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Bromoselenate(IV) Equilibria in Aqueous Hydrobromic Acid

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Solutions of selenium dioxide in hydrobromic acid, 0–15.74 M, have been shown to contain H_2SeO_3, $HSeO_2Br$, $SeOBr_3^-$, $SeBr_5^-$, and $SeBr_6^{2-}$ on the basis of their Raman spectra. The equilibrium constants for $H_2SeO_3 + H^+ + Br^- \rightleftharpoons HSeO_2Br + H_2O$ (K_1) and $HSeO_2Br + H^+ + 2Br^- \rightleftharpoons SeOBr_3^- + H_2O$ (K_2) have been determined by quantitative Raman spectroscopy to be 4.9 (±0.5) $L^2\ mol^{-2}$ and 9.5 (±0.5) $\times 10^{-4}\ L^3\ mol^{-3}$, respectively. The constants for the equilibria $SeOBr_3^- + 2H^+ + 2Br^- \rightleftharpoons SeBr_5^- + H_2O$ (K_3) and $SeBr_5^- + Br^- \rightleftharpoons SeBr_6^{2-}$ (K_4) have been determined from UV–visible spectra to be 8 (±1) $\times 10^{-8}\ L^4\ mol^{-4}$ and 0.3 (±0.1) $L\ mol^{-1}$, respectively, and have been shown to be consistent with quantitative Raman measurements. The ease of formation of haloselenate species in aqueous HX solutions, HBr > HCl > HF, correlates directly with the magnitude of the HX activities in water.

Introduction

The preparation of pentafluorotellurate(IV) and hexabromo- and hexachloroselenate(IV) and -tellurate(IV) salts from aqueous hydrohalic acid solutions is standard in the laboratory, but the determination of the precise nature of the halo–chalcogen species formed in these solutions is more recent. Tellurium dioxide dissolves in hydrofluoric acid to give TeF_5^- and $Te(OH)F_4^-$ [1] while in hydrochloric acid it forms $TeCl_6^{2-}$ and $Te(OH)Cl_4^-$, as well as a monochloro species.[2] Selenium dioxide dissolves in both hydrofluoric and hydrochloric acids to form seleninyl halides,[3,4] but in the latter solution, $SeCl_5^-$ and perhaps $SeCl_6^{2-}$ are formed at high HCl concentrations, whereas only $SeOF_2$ is present even in 100% HF. The nature of solutions of SeO_2 in hydrobromic acid has been studied by two groups[5,6] using Raman spectroscopy, but the conclusions of the two are contradictory. Futekov and Specker[6] report that the two species present are $SeOBr_2$ and $SeBr_6^{2-}$, while Hendra and Jovic[5] interpret their spectra in terms of $SeBr_5^-$ and $SeBr_6^{2-}$. Crystals of hydronium hexabromoselenate(IV) may be isolated from solutions of SeO_2 in concentrated HBr,[7] suggesting the presence of significant amounts of the $SeBr_6^{2-}$ ion in solution. More recently, it has been reported[8] that a tribromoselenate(IV) can be isolated from aqueous hydrobromic acid solutions, which indicates that this anion may also be present. In view of the contradictory conclusions concerning these solutions and in view of the recent spectroscopic characterization of the $SeOBr_3^-$ anion,[8] it was considered of interest to carry out a further study of these solutions by Raman and UV–visible spectroscopy.

Experimental Section

Selenium dioxide (Alfa) was dried under vacuum before use. Hydrobromic acid (Fisher) was analyzed by titration against sodium carbonate. Traces of elemental bromine were removed by stirring the acid over clean mercury and decanting. Acetonitrile (Fisher) was distilled, after refluxing, from phosphorus pentoxide. Tetra-*n*-butylammonium bromide (Aldrich) was recrystallized from a 3:1 mixture of ethyl acetate–ethyl ether and stored over phosphorus pentoxide in a vacuum desiccator. Selenium tetrabromide was prepared according to Brauer.[9] Solutions of penta- and hexabromoselenate(IV) in acetonitrile were prepared from stoichiometric mixtures of selenium tetrabromide and quaternary ammonium bromide in acetonitrile. These solutions and the solids derived from them are the subject of further study.[10]

The methods used for obtaining quantitative Raman spectra and UV–visible spectra have been described elsewhere.[2,4] Raman spectra were excited at 632.8 nm, and the normalization assumption was that the 925-cm^{-1} band of 1 M $HClO_4$ had an area intensity of 6.45 $cm^2\ L\ mol^{-1}$. Each area was measured 10 times with a planimeter, and the average was taken. The average deviation of areas measured in this way was ±0.2 cm^2, and the values agreed well with those determined by weight and by counting squares under the band envelope. The highest concentration solution of HBr was obtained by saturating the solution with HBr at 0 °C. The concentration was calculated from data in ref 11 and 12 to be 15.74 M. The Raman spectrum was run at 0 °C.

Results and Discussion

Raman Spectra. The Raman spectra of solutions of 1 M SeO_2 in 0.0–5.0 M HBr are shown in Figure 1. As the concentration of HBr is increased from 0.0 to 3.0 M with Se(IV) concentration constant at 1.0 M, there is a broad increase in intensity in the region 110–180 cm^{-1}, where SeBr stretching bands are expected. At the same time, the SeO single-bond stretching band at 700 cm^{-1} increases in intensity, while that for SeO double-bond stretching shifts to lower frequency and broadens. Apparently a bromoselenium(IV) species is being formed, and this species has an SeOH group. The SeBr stretching envelope, which is also due in part to the weak deformation modes of H_2SeO_3 and the new species, is near the SeBr stretching frequency for the SeO_2Br^- anion (139 cm^{-1}).[13] In view of the increasing intensity of the SeO single-bond stretch, however, the new species is more likely to be the parent acid $HSeO_2Br$, whose SeBr stretching mode is not expected to differ greatly from that of the SeO_2Br^- anion and which would contribute to the SeO single-bond stretching envelope and cause the slight shift and broadening of the SeO double-bond band. The analogous monohaloselenious acids are also observed in the $HF–SeO_2$[14] and $HCl–SeO_2$[15] systems. The observed spectra in this region of HBr concentration are therefore consistent with the equilibrium

$$H_2SeO_3 + H^+ + Br^- \overset{K_1}{\rightleftharpoons} HSeO_2Br + H_2O \qquad (1)$$

As the HBr concentration is increased from 3.0 to 5.0 M, the SeBr stretching region increases in intensity and becomes more structured with bands at 190 and 265 cm^{-1} and a shoulder at 150 cm^{-1} and the SeO double-bond stretching mode near 900 cm^{-1} increases in intensity relative to that of the SeO single-bond stretching peak near 700 cm^{-1}, which falls in intensity. The $HSeO_2Br$ is obviously being replaced by a bromoselenium(IV) species with an SeO double bond for which two candidates are possible, $SeOBr_2$ and $SeOBr_3^-$. The strongest bands of $SeOBr_2$ in solution in acetonitrile[16] lie at 223 (10), 284 (9), and 96 (7)

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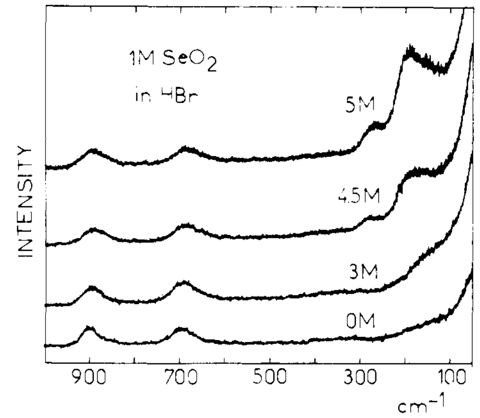

Figure 1. Raman spectra of solutions of 1 M SeO_2 in 0–5 M HBr.

cm^{-1} (relative intensities given in parentheses); the presence of this species would not account for the broad increased intensity observed at 150 cm^{-1}. The simplest interpretation of the Raman spectra is in terms of formation of the $SeOBr_3^-$ anion,[8] which has its strongest bands at 138 (8), 155 (7), 194 (10), and 265 (3) cm^{-1} and which presents a profile in this part of the spectrum that matches best the observed profile of the 5 M HBr solution shown in Figure 1. Moreover, the small shift in the SeO double-bond peak from 900 to 890 cm^{-1}, which persists even with the decrease in $HSeO_2Br$ concentration, suggests that $SeOBr_3^-$ is formed in solution, since estimation of the position of the SeO stretch of $SeOBr_2$ in aqueous solution is 915 cm^{-1}. This value is obtained by comparing the relative positions of this band in the spectra of $SeOBr_2$ and $SeOCl_2$ in acetonitrile[16] and relating this difference to the value for $SeOCl_2$ in water.[4] The SeO stretching mode of $SeOCl_3^-$ in acetonitrile lies 21 cm^{-1} below that of $SeOCl_2$ in the same solvent. The Raman spectra in the region of 3.0–5.0 M HBr concentration are thus best accounted for by the equilibrium

$$HSeO_2Br + H^+ + 2Br^- \overset{K_2}{\rightleftharpoons} SeOBr_3^- + H_2O \qquad (2)$$

The Raman spectra of 1.0 M SeO_2 solutions with HBr concentrations from 6.0 to 15.74 M are shown in Figure 2. As the concentration of HBr is increased above 5.0 M, the band at 700 cm^{-1} decreases in intensity, indicating a fall in the concentration of $HSeO_2Br$, which becomes undetectable by Raman spectroscopy when the HBr concentration reaches 8.9 M. At the same time, the SeO double-bond stretching band near 900 cm^{-1} reaches a maximum in intensity at 7.0 M HBr and then decreases. Apparently equilibrium 2 is shifted further toward $SeOBr_3^-$, but both $SeOBr_3^-$ and $HSeO_2Br$ are being replaced by another Se(IV) species; the change in the intensity and the profile of the SeBr stretching region also indicates this. Corresponding to the band near 900 cm^{-1}, the band at 265 cm^{-1} due to the $SeOBr_3^-$ anion decreases in intensity as the HBr concentration increases from 7.0 to 15.74 M. Over the range of HBr concentrations from 5.0 to 15.74 M, a new peak near 160 cm^{-1} and a shoulder to low frequency of this appear in the spectra; accompanying this is a peak at 210 cm^{-1} which replaces that at 190 cm^{-1} due to $SeOBr_3^-$. The $SeOBr_3^-$ band at 190 cm^{-1} must be completely absent from the spectrum in 15.74 M HBr in which the SeO double-bond stretching band at 900 cm^{-1} due to $SeOBr_3^-$ is completely missing. The new species being formed in this range of concentration cannot be the $SeOBr_4^{2-}$ ion, for which a band near 900 cm^{-1} would be expected. Another possible species, $SeBr_4$, is expected to accept Br^- to form $SeBr_5^-$ or $SeBr_6^{2-}$ in these solutions. However, the band at 210 cm^{-1} is not consistent with the spectrum of the $SeBr_6^{2-}$ ion, which has peaks at 160 (7), 143 (10), and 90 (3) cm^{-1}.[5,10] The spectrum of the $SeBr_5^-$ anion in acetonitrile consists of bands at 247 (2), 180 (2), 151 (10), and 112 (1) cm^{-1} [10] and accounts for the bands that replace those of $SeOBr_3^-$ and $HSeO_2Br$ in the HBr solutions over this range of concentrations. In addition, at the higher HBr concentrations (8.0–15.74 M) the presence of the $SeBr_6^{2-}$ ion is indicated by the growth of a peak at 85 cm^{-1} as well as an increase in intensity of the peak near 160 cm^{-1} relative to that of the band at 210 cm^{-1}. The spectra of solutions of 1.0 M SeO_2 in 7.0–15.74 M HBr are best accounted for by the equilibria

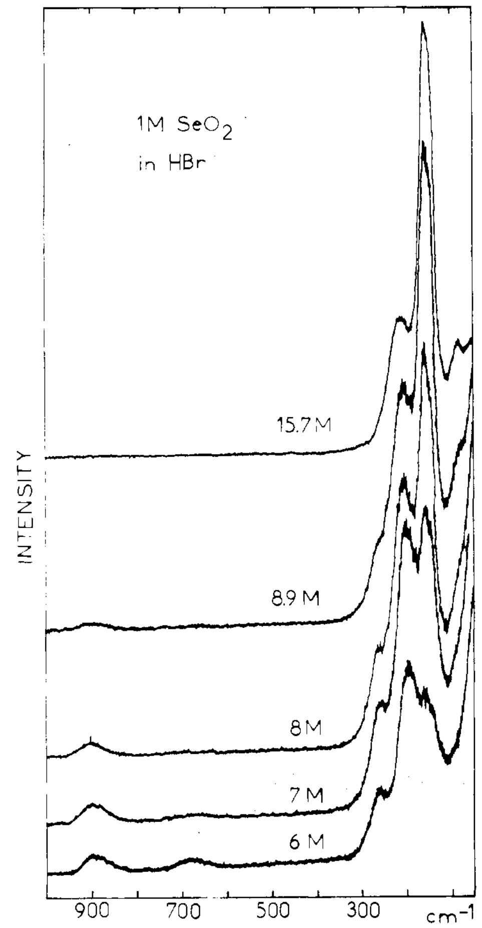

Figure 2. Raman spectra of solutions of 1 M SeO_2 in 6–15.74 M HBr.

$$SeOBr_3^- + 2H^+ + 2Br^- \overset{K_3}{\rightleftharpoons} SeBr_5^- + H_2O \qquad (3)$$

$$SeBr_5^- + Br^- \overset{K_4}{\rightleftharpoons} SeBr_6^{2-} \qquad (4)$$

Evaluation of K_1 and K_2 from Raman Spectra: HBr Concentration (c_{HBr}) 0.0–5.0 M. The formation constant for equilibrium 1 is given by the expression

$$K_1 = \frac{[HSeO_2Br]a}{[H_2SeO_3][H^+][Br^-]y^2} \qquad (5)$$

where a represents water activity and y, the mean molar ionic activity coefficient for HBr. K_1 may be evaluated from the Raman intensity data listed in Table I. For this purpose it is assumed that the activity coefficients of the molecular species H_2SeO_3 and $HSeO_2Br$ are unity and that dissociation of these acids is negligible. It is possible to determine K_1 from the SeBr stretching (100–350 cm^{-1}), SeO single-bond stretching (700 cm^{-1}), and SeO double-bond stretching (900 cm^{-1}) regions of the spectra. The procedure used is illustrated by the following treatment for the SeO single-bond stretching region. The normalized band intensity for this region, i_{Se-O}, is given by

$$i_{Se-O} = {}^1I_{Se-O}[HSeO_2Br] + {}^0I_{Se-O}[H_2SeO_3] \qquad (6)$$

where ${}^1I_{Se-O}$ is the molar intensity of the band at 700 cm^{-1} for $HSeO_2Br$ and ${}^0I_{Se-O}$, the molar intensity of the SeO single-bond stretching modes (ν_2 and ν_5) of H_2SeO_3 in the same region. For 632.8-nm excitation, ${}^0I_{Se-O}$ = 6.02 cm^2 L mol^{-1}. Combination of eq 6 and the mass balance expression

$$c_{IV} = [HSeO_2Br] + [H_2SeO_3] \qquad (7)$$

Table I. Raman Band Intensities, Concentrations, and Equilibrium Constants for 1.0 and 3.0 M HBr Solutions (Stoichiometric Se(IV) Concentration, c_{HBr}, 1.0 M)

spectral region	c_{HBr}, mol L^{-1}	i,[a] cm^2	[H$^+$], mol L^{-1}	a/y^2	[HSeO$_2$Br], mol L^{-1}	[H$_2$SeO$_3$], mol L^{-1}	K_1,[b] L^2 mol^{-2}	^1I,[c] cm^2 L mol^{-1}
SeBr (100-300 cm^{-1})	1.0	3.25	0.513	1.579	0.487	0.513	5.70	4.04
	3.0	4.00	2.03	0.603	0.974	0.026	5.51	
Se-O (700 cm^{-1})	1.0	6.37	0.540	1.565	0.458	0.542	4.48	6.79
	3.0	6.76	2.03	0.603	0.967	0.033	4.32	
Se=O (900 cm^{-1})	1.0	4.75	0.535	1.567	0.465	0.535	4.77	4.33
	3.0	4.35	2.03	0.603	0.969	0.031	4.57	

[a] Observed band intensity for the corresponding spectral region. [b] Average K_1 = 4.9 (±0.5) L^2 mol^{-2}. [c] Assumed molar intensity for HSeO$_2$Br for the corresponding spectral region.

Table II. Raman Band Intensities, Concentrations, and Equilibrium Constants for 1.0 M SeO$_2$ Solutions in 3.5-5.0 M HBr

c_{HBr}, mol L^{-1}	i_{SeBr}, cm^2	[HSeO$_2$Br], mol L^{-1}	[SeOBr$_3^-$], mol L^{-1}	[Br$^-$], mol L^{-1}	[H$^+$], mol L^{-1}	a/y^2	10^4K_2,[a] L^3 mol^{-3}
3.50	6.70	0.967	0.033	2.43	2.47	0.403	9.5
4.00	10.70	0.917	0.083	2.83	2.92	0.248	9.5
4.50	17.40	0.835	0.165	3.17	3.33	0.155	9.2
5.00	27.90	0.705	0.295	3.41	3.70	0.100	9.7

[a] Mean K_2 = 9.5 (±0.5) × 10^{-4} L^3 mol^{-3}; $^3I_{SeBr}$ = 85 (±3) cm^2 L mol^{-1}.

where C_{IV} represents the stoichiometric concentration of Se(IV), which is 1.0 M in all cases, yields

$$[\mathrm{HSeO_2Br}] = \frac{i_{Se-O} - {}^0I_{Se-O}}{{}^1I_{Se-O} - {}^0I_{Se-O}} \qquad (8)$$

For the other spectral regions, expressions analogous to (6) and (8) are used. The concentration of selenious acid, [H$_2$SeO$_3$], may now be determined from (7), and [H$^+$] (=[Br$^-$]), from

$$[\mathrm{H^+}] = c_{HBr} - [\mathrm{HSeO_2Br}] \qquad (9)$$

where c_{HBr} represents the stoichiometric concentration of HBr. The activity factor a/y^2 in the expression for K_1, (5), may be evaluated for the H$^+$ concentration from reported H$_2$O and HBr activities,[17] by using densities given in ref 12. The equilibrium constant K$_1$ was determined for various guessed values of $^1I_{Se-O}$, which permitted calculation of [HSeO$_2$Br] by eq 8 and calculation of K_1 for 1.0 and 3.0 M HBr solutions. The value of $^1I_{Se-O}$ that gave reasonable agreement in K_1 for both HBr concentrations was accepted as correct. The same procedure was followed for the SeO double-bond and SeBr spectral regions of the spectra, for which the molar intensities for H$_2$SeO$_3$ with 632.8-nm radiation, $^0I_{Se=O}$ (900 cm^{-1}) and $^0I_{def}$ (100-300 cm^{-1}), are 5.12 and 2.50 cm^2 L mol^{-1}, respectively. The observed normalized Raman intensities for 1.0 and 3.0 M HBr solutions for the three spectral regions are listed in Table I along with the calculated values of K_1, the corresponding values of the molar intensities (^1I) assumed for HSeO$_2$Br for each region ($^1I_{Se-O}$, $^1I_{Se=O}$, $^1I_{SeBr}$), [H$^+$], a/y^2, and the concentrations of the Se(IV) species present. The agreement between the values of K_1 from calculations for the three regions is good, considering the variation in individual area measurements (±0.2 cm^2) for a single band, and gives a value for K_1 of 4.9 ± 0.5 L^2 mol^{-2}.

It may be seen from Table I that, at c_{HBr} = 3.0 M, HSeO$_2$Br accounts for about 97% of the total Se(IV) concentration, and for purposes of evaluation of K_2, selenious acid concentration may be ignored. The constant for SeOBr$_3^-$ formation, equilibrium 2, is given by

$$K_2 = \frac{[\mathrm{SeOBr_3^-}]a}{[\mathrm{HSeO_2Br}][\mathrm{H^+}][\mathrm{Br^-}]^2y^2} \qquad (10)$$

for which it has been assumed that the ionic activity coefficients of SeOBr$_3^-$ and Br$^-$ are equal and cancel. The value of K_2 was determined from Raman intensity data for the range of c_{HBr} from 3.5 to 5.0 M, given in Table II. The procedure was similar to that for the evaluation of K_1. In this case, however, only the band envelope in the 100-350-cm^{-1} region was used, since the areas here were larger and afforded greater accuracy. The normalized intensity is given by

$$i_{SeBr} = {}^1I_{SeBr}[\mathrm{HSeO_2Br}] + {}^3I_{SeBr}[\mathrm{SeOBr_3^-}] \qquad (11)$$

where $^3I_{SeBr}$ represents the molar intensity for the SeOBr$_3^-$ anion. This equation may be combined with the mass balance equation

$$c_{IV}\ (=1.0) = [\mathrm{HSeO_2Br}] + [\mathrm{SeOBr_3^-}] \qquad (12)$$

to give

$$[\mathrm{SeOBr_3^-}] = \frac{i_{SeBr} - {}^1I_{SeBr}}{{}^3I_{SeBr} - {}^1I_{SeBr}} \qquad (13)$$

where $^1I_{SeBr}$ = 4.04 cm^2 mol L^{-1} (Table I). The concentrations of H$^+$ and Br$^-$ may be calculated from

$$[\mathrm{H^+}] = c_{HBr} - [\mathrm{HSeO_2Br}] - 2[\mathrm{SeOBr_3^-}] \qquad (14)$$

$$[\mathrm{Br^-}] = c_{HBr} - [\mathrm{HSeO_2Br}] - 3[\mathrm{SeOBr_3^-}] \qquad (15)$$

From the data listed in Table II and assumed values for $^3I_{SeBr}$, K_2 was calculated for each c_{HBr} by use of the following sequence of equations: (13), (12), (14), (15), (10). The activity factor, a/y^2, was determined from [H$^+$] as for K_1. This assumes that the same factor applies to both H$^+$Br$^-$ and H$^+$SeOBr$_3^-$, which is reasonable since the H$^+$SeOBr$_3^-$ concentration is small compared to that of H$^+$Br$^-$. The best value of K_2 was arrived at by assuming $^3I_{SeBr}$ = 85 (±3) cm^2 L mol^{-1}, for which K_2 was 9.5 (±0.5) × 10^{-4} L^3 mol^{-3}, where the error is determined by the incremental changes in the assumed values of $^3I_{SeBr}$. The values of K_2 for the various c_{HBr} values are listed in Table II along with concentrations of various species and the activity factor, a/y^2. The agreement in K_2 values is good, but extension of this approach to solutions where $c_{HBr} > 5$ M gives [SeOBr$_3^-$] > c_{IV}, indicating that other equilibria are involved.

Calculation of K_3 and K_4, as well as the SeBr stretching molar intensities for the SeBr$_5^-$ and SeBr$_6^{2-}$ ions in the solutions where $c_{HBr} > 5.0$ M, is a complex task due to the fact that equilibria 2, 3, and 4 must be allowed for in each of the solutions; in addition, graphical evaluation of y and a has to be carried out for each approximation. For this reason UV-visible spectral measurements were made on solutions where c_{IV} was sufficiently small that y and a could be taken directly from c_{HBr}, simplifying the interpretation and calculation. Equilibrium constants calculated in this way were shown to be consistent with the quantitative Raman spectra.

UV-Visible Spectra. The UV-visible spectra of solutions 0.001 M in SeO$_2$ show insignificant change above 300 nm until the HBr

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Table III. Absorbances at 385 nm and Anion Concentrations for 0.001 M SeO_2 Solutions of Varying HBr Concentration

c_{HBr}, mol L^{-1}	obsd A_{385}	calcd A_{385}	$10^4 \times$ $[HSeO_2Br]$, mol L^{-1}	$10^4 \times$ $[SeOBr_3^-]$, mol L^{-1}	$10^5 \times$ $[SeBr_5^-]$, mol L^{-1}	$10^5 \times$ $[SeBr_6^{2-}]$, mol L^{-1}	$10^3 a_{H_2O}/y^2$	$10^5 a_{H_2O}/y^4$
4.50	0.070	0.065	2.85	6.87	1.18	1.59	35.9	191
5.00	0.250	0.252	1.13	7.23	6.57	9.85	18.6	55.0
5.50	0.760	0.774	0.246	4.17	21.1	34.8	9.33	14.5
6.00	1.19	1.20	0.0252	1.15	31.5	56.7	4.47	3.80
7.00	1.34	1.34		0.0305	32.2	67.5	0.891	0.182
8.00	1.36	1.34			29.4	70.6	0.150	0.00661
8.90	1.32	1.34			27.2	72.8	0.0457	0.000759

Table IV. SeO Single-Bond Intensities and Concentrations for Raman Spectra of 1.0 M SeO_2 Solutions in 6.0–8.9 M HBr

c_{HBr}, mol L^{-1}	c_{IV}, mol L^{-1}	$[H^+]$, mol L^{-1}	$10^3 a/y^4$	$10^2 a/y^2$	$[Br^-]$, mol L^{-1}	$[HSeO_2Br]$, mol L^{-1}	$[SeOBr_3^-]$, mol L^{-1}	$[SeBr_5^-]$, mol L^{-1}	$[SeBr_6^{2-}]$, mol L^{-1}	calcd i_{Se-O}, cm^2	obsd i_{Se-O}, cm^2
6.00	0.513	4.92	0.661	1.972	4.485	0.0796	0.3815	0.0239	0.321	0.54	1.27
6.00	0.776	4.62	1.413	3.055	4.055	0.2232	0.5266	0.0105	0.0127	1.52	2.45
6.00	1.00	4.37	2.630	4.315	3.777	0.4124	0.5779	0.0048	0.0054	2.80	3.60
7.00	1.00	4.99	0.562	1.884	4.109	0.1732	0.7349	0.0440	0.542	1.18	2.18
8.00	1.00	5.41	0.186	1.035	4.294	0.0665	0.6111	0.1417	0.1825	0.45	0.40
8.90	1.00	5.74	0.078	0.668	4.423	0.0239	0.3818	0.2532	0.3359	0.16	...

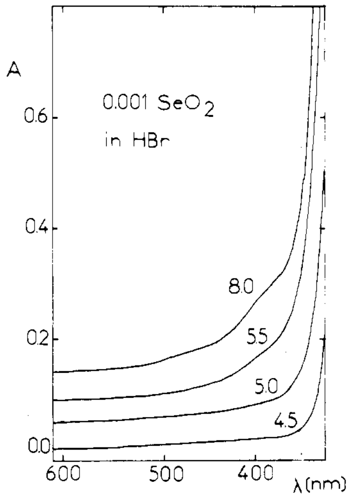

Figure 3. UV–visible spectra of solutions of 0.001 M SeO_2 in 4.5, 5.0, 5.5, and 8.0 M HBr.

concentration reaches 4.5 M. Above this HBr concentration there is a general increase in absorbance with no actual peaks being visible until 5.5 M HBr is reached, after which two shoulders at 385 and 480 nm become apparent as shown in Figure 3. The increase in absorbance is due to the $SeBr_5^-$ and $SeBr_6^{2-}$ ions. Apparently $HSeO_2Br$ and $SeOBr_3^-$, which are being formed over the range $c_{HBr} = 0.0–4.5$ M, absorb only weakly above 300 nm. Absorbances at 385 nm are listed in Table III, and these may be used to evaluate equilibrium constants K_3 and K_4 in eq 3 and 4. The equilibrium constants are given by

$$K_3 = \frac{[SeBr_5^-]a}{[SeOBr_3^-][H^+]^2[Br^-]^2 y^4} \frac{y_{SeBr_5^-}}{y_{SeOBr_3^-}} \qquad (16)$$

$$K_4 = \frac{[SeBr_6^{2-}]}{[SeBr_5^-][Br^-]} \frac{y_{SeBr_6^{2-}}}{y_{SeBr_5^-} y_{Br^-}} \qquad (17)$$

The ionic activity coefficients for the bromoselenate(IV) ions are assumed to cancel in the case of K_3. This assumption is reasonable since both ions are uninegative. It is assumed for K_4 that $y_{SeBr_6^{2-}} = y_{SeBr_5^-} y_{Br^-}$, which is more dangerous but has some basis in Debye–Hückel theory.[18] From eq 10, 16, and 17 and the mass balance equation

$$c_{IV} = [HSeO_2Br] + [SeOBr_3^-] + [SeBr_5^-] + [SeBr_6^{2-}] \qquad (18)$$

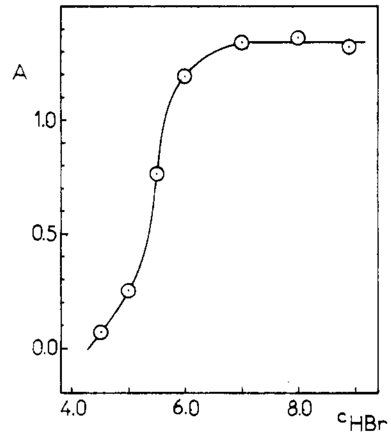

Figure 4. Comparison of observed absorbances at 385 nm (⊙) for 0.001 M SeO_2 in HBr with calculated values, assuming $K_2 = 9.5 \times 10^{-4}$ L^2 mol^{-2}, $K_3 = 8.0 \times 10^{-8}$ L^4 mol^{-4}, $K_4 = 0.3$ L mol^{-1}, ${}^5\epsilon_{385} = 1450$ L mol^{-1} cm^{-1}, ${}^6\epsilon_{385} = 1300$ L mol^{-1} cm^{-1}, and ${}^3\epsilon_{385} = 40$ L mol^{-1} cm^{-1}.

the concentrations of all species can be calculated, given K_2 and the assumed values of K_3 and K_4. An initial estimate of K_3, made from the Raman intensities, produces a value of $\sim 10^{-7}$ L^4 mol^{-4}. As a starting point, K_4 may be estimated from the relative intensities of the bands due to the $SeBr_5^-$ and $SeBr_6^{2-}$ ions in the Raman spectrum of the most concentrated HBr solution, assuming equal SeBr stretching intensities. This gives the value $K_3 \sim 0.2$ L mol^{-1}. From the concentrations calculated, the absorbance at 385 nm is determined from

$$A_{385} = {}^5\epsilon_{385}[SeBr_5^-] + {}^6\epsilon_{385}[SeBr_6^{2-}] + {}^3\epsilon_{385}[SeOBr_3^-] \qquad (19)$$

where ${}^3\epsilon_{385}$, ${}^5\epsilon_{385}$, and ${}^6\epsilon_{385}$ are the extinction coefficients at this wavelength for $SeOBr_3^-$, $SeBr_5^-$, and $SeBr_6^{2-}$, respectively. By the use of various values for the equilibrium constants and extinction coefficients, a fit to the variation of absorbance (A_{385}) and c_{HBr} was found. The optimal fit to the data required a small contribution to the absorbance from $SeOBr_3^-$ ion, to improve the fit to the lowest c_{HBr} absorbance. The final values were $K_3 = 8$ (± 1) $\times 10^{-8}$ L^4 mol^{-4}, $K_4 = 0.3$ (± 0.1) L mol^{-1}, ${}^3\epsilon_{385} = 40$ (± 10) L mol^{-1} cm^{-1}, ${}^5\epsilon_{385} = 1450$ (± 50) L mol^{-1} cm^{-1} and ${}^6\epsilon_{385} = 1300$ (± 50) L mol^{-1} cm^{-1}. This fit is shown in Figure 4. The error limits represent the increments taken to obtain the fit. The various concentrations for each solution are given in Table III as well as the calculated absorbances at 385 nm.

From this set of equilibrium constants, it is possible to calculate the concentrations of all species in solution, and from ${}^1I_{Se-O}$ (6.79 cm^2 L mol^{-1}) and the concentration of $HSeO_2Br$, i_{Se-O} may be calculated for comparison with the observed intensity at 700 cm^{-1}.

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The concentrations of the various species and the calculated and observed intensities are given in Table IV. The agreement between calculated and observed intensities is reasonable, considering the assumptions made and the accuracy of measurement with relatively weak peaks. It should be recalled that two serious assumptions have been made: (a) $f_{SeBr_6^{2-}} = f_{SeBr_5^-}f_{Br^-}$; (b) the activity factors, a/y^4 and a/y^2, calculated for pure HBr solutions are applicable to mixtures of the strong acids HBr, $HSeOBr_3$, $HSeBr_5$, and H_2SeBr_6. Both of these assumptions will be more dangerous with increasing concentration, particularly where the Se(IV) acids assume a greater proportion of total acid concentration.

Conclusion

The principal species present in solutions of SeO_2 in hydrobromic acid are H_2SeO_3, $HSeO_2Br$, $SeOBr_3^-$, $SeBr_5^-$, and $SeBr_6^{2-}$. While the Raman spectra give no clear evidence for the presence of SeO_2Br^-, $SeOBr_2$, and $SeOBr_4^{2-}$, their presence in low concentration cannot be ruled out. It is interesting that $SeBr_4$ decomposes to Se_2Br_2, $SeBr_2$, and Br_2 in nonaqueous solvents, yet no evidence for such decomposition is found in this work. Apparently coordination by the bromide ion stabilizes the Se(IV) oxidation state. In comparison to chloroselenates in hydrochloric acid, bromoselenates in hydrobromic acid are formed more readily. For instance, in 5 M HCl (1 M SeO_2), all of the Se(IV) is still present as H_2SeO_3,[4] whereas in 5 M HBr (1 M SeO_2), no H_2SeO_3 remains, all of the Se(IV) being present as $HSeO_2Br$ and $SeOBr_3^-$. Moreover, the chloro species formed in HCl is $SeOCl_2$, while in HBr, $SeOBr_3^-$ is formed. In the SeO_2–HF system, even at 26 M HF, no bands for fluoroselenate(IV) species can be seen in the Raman spectrum.[14] Thus, the order of ease of haloselenate(IV) formation, Br > Cl > F, follows the order of HX activities in water.[1,4,17] Both hexabromo-[7] and tribromoselenate(IV)[8] compounds can be isolated from the HBr solutions of SeO_2, thus reflecting the presence of these anions as the predominant forms of bromoselenate found in these solutions, depending upon the HBr concentration involved (Table IV). On the basis of the relatively low concentration of pentabromoselenate(IV) in these solutions, it appears unlikely that compounds containing this anion can be prepared from aqueous HBr solutions.

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Registry No. H_2SeO_3, 7783-00-8; $HSeO_2Br$, 88212-41-3; $SeOBr_3^-$, 86238-39-3; $SeBr_5^-$, 94598-25-1; $SeBr_6^{2-}$, 20130-45-4; SeO_2, 7446-08-4; HBr, 10035-10-6.

Contribution from the Istituto Chimico "G. Ciamician" and Istituto di Scienze Chimiche,
University of Bologna, Bologna, Italy, and Istituto FRAE—CNR, Bologna, Italy

Electron-Transfer Photosensitization via Ion Pairs. Co(sepulchrate)$^{3+}$–Iodide Ion System

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The Co(sep)$^{3+}$ complex (sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) in aqueous solution forms ion pairs with I^- ions that exhibit a relatively intense charge-transfer absorption. In deoxygenated solutions at natural pH, light excitation of the ion pair does not cause any net reaction. In deoxygenated acid solutions a photochemical reaction takes place with formation of I_3^- and Co_{aq}^{2+} in a 1:2 stoichiometric ratio, with quantum yield 3.4×10^{-3} at pH 1. In oxygen-saturated solutions at natural pH, a photoassisted oxidation of I^- to I_3^- by O_2 is obtained with turnover number >40 for Co(sep)$^{3+}$ and quantum yield 1.6×10^{-3} for $^1/_2$ I_3^- formation. The quantum yield increases with increasing H^+ and I^- concentrations, and in acid solution, it also increases with irradiation time. The results obtained are interpreted on the basis of a mechanism in which the primary photoproducts Co(sep)$^{2+}$ and I are involved in the following secondary reactions: (i) The I radical is scavenged by I^- to yield I_2^-, which then undergoes disproportionation to I_3^- and I^-. (ii) In deoxygenated neutral solutions Co(sep)$^{2+}$ is quantitatively reoxidized to Co(sep)$^{3+}$ by I, I_2^-, or I_3^-. (iii) In deoxygenated acid solution Co(sep)$^{2+}$ undergoes a decomposition reaction, yielding Co_{aq}^{2+}. (iv) In the presence of oxygen, Co(sep)$^{2+}$ can be oxidized to Co(sep)$^{3+}$ with concomitant formation of H_2O_2, which in acid solution oxidizes I^- to I_3^-. The potentiality of the ion-pair approach to the design of photosensitizers for cyclic redox processes is briefly discussed.

Introduction

The recently synthesized[2] Co(sep)$^{3+}$ complex (Figure 1) (sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) exhibits interesting electron-transfer properties[2,3] and has already been used as a relay species in homogeneous[4–6] and heterogeneous[7,8] photochemical cyclic processes for solar energy conversion. We have found that Co(sep)$^{3+}$ can give ion pairs with a variety of anions, and that, once involved in such ion pairs, it can play the role of an electron-transfer photosensitizer. In this paper we report the results obtained on light excitation of the Co(sep)$^{3+}$,I^- ion pair under a variety of experimental conditions.

Experimental Section

Co(sep)$Cl_3 \cdot H_2O$ was prepared following the method of Sargeson et al.[2] as modified by Indelli et al.[9] The absorption spectrum and the electrochemical behavior of the compound so obtained were in full agreement with the data reported in the literature.[2]

The experiments were carried out in aqueous solutions that were air equilibrated or nitrogen or oxygen saturated by continuous bubbling. The absorption spectra were recorded with a Cary 19 spectrophotometer, and the electrochemical measurements were performed by an AMEL Model 563 Electrochemolab equipment.

Light excitation at 254 or 313 nm was carried out by low- and medium-pressure Hg lamps as previously described.[10] The incident light

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