Weak Complexes of Sulphur and Selenium. Part III.[1] Effect of Solvent on the Stability of 1 : 1 Complexes of Sulphur Dioxide, Sulphinyl Dichloride, and Sulphonyl Dichloride with Halogen Ions

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The complex species SO_2,X^-, $SOCl_2,X^-$, and SO_2Cl_2,X^- (X = Cl, Br, and I) have been studied in acetonitrile, dimethyl sulphoxide (dmso), and water (for SO_2,X^- species only). It appears that solvation of halide ions by dmso is important in deciding the stabilities of the different species.

SOLVENT molecules are not impartial in chemical processes, the extent to which they participate sometimes overshadowing that of the other species in the reaction media. This is because the solvent represents the environment in which a chemical reaction takes place and in most cases plays the role of electron donor or acceptor. The role of the environment and solvent effects in chemical reactions has been discussed by a number of workers in recent years.[2-7] The purpose of this paper is to study the role of solvent on the stability of some weak complexes which were reported recently.[8a]

EXPERIMENTAL

The preparation of solutions, spectral measurements, and data processing was as outlined previously.[1,8a] The experimental conditions were such that all the reported species had 1 : 1 stoicheiometries. A number of solvents were used; dioxan, tetrahydrofuran, and ethylene dichloride were unsuitable because of solubility problems of the halide salts (mostly quaternary ammonium salts). *NN*-Dimethylformamide was also unsatisfactory because a yellow colour appeared with $SOCl_2$ and SO_2Cl_2 indicating probable oxidation. Dimethyl sulphoxide (dmso) was the principal solvent and is compared with earlier data with acetonitrile.[8a] Water was limited to SO_2,X^- species as the other acceptors, *i.e.* $SOCl_2$ and SO_2Cl_2, are hydrolysed. All compounds used were B.D.H. AnalaR grade and were treated as outlined before.[8a] A Unicam SP 8000 spectrophotometer was used in which the cell compartment could be thermostatted to ±0·05 °C.

Absorption peaks of the complex species in the three solvents used are listed in Table 1, the detailed experimental data for evaluating the complex formation constant K_c in Table 2, a summary of all the K_c data at 25 °C in Table 3, ratios of K_c in acetonitrile and dmso in Table 4. The K_c data in acetonitrile were taken from ref. 8*a*.

RESULTS AND DISCUSSION

Water, being unsuitable as a solvent for $SOCl_2$ and SO_2Cl_2 because of hydrolysis, has been excluded from Table 4 and comparison of K_c data is therefore limited to

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TABLE 1

Absorption spectra ($\lambda_{max.}$/nm) of the complexes in dmso, acetonitrile, and water

Complex \ X	Cl[a]	Br[a]		I[b]	
	c	*c*	*d*	*c*	*d*
SO_2,X^-	292	320	284	380	344
$SOCl_2,X^-$	292	321		381	
SO_2Cl_2,X^-	276	323		375	

[a] Values of K_c at 25 °C were evaluated using an equation cited by J. A. A. Ketelaar, *Rec. Trav. chim.*, 1952, **71**, 1104. [b] As in (*a*) from H. A. Benezi and J. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703. [c] MeCN and dmso. [d] H_2O.

TABLE 2

Stability constants of the complexes in dmso at 25 °C

SO_2,I^-				
$10^3[I^-]$/M	1·792	2·240	2·688	3·136
$10^3[SO_2]$/M	2·210	2·210	2·210	2·210
D_{obs}	0·085	0·103	0·128	0·145
$K_c = 12{\cdot}1 \pm 0{\cdot}1$ l mol^{-1}				
SO_2,Br^-				
$10^2[Br^-]$/M	2·148	2·685	3·222	3·759
$10^5[SO_2]$/M	5·000	5·000	5·000	5·000
D_{obs}	0·151	0·170	0·183	0·205
$\varepsilon_A = 400$ l mol^{-1} cm^{-1},* $K_c = 21 \pm 0{\cdot}4$ l mol^{-1}				
SO_2,Cl^-				
$10^2[Cl^-]$/M	1·147	1·434	1·721	
$10^5[SO_2]$/M	5·000	5·000	5·000	
D_{obs}	0·285	0·305	0·325	
$\varepsilon_A = 4\ 000$ l mol^{-1} cm^{-1}, $K_c = 26 \pm 0{\cdot}5$ l mol^{-1}				
$SOCl_2,I^-$				
$10^3[I^-]$/M	3·860	5·790	7·720	9·650
$10^4[SOCl_2]$/M	4·768	4·768	4·768	4·768
D_{obs}	0·055	0·080	0·100	0·120
$K_c = 35 \pm 0{\cdot}7$ l mol^{-1}				
$SOCl_2,Br^-$				
$10^3[Br^-]$/M	3·330	5·000	6·660	8·330
$10^4[SOCl_2]$/M	4·768	4·768	4·768	4·768
D_{obs}	0·330	0·390	0·450	0·500
$\varepsilon_A = 4\ 420$ l mol^{-1} cm^{-1}, $K_c = 21 \pm 0{\cdot}4$ l mol^{-1}				
$SOCl_2,Cl^-$				
$10^3[Cl^-]$/M	2·950	6·220	9·490	12·760
$10^5[SOCl_2]$/M	3·560	3·560	3·560	3·560
D_{obs}	0·150	0·170	0·185	0·200
$\varepsilon_A = 3\ 652$ l mol^{-1} cm^{-1}, $K_c = 18 \pm 0{\cdot}5$ l mol^{-1}				
SO_2Cl_2,I^-				
$10^3[I^-]$/M	4·490	8·990	13·480	17·980
$10^4[SO_2Cl_2]$/M	6·700	6·700	6·700	6·700
D_{obs}	0·070	0·130	0·200	0·260
$K_c = 6 \pm 0{\cdot}2$ l mol^{-1}				
SO_2Cl_2,Br^-				
$10^3[Br^-]$/M	4·350	8·710	13·060	17·420
$10^4[SO_2Cl_2]$/M	6·700	6·700	6·700	6·700
D_{obs}	0·400	0·590	0·780	0·980
$\varepsilon_A = 268{\cdot}5$ l mol^{-1} cm^{-1}, $K_c = 14 \pm 0{\cdot}5$ l mol^{-1}				
SO_2Cl_2,Cl^-				
$10^3[Cl^-]$/M	3·270	6·550	9·820	13·090
$10^5[SO_2Cl_2]$/M	6·700	6·700	6·700	6·700
D_{obs}	0·300	0·335	0·360	0·380
$\varepsilon_A = 3\ 728$ l mol^{-1} cm^{-1}, $K_c = 36 \pm 0{\cdot}8$ l mol^{-1}				
SO_2,I (in water)				
$[I^-]$/M	0·1214	0·1518	0·1822	0·2125
$10^2[SO_2]$/M	1·175	1·175	1·175	1·175
D_{obs} (20 °C)	0·475	0·600	0·698	0·797
D_{obs} (40 °C)	0·528	0·670	0·770	0·870
K_c (20 °C) = 0·35, K_c (40 °C) = 0·39 l mol^{-1}				
SO_2,Br^- (in water at 25 °C)				
$[Br^-]$/M	0·2578	0·3094	0·3609	0·4125
$10^3[SO_2]$/M	6·180	6·180	6·180	6·180
$\varepsilon_A = 70$ l mol^{-1} cm^{-1}, $K_c = 0{\cdot}22$ l mol^{-1}				

* ε_A = *Absorption coefficient of acceptor at the absorption maximum for the complex.*

TABLE 3

Summary of stability-constant data in acetonitrile, dmso, and water at 25 °C

Complex \ X	Cl		Br			I		
	a	*b*	*a*	*b*	*c*	*a*	*b*	*c*
SO_2,X^-	372	26	160	21	0·22	38	12	0·36
$SOCl_2,X$	362	18	241	21		150	35	
SO_2Cl_2,X^-	10	36	41	14		76	6	

[a] MeCN. [b] dmso. [c] H_2O.

TABLE 4

Comparison of stability constants K_c at 25 °C in acetonitrile and dmso

Complex \ X	K_c(MeCN) : K_c(dmso)		
	Cl	Br	I
SO_2,X^-	15	8	3
$SOCl_2,X^-$	20	11	4
SO_2Cl_2,X^-	0·3	3	13

the values in acetonitrile and dmso. Reference will be given later to the data in water. With the exception of the SO_2Cl_2,Cl^- species, the stability constants of the different complexes decreased by a factor of between 3 and 20 in dmso as compared to acetonitrile. It should be noted that the reference solvent, in all spectral measurements, consisted of the solvent and donor ligand in similar concentration to that in the experimental solution mixture which includes the acceptor. This procedure was designed to filter out any spectral effects which might arise from possible interaction between the halide ions and the solvent.

The data in Table 4, therefore, express the significant reduction in stability of the complex species in dmso. There are at least two possible roles that can be played by dmso (or water) in affecting the stabilities of the complex species. It may solvate the donor halide ligands and thus prevent them from interacting with the acceptors or act as a competing acceptor towards the halide ions, or perhaps both, to extents depending on the environmental conditions.

Table 4 shows some vertical and horizontal trends. The data in column (1) show maximum decrease in K_c for the species SO_2,Cl^- and $SOCl_2,Cl^-$ in dmso. This can be attributed to solvation of the Cl^- ligand and possibly ion–dipole interaction. The greater polarity of dmso (μ 4·3 D) [8b,9] than SO_2 and $SOCl_2$ (μ 1·61 and 1·60 D respectively) favours this.* In these species, stabilisation results from back donation [10-12] from sulphur 3*d* orbitals to the donor ligand. Minimum effect is shown for SO_2Cl_2,Cl^- where K_c(MeCN) : K_c(dmso) = 0·3 : 1 and this shows the important role of polarisation, not back donation, in stabilising this species. In column (2) the ratios for SO_2,Br^- and $SOCl_2,Br^-$ are nearly half those in (1) for the Cl^- species. This is regarded as reflecting the

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* 1D ≈ 3·34 × 10^{-30} C m.

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[12] C. A. Coulson and F. A. Gianturco, *J. Chem. Soc. (A)*, 1968, 1618.

lower tendency to solvation of the Br^- ligand as compared to Cl^- by dmso. In column (3) the ratios for SO_2,I^- and $SOCl_2,I^-$ are nearly $\frac{1}{4}$ of the values for the Cl^- species. This shows the lower tendency of the I^- ligands to solvate and is not unexpected due to their larger ionic size.

The horizontal trends in SO_2,X^- and $SOCl_2,X^-$ appear to agree with the conclusion that solvation of the donor ligands by dmso is important in decreasing the stability constants compared with those in acetonitrile and that this lowering is maximal with Cl^- and minimal with I^-. The K_c data in water for SO_2,X^- appear to support this view. From Table **3** it can be seen that SO_2,Cl^- could not be detected but SO_2,Br^- and SO_2,I^- were stable enough for their K_c data to be determined. The data in Table **3** also show that I^- is less solvated than Br^- in water as is the case in dmso. For SO_2Cl_2,X^- species the horizontal trend observed is reversed compared to that shown for SO_2,X^- and $SOCl_2,X^-$. This supports an earlier view [1,8a] that the nature of the association in SO_2Cl_2,X^- species is different from that in SO_2,X^- and $SOCl_2,X^-$, the former being mainly ion–dipole interaction and the latter back donation from sulphur 3*d* orbitals to the donor ligands. The lowering in stability of SO_2Cl_2,I^- and SO_2Cl_2,Br^- is evidence that ion–dipole interaction is particularly strong between dmso and I^-, which is understandable in view of the higher dipole moment of dmso than SO_2Cl_2. The data in column (3), Table **4**, for the iodide species show that ion–dipole interaction outweighs solvation, while those of column (1) show that solvation has the greater effect.

We thank Dr. A. Katrib of this department for assistance.

[4/007 *Received, 2nd January,* 1974]