Benesi–Hildebrand results.

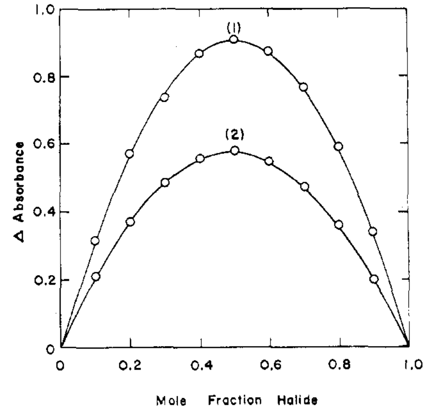

Figure 1.—Job plots for tetraethylammonium halide–sulfur dioxide mixtures in acetonitrile at 25°. Salt, observation wavelength, and total concentration (salt plus SO_2): (1) $(C_2H_5)_4NCl$, 294 nm, 1.305 × 10^{-3} M; (2) $(C_2H_5)_4NBr$, 321 nm, 1.505 × 10^{-3} M.

Absorbances were measured for mixtures in acetonitrile of sulfur dioxide with tetraethylammonium chloride, bromide, and iodide, respectively, at 15, 25, and 35° and in the concentration ranges indicated in the Experimental Section. From these data, plots of eq 1 were prepared, and from the equation, values of the

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(24) P. Job, *Ann. Chim. (Paris)*, [10] **9**, 113 (1928).

molar extinction coefficients and the formation constants were calculated. The good linearity of the plots found in all cases further substantiates the 1:1 complex stoichiometries. The molar extinction coefficients were found to be essentially temperature independent. Figure 2 shows, for the chloride complex, the final refined plots at 295 nm (λ_{max} 294 nm), assuming a constant, average extinction coefficient. Calculations based on eq 2 yielded complex formation enthalpies and entropies. Table I summarizes the optical and formation equilibria data obtained. Figure 3 shows the absorption spectra of the complexes themselves, derived from these data, based on the average extinction coefficients.

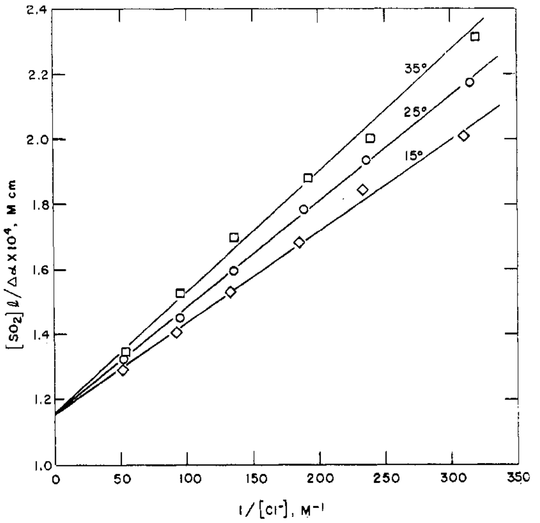

Figure 2.—Benesi–Hildebrand plots for tetraethylammonium chloride–sulfur dioxide mixtures in acetonitrile. $[SO_2] \approx 1.6 \times 10^{-4}$ *M*; λ 295 nm.

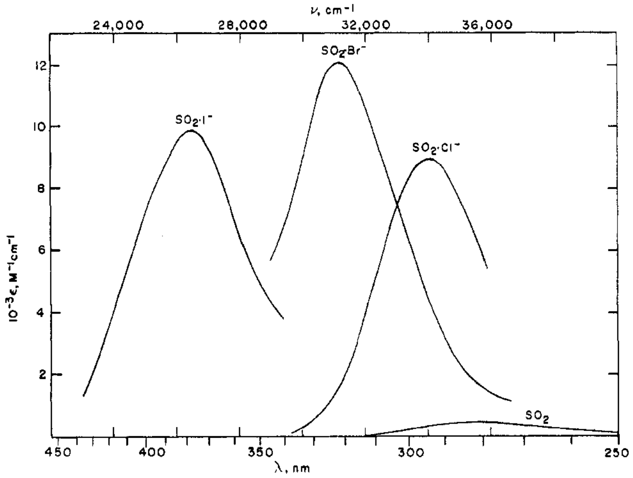

Figure 3.—Molar extinction coefficients of sulfur dioxide–tetraethylammonium halide complexes in acetonitrile.

Sulfur Dioxide–Fluoride Complex.—A preliminary uv spectral investigation was also made of mixtures of tetraethylammonium fluoride and sulfur dioxide in acetonitrile. These solutions showed no strong absorbance band above 220 nm, which could be ascribed to the complex, although the spectra did suggest the occurrence of a tail of an absorbance band (not yet further studied) at shorter wavelengths. The presence of fluoride ion did, however, essentially eliminate the sulfur dioxide band at 282 nm, this band only appearing at a $SO_2:F^-$ mole ratio greater than unity and increasing linearly with excess sulfur dioxide (with ε 471). The data thus correspond to 1:1 complex formation. They also suggest a formation constant much greater than those of the other halide complexes.

Preparation and Uv Spectrum of $(CH_3)_4NCl \cdot SO_2$.—Since Jander and Mesech[10] reported the formation of the solid solvates $(CH_3)_4NCl \cdot 2SO_2$ and $(CH_3)_4NCl \cdot SO_2$, with respective decomposition temperatures of 35 and 88°, it seemed of interest to repeat the preparation of the latter to see if its solutions gave spectral results comparable to those quoted above. As indicated in the Experimental Section, a dry solid corresponding closely to the 1:1 sulfur dioxide solvate was obtained. This material was then used to prepare a series of solutions in acetonitrile over the concentration range 7.77×10^{-5} to 4.97×10^{-3} *M*. For these solutions, then, the observed absorbances at the complex peak were compared to those expected on the basis of the known complex formation constant and extinction coefficient (assumed the same as for the tetraethylammonium salt) and the sulfur dioxide extinction coefficient (for SO_2, $\epsilon_{294} = 0.74\epsilon_{282}$). The solutions, covering an absorbance range from 0.04 to ~20 (high values, observed at shorter path length, corrected to 1-cm path) showed complete agreement, within experimental error, between calculated and expected values.

Infrared Spectra.—The work of Lippincott and Welsh[17] on solutions of potassium iodide and sulfur dioxide in acetonitrile was repeated and confirmed in the range 4000–650 cm^{-1}. Sulfur dioxide alone in solution showed bands at 1330 (strong, asym str) and 1148 cm^{-1} (medium, sym str). The solutions including potassium iodide showed the same bands and, in addition, a shoulder at 1290 cm^{-1} and a new band at 1115 cm^{-1}. The latter are presumably to be associated, as inferred by Lippincott and Welsh, with iodide–sulfur dioxide complex formation in solution.

The solvate $(CH_3)_4NCl \cdot SO_2$, prepared as indicated above, was examined as a solid. In the range 4000–650 cm^{-1} the solvate had two bands, not present in the pure halide salt, at 1305 cm^{-1} (strong, shoulder at 1290 cm^{-1}) and 1135 cm^{-1} (medium). These bands presumably correspond to the sulfur dioxide antisymmetric and symmetric stretches, respectively. In the range 740–340 cm^{-1} the solvate showed a band, not present in the pure chloride, at 530 cm^{-1}, presumably corresponding to sulfur dioxide bending. No second band which might be ascribed to a sulfur–halogen stretching frequency was found in this latter range, in marked contrast to the observation of Paetzold and Aurich[25] with the related fluoride species, potassium fluorosulfite, KSO_2F.

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(25) R. Paetzold and K. Aurich, *Z. Anorg. Allg. Chem.*, **335**, 281 (1965).

Discussion

The results show that 1:1 complexes are formed in acetonitrile between sulfur dioxide and halide salts with all four halides. These findings are consistent with Lichtin's[15,16] observations in aqueous solution. It seems probable that Lippincott and Welsh's[17] failure to observe the chloride and bromide complexes is to be traced to the very low solubilities in acetonitrile of the potassium salts used.

The data in Table I indicate complex stabilities much greater than those in water and a stability trend opposite to the general one in water. Thus Jander and Türk[14] cited a formation constant of $\sim 1.0\ M^{-1}$ (20°) for ISO_2^- in water, Witekowa and Witek[13c] reporting a constant of 0.319 (25°) for $HI \cdot SO_2$. Lichtin's[16] data suggest a lesser stability for the chloride than for the bromide complex in water, and Seel's[11] work has shown the fluoride complex to hydrolyze completely in water, a quite low formation constant hence being implied.

It seems probable that the lesser stabilities of the complexes in water, as compared to acetonitrile solution, are to be related to the much greater stabilization by high solvation energies of the free halide ions, relative to the complexed ions. The same effect would account for the general stability trend in water, the free halide ion hydration energies increasing markedly with decreasing ion size.

In acetonitrile solution, on the other hand, solvation energies are less important, while entropy effects become more significant. The data in Table I show that the general increase in stability from iodide to chloride is to be related primarily to changes in entropy, ΔH° values remaining roughly constant. Presumably an increasing halide ion solvation trend with decreasing ion size, while not manifest in the ΔH° values, leads to a significant change in the entropy terms. This trend would be in a sense favorable to complex formation, a process which would free solvent molecules ordered around the free halide ions. Such an effect is, of course, less important in water because of the greater order in the solvent itself that replaces the order of solvent molecules around the free ions.

The exact nature of the bonding in these complexes[26] remains, unfortunately, undefined by the present results. A charge-transfer character for the species, however, indicated by the work of Lippincott and Welsh[17] as well as of Lichtin[15,16] also seems suggested (for the chloride, bromide, and iodide) by the present results. Our infrared observations with potassium iodide–sulfur dioxide solutions have corroborated those of Lippincott and Welsh. Furthermore, the high extinction coefficients and low heats of formation for the complexes are generally consistent with this feature.

If charge-transfer complexes are here involved and if the complexing is between sulfur dioxide and the halide anions, as the work of Lippincott and Welsh and the general character of the present results appear to show, it is inviting to seek a correlation between the frequencies of the absorption maxima, $\nu_{\max}$, and the ionization potentials, I_D, of the halide ions. On the basis of Mulliken's concepts, such a relationship may be expressed in the form[27,28]

$$h\nu_{\max} = I_D - E_A - \Delta \tag{3}$$

where E_A is the electron affinity of the acceptor, sulfur dioxide. The term Δ represents the difference in binding energies between ground and excited states. In Figure 4[29] a plot of $h\nu_{\max}$ *vs.* I_D does show a correlation, though not with unit slope as might be expected, were Δ constant in eq 3. The correlation appears to be consistent with both the charge-transfer nature of and the involvement of halide ions in the complexes.

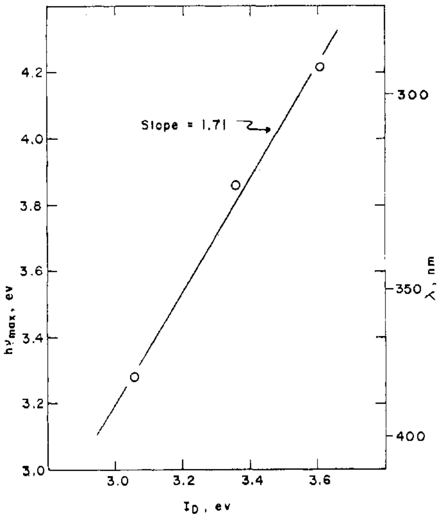

Figure 4.—Plot of absorption energies of complexes *vs.* ionization potentials of halide ions. Data from Berry and Reimann.[29]

Employing a value of 2.8 eV for E_A,[30] we calculate values of Δ: −3.4 eV ($SO_2 \cdot Cl^-$), −3.3 eV ($SO_2 \cdot Br^-$), and −3.0 eV ($SO_2 \cdot I^-$). The negative quantities contrast with the more familiar positive ones associated with complexes between neutral species, where the excited state is electrostatically stabilized relative to the ground state. However, if ion–dipole interaction is important in the ground state of the present complexes, it seems possible that electron transfer could lead to a decrease in binding energy and hence the negative Δ values.

The formation of these halide complexes helps to explain the moderate solubility of ionic halides in liquid sulfur dioxide as well as (as Lichtin[15] has pointed out) the unusual ionizing power of this medium. It also stands in at least qualitative agreement with the inference from the studies in this laboratory of halide catalysis of the sulfur dioxide–thionyl chloride radiosulfur exchange. Quantitatively, however, the situation here is not yet entirely clear. In the original chloride catalysis study in liquid sulfur dioxide–thionyl

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[26] *Cf.* R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley-Interscience, New York, N. Y., 1969, p 245.

[27] H. McConnell, J. S. Ham, and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

[28] L. E. Orgel, *Quart. Rev., Chem. Soc.*, **8**, 422 (1954).

[29] R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, **38**, 1540 (1963).

[30] G. Piccardi, *Z. Phys.*, **43**, 899 (1927).

chloride mixtures,[18b] it was assumed that the $SO_2\cdot Cl^-$ formation constant was very small, no adequate explanation being offered for the increase in rate constant in excess thionyl chloride as compared to excess liquid sulfur dioxide. More recently, we have assumed the absence of important medium effects on the rate and equilibrium constants as the solution components are varied from one extreme to the other. Thus we have been able, by nonlinear least-squares procedures, to employ the variation in the apparent third-order rate constant (k_3 in ref 18b) to obtain values for (1) the bimolecular rate constant for radiosulfur exchange between $SO_2\cdot Cl^-$ and $SOCl_2$ and (2) the formation constant for $SO_2\cdot Cl^-$ (K).[31] The K value at 0.0° is 0.17 ± 0.03. The meager data at other temperatures give ~0.18 (25.2°) and ~0.27 (~−21°). The apparent approximate formation enthalpy and entropy are $\Delta H^\circ \approx -1.6$ kcal/mol and $\Delta S^\circ \approx -9$ eu. Since the original study in the mixed reactants, a further rough preliminary investigation has been made of the same exchange study in the solvent acetonitrile.[32] The same rate law has been found as in the original work, and, furthermore, roughly comparable values for both rate and formation constants are suggested, the value for the latter being ~0.12 (25.2°). Thus some support is provided for the assumption that medium effects are not large, and, further, a basis is furnished for comparison of results from the exchange studies with those in the present research. This comparison leaves us with the observation that the formation constants calculated from the former studies present an apparent quantitative disagreement with the much larger figures of 418–321 (15–35°) now found.

Two possible explanations for this apparent anomaly present themselves. As one possibility, it might be that the complex spectroscopically observed is not catalytically effective, perhaps with an excessive S–Cl bond length and/or an unfavorable geometry. Then the formation constant for the catalytically effective form might be much smaller than for the ineffective. As a second possibility, it might be that further chloride ion complexes besides the 1:1 complex here treated, with either sulfur dioxide or thionyl chloride, may be involved in the kinetics experiments. (Substantially higher concentrations of the sulfur compounds prevailed as compared to sulfur dioxide in the present study.) In such a case the formation constant estimates derived from the exchange studies become quite meaningless. Further work is planned.

Acknowledgment.—We are greatly indebted to Professor N. N. Lichtin for a preliminary report of his complex studies prior to publication.

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[31] (a) N. D. Potter, Ph.D. Thesis, Oregon State University, 1962; (b) T. H. Norris, unpublished data.

[32] T. G. Cooper and T. H. Norris, to be submitted for publication.

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Thermodynamic Properties of the Aqueous Sulfide and Bisulfide Ions and the Second Ionization Constant of Hydrogen Sulfide over Extended Temperatures[1,2]

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The heat of formation and entropy for the aqueous sulfide ion and the heat capacity functions for S^{2-}(aq) and HS^-(aq) have been determined calorimetrically by measuring the heat of solution of KHS(c) in basic solutions at 25 and 95°. The value determined for $\bar{S}^\circ(25^\circ)$ for S^{2-}(aq) is −4.1 ± 2 cal mol^{-1} deg^{-1} and the heat capacity function $\bar{C}_p^\circ|_{25}^{100}$ for S^{2-}(aq) and HS^-(aq) was found to be −105 ± 9 and −48.8 ± 2 cal mol^{-1} deg^{-1}, respectively. The entropy and heat capacity of aqueous sulfide are incorrectly predicted from empirical considerations based on other simple ions. This fact suggests aqueous sulfide is a complex species or that its hydration sphere is not as tightly bound as would be predicted from its charge density.

I. Introduction

A procedure for determining accurate thermal data over extended temperatures for an aqueous ionic species which can only be formed in equilibrium with other species has been described in a preceding paper of this series.[5] The method involved a simple extension of the integral heat method,[6] and it has been further modified in the present research to obtain thermal data on the chemically important sulfide and bisulfide ions. Measurements have been made of the heat of solution of crystalline potassium bisulfide in aqueous solutions of potassium hydroxide. The resulting heat is the sum of the heat of solution of KHS(c) and the heat of reaction of HS^-(aq) with OH^-(aq) to form an equilib-

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[1] This communication constitutes paper XIII of a series of communications from these laboratories on the thermodynamic properties of high-temperature aqueous solutions.

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[3] From the Ph.D. Thesis of H. P. Stephens, Purdue University, June 1970.

[4] National Science Foundation Predoctoral Fellow, 1966–1969.

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