Weak Complexes of Sulphur and Selenium. Part 5.[1] Halide-ion Replacement in 1:1 Complexes of Sulphur Dioxide, Thionyl Chloride, and Sulphonyl Choride with Halide Ions in Acetonitrile and Dimethyl Sulphoxide

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The replacement of the iodide ligand in the complex species $SO_2{\cdot}I^-$, $SOCl_2{\cdot}I^-$, and $SO_2Cl_2{\cdot}I^-$ by chloride, bromide, and thiocyanate ions has been studied spectrophotometrically. The extent of replacement depends on complex stability, the nature of the replacing ligand, and on the solvent used.

THE nature of weak charge-transfer complexes of the type $SO_2{\cdot}X^-$, $SOCl_2{\cdot}X^-$, and $SO_2Cl_2{\cdot}X^-$ was discussed recently.[2-4] The stability constants in acetonitrile and dimethyl sulphoxide (dmso) display differences which depend on the nature of the sulphur compound (acceptor), the halide ion (donor), and the solvent used.

Since more than one halide ion can co-ordinate to the same sulphur acceptor it was of interest to examine the effect of adding a ligand to a complex in solution. This study can be extended to substitution reactions in metal complexes which might be useful in many chemical processes involving transition metals.

EXPERIMENTAL

In all the experiments a solution of the replacing ligand (Cl^-, Br^-, or $[SCN]^-$) was added progressively to a solution of the iodide complex species $SO_2{\cdot}I^-$, $SOCl_2{\cdot}I^-$, and $SO_2Cl_2{\cdot}I^-$. Replacement of iodide ion was followed by recording the disappearance of the visible spectrum of the iodide complex and the emergence of a new peak resulting from the formation of the new complex species. Figure 1 shows the growth of $SO_2{\cdot}SCN^-$ and decay of $SO_2{\cdot}I^-$ in MeCN.

In all experiments the concentration of the iodide ion was kept at 0.002 5 mol dm^{-3}. The mol ratio $[L^-]:[I^-]$ varied from 0.1 to 10 : 1. The concentration of the sulphur compound was *ca.* 10^{-4} mol dm^{-3}. All the solutions were prepared as outlined before.[2-4] Spectra were recorded immediately after the preparation of solutions using a Pye–Unicam SP 8000 spectrometer in which the cell compartment was thermostatted at 25 ± 0.1 °C.

For each experiment a spectrum was recorded for the solution of the iodide complex before adding the solution of the replacing halide ligand. The observed absorbance $d^0_{\text{obs.}}$ represents the reference to which all the other spectra

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[1] Part 4; S. Wasif and S. B. Salama, *J.C.S. Dalton*, 1975, 2239.

[2] A. Salama, S. B. Salama, M. Sobeir, and S. Wasif, *J. Chem. Soc.* (*A*), 1971, 1112.

[3] S. B. Salama and S. Wasif, *J.C.S. Dalton*, 1973, 2139.

[4] S. B. Salama and S. Wasif, *J.C.S. Dalton*, 1975, 151.

are compared after adding the replacing ligand. If the new absorbance equals $d'_{\text{obs.}}$ then the percentage disappearance of iodide complex = $[(d^0_{\text{obs.}} - d'_{\text{obs.}})/d^0_{\text{obs.}}] \times 100$. Table 1 includes data for one experiment in which Cl^- is added to $SO_2{\cdot}I^-$ in MeCN at 25 °C, and Table 2 includes a summary of all the replacement reactions investigated.

TABLE 1

Data for the reaction $SO_2{\cdot}I^- + Cl^- \longrightarrow SO_2{\cdot}Cl^- + I^-$ in MeCN at 25 °C

$10^3[Cl^-]$/mol dm^{-3}	0.00	0.50	1.00	1.50	2.50	3.50	5.00	6.50	10.0
$[Cl^-] : [I^-]$		0.20	0.40	0.60	1.00	1.40	2.00	2.60	4.0
$d_{\text{obs.}}$	0.66	0.56	0.51	0.47	0.42	0.37	0.29	0.27	0.19
% Replacement		15	23	29	37	44	56	60	70

$[SO_2] = 1.6 \times 10^{-4}$, $[I^-] = 2.5 \times 10^{-3}$ mol dm^{-3}

The experimental solution gave a negative test for I_2 showing that I^- was released according to equation (1)

$$SO_2{\cdot}I^- + X^- \longrightarrow SO_2{\cdot}X^- + I^- \qquad (1)$$

($X = Cl^-$, Br^-, or $[SCN]^-$). Similar reactions occurred with $SOCl_2{\cdot}I^-$ and $SO_2Cl_2{\cdot}I^-$ confirming the generality of this equation. All the chemicals were reagent grade, and the solvents were for spectroscopic use.

DISCUSSION

The Nature of the Complex Species.—In order to be able to interpret the trends in Table 2 reference may be made to the stabilities of the complexes involved in different reactions. Table 3 includes K_c data for $SO_2{\cdot}X^-$, $SOCl_2{\cdot}X^-$, and $SO_2Cl_2{\cdot}X^-$ in MeCN at 25 °C. The magnitude and order of the K_c values depends on the Lewis-base character of the halide ligands [5,6] and on the Lewis-acid character of the sulphur acceptors, $SO_2{\cdot}Cl^-$, $SOCl_2{\cdot}Cl^-$, and $SO_2Cl_2{\cdot}I^-$ being the most stable species in the three series.[2]

TABLE 2

Replacement reactions at 25 °C *

	Reaction	
(*a*) In MeCN		$[Cl^-] : [I^-]$
	(1) $Cl^- + SO_2{\cdot}I^-$	0.05(5), 0.10(8), 0.15(12), 0.20(15), 0.30(19), 0.40(23)
	(2) $Cl^- + SOCl_2{\cdot}I^-$	0.05(4), 0.10(7), 0.15(11), 0.20(15), 0.30(18), 0.40(22)
	(3) $Cl^- + SO_2Cl_2{\cdot}I^-$	0.05(2), 0.10(3.5), 0.15(5.5), 0.20(8), 0.30(10), 0.40(12.5)
		$[Br^-] : [I^-]$
	(4) $Br^- + SO_2{\cdot}I^-$	0.05(1.5), 0.10(3), 0.20(5), 0.30(8), 0.40(10)
	(5) $Br^- + SOCl_2{\cdot}I^-$	0.05(2), 0.10(3.6), 0.20(5.8), 0.30(7.7), 0.40(9.3)
	(6) $Br^- + SO_2Cl_2{\cdot}I^-$	0.05(2.5), 0.10(4), 0.20(6), 0.30(8), 0.40(9.4)
		$[SCN^-] : [I^-]$
	(7) $[SCN]^- + SO_2{\cdot}I^-$	0.20(—), 0.50(2), 1.0(3), 2.5(4), 4.0(6)
	(8) $[SCN]^- + SOCl_2{\cdot}I^-$	0.20(—), 0.50(1.8), 1.0(2.9), 2.5(4), 4.0(5.9)
(*b*) In dmso		$[Cl^-] : [I^-]$
	(9) $Cl^- + SO_2{\cdot}I^-$	0.503), 1.0(5), 1.5(7), 2.0(10), 3.0(13), 4.0(17)
	(10) $Cl^- + SOCl_2{\cdot}I^-$	0.50(3), 1.0(4), 1.5(6), 2.0(9), 3.0(12), 4.0(15)
	(11) $Cl^- + SO_2Cl_2{\cdot}I^-$	2.0(8), 4.0(16)
		$[Br^-] : [I^-]$
	(12) $Br^- + SO_2{\cdot}I^-$	0.50(4), 1.0(6), 2.0(11), 4.0(13)
	(13) $Br^- + SOCl_2{\cdot}I^-$	0.50(4), 1.0(5), 1.5(7), 2.0(10)
(*c*) In water	$Cl^- + SO_2{\cdot}I^-$	4(3), 8(5), 12(7)

* No replacement was observed by $[SCN]^-$ in dmso. Percentage replacements of the iodide species are given in parentheses.

Correlation of Stability Constants with Ligand Replacements.—(*a*) *The Cl^-–I^- reaction.* The data in Table 3 show that in the presence of two halide ligands such as Cl^- and I^- and acceptors such as SO_2 and $SOCl_2$ (in MeCN) the thermodynamics would be more favourable for $SO_2{\cdot}Cl^-$ and $SOCl_2{\cdot}Cl^-$ than for $SO_2{\cdot}I^-$ and $SOCl_2{\cdot}I^-$. Also, $K_c(SO_2{\cdot}Cl^-) \approx K_c(SOCl_2{\cdot}Cl^-)$ and these values are much higher than $K_c(SO_2Cl_2{\cdot}Cl^-)$, in the ratio 37 : 36 : 1. Such a large difference in stability makes replacement of

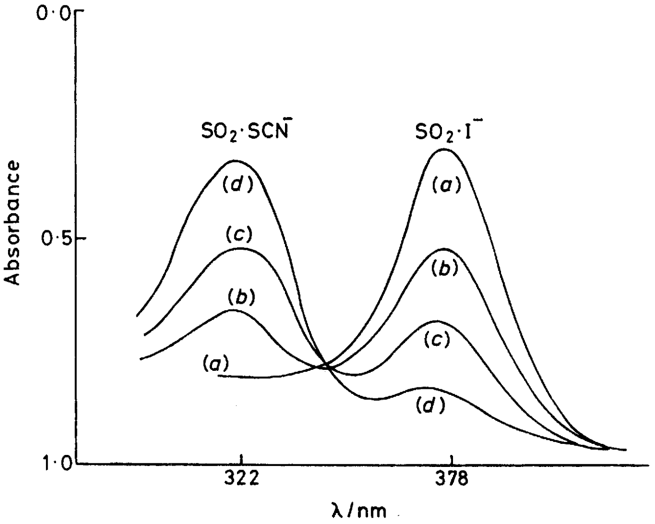

FIGURE 1 Substitution of I^- in $SO_2{\cdot}I^-$ by $[SCN]^-$: no $[SCN]^-$ added (*a*); $[SCN^-] : [I^-]$ = 0.4 (*b*), 1.0 (*c*), and 2.0 : 1 (*d*)

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[5] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

[6] M. C. Day and J. Selbin, 'Theoretical Inorganic Chemistry,' Rheinhold, New York, 1969.

TABLE 3

Stability constants (dm^3 mol^{-1}) * in MeCN at 25 °C

X$^-$ / Complex	Cl$^-$	Br$^-$	I$^-$	[SCN]$^-$
$SO_2{\cdot}X^-$	372	160	38	65
$SOCl_2{\cdot}X^-$	362	241	150	77
$SO_2Cl_2{\cdot}X^-$	10	41	77	298

* Ref. 2.

the I$^-$ by added Cl$^-$ much easier for $SO_2{\cdot}I^-$ and $SOCl_2{\cdot}I^-$ than it is for $SO_2Cl_2{\cdot}I^-$. The data in Table 2 and Figure 2 illustrate this observation, and we note that the percentage replacements in $SO_2{\cdot}I^-$ and $SOCl_2{\cdot}I^-$ fall (at low [Cl$^-$] : [I$^-$]) on the same curve and are much higher than for $SO_2Cl_2{\cdot}I^-$.

The replacement reaction (2) seems anomalous, since

$$SO_2Cl_2{\cdot}I^- + Cl^- \longrightarrow SO_2Cl_2{\cdot}Cl^- + I^- \qquad (2)$$

$K_c(SO_2Cl_2{\cdot}I^-)/K_c(SO_2Cl_2{\cdot}Cl^-) \approx 8$. That reaction (2) can be carried out despite the reversed order of stability constants, which permits easy replacement, between product and reactant, can only be due to the relative abundance of the chloride ligand which seems to outweigh the difference in stability constants. Table 2 shows that a 20% disappearance of $SO_2{\cdot}I^-$ requires a ligand ratio of [Cl$^-$] : [I$^-$] = 0.35 : 1, while in the case of $SO_2Cl_2{\cdot}I^-$ a ligand ratio of [Cl$^-$] : [I$^-$] = 1 : 1 was necessary for the same percentage replacement. By changing the ligand ratio from 0.35 to 1 : 1 we are merely increasing the chances of effective collisions leading to replacement by the more abundant ligand.

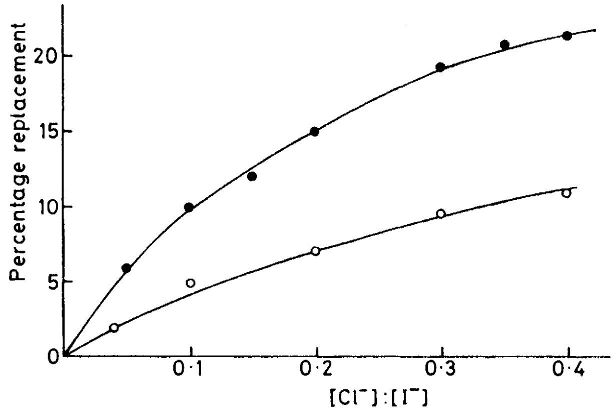

FIGURE 2 Comparison of replacement reactions by added Cl$^-$; (●) $SO_2{\cdot}I^-$ and $SOCl_2{\cdot}I^-$; (○) $SO_2Cl_2{\cdot}I^-$; MeCN, 25° C

(*b*) *The* Br$^-$–I$^-$ *and* SCN$^-$–I$^-$ *reactions.* Table 2 includes data for replacement reactions by the Br$^-$ and [SCN]$^-$ ligands. For both ligands the magnitudes of replacement are not widely different. This is not unexpected since the stability constants of $SO_2{\cdot}Br^-$, $SOCl_2{\cdot}Br^-$, and $SO_2Cl_2{\cdot}Br^-$ are in the ratio 4 : 6 : 1 and for $SO_2{\cdot}SCN^-$, $SOCl_2{\cdot}SCN^-$, and $SO_2Cl_2{\cdot}SCN^-$ are in the ratio 1 : 1.2 : 2.4. A comparison of the replacing ability of the [SCN]$^-$ ligand with that of Cl$^-$ and Br$^-$, for reaction (1), is shown in Figure 3. The ligands fall in the order Cl$^-$ > Br$^-$ > [SCN]$^-$ which parallels their Lewis-base character as hard, borderline, and soft, respectively.

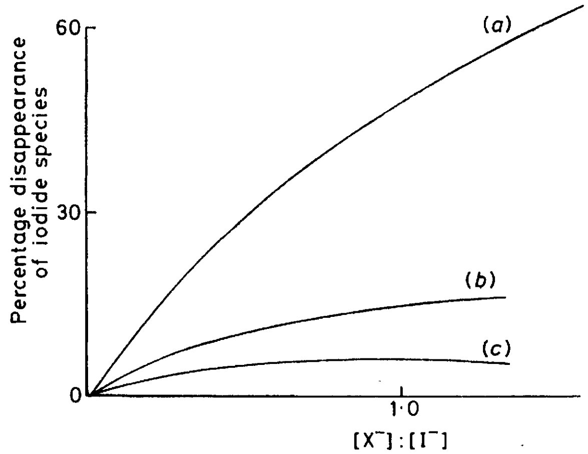

FIGURE 3 Comparison of amount of substitution of I$^-$ in $SOCl_2{\cdot}I^-$. X = Cl$^-$ (*a*), Br$^-$ (*b*), or [SCN]$^-$ (*c*)

The Role of Solvent in Replacement Reactions.—Table 2 and Figure 4 show the effect of the solvent on reaction (1) (X$^-$ = Cl$^-$). For a ligand ratio [Cl$^-$] : [I$^-$] = 4 : 1 in MeCN there is 70% replacement of I$^-$ but only 16% in dmso (and less than 3% in water). Clearly, a change of solvent greatly affects the degree of replacement.

In dmso two factors are operative: (*a*) dmso may solvate the Cl$^-$ ligand and so prevent its co-ordination to SO_2 radicals; and (*b*) dmso may act as a potential acceptor at its S atom and compete with the sulphur acceptors (as SO_2) in solution. The conclusion that dmso probably acts as a potential acceptor was reached from the observation of the spectrum of a solution of dmso containing Cl$^-$ and I$^-$. This solution shows the slow growth of two peaks at 292 and 365 nm, the rate of growth being dependent on the halide-ion concentration; a rate constant of 2×10^{-2} min^{-1} was found at 25 °C.

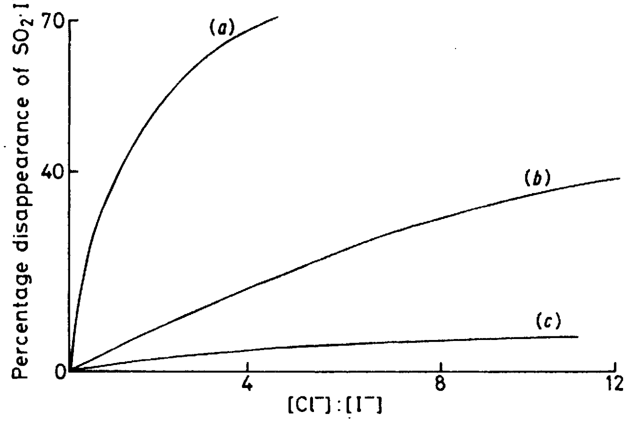

FIGURE 4 Solvent effect on the reaction $SO_2{\cdot}I^- + Cl^- \longrightarrow SO_2{\cdot}Cl^- + I^-$. Solvent = MeCN (*a*), dmso (*b*), or water (*c*)

The replacement reaction (1) ($X^- = Cl^-$) in dmso is ionic and has a rate constant of *ca.* 10^{10} s^{-1}; therefore the addition of Cl^- to $SO_2{\cdot}I^-$ (in dmso) is accompanied, at first, by the disappearance of the peak at 378 nm ($SO_2{\cdot}I^-$) and the emergence of a new peak at 292 nm ($SO_2{\cdot}Cl^-$). If this solution is left for a few days the peaks at 365 and 292 nm grow slowly. The appearance of the peaks at 292 and 365 nm probably shows that dmso gives rise to new complex species with Cl^- and I^- respectively. By analogy of the observed peaks with those reported for $SO_2{\cdot}X^-$, $SOCl_2{\cdot}X^-$, and $SO_2Cl_2{\cdot}X^-$ it is logical to assume the formation of a chloride and an iodide complex species of dmso. Since dmso has a quadrivalent S atom, like SO_2 and $SOCl_2$, its acceptor centre will be the sulphur atom and the complex species would have a similar structure to that reported earlier for SO_2 and $SOCl_2$ and would therefore be $SMe_2O{\cdot}Cl^-$ and $SMe_2O{\cdot}I^-$. Recent work on the photoelectron spectroscopy of sulphur compounds favours this view.[7-15] A solution of dmso containing Cl^- or I^- alone does not show any new peaks. The presence of two ligands appears to excite the dmso molecule to form the new complex species in a manner which is not yet clear. Similar ' catalysis ' by ligands was reported recently.[16]

Water appears to be a more drastic solvating agent towards the Cl^- ligand and this results in only a low degree of replacement up to a high ratio of $[Cl^-] : [I^-] = 12 : 1$. Attempts to carry out replacements by $[SCN]^-$ in dmso failed, no reaction being noticeable.

Replacement Reactions in Mixed Solvents.—Various mixtures of MeCN and dmso were used to study reaction (1) ($X^- = Cl^-$) and the data are given in Table 4. As the percentage of dmso in the solvent increases the ability of Cl^- to replace I^- diminishes. Here it is possible that the solvating power of dmso towards Cl^- makes it sterically difficult to replace the I^- in $SO_2{\cdot}I^-$.

TABLE 4

Replacement reaction of $SO_2{\cdot}I^- + Cl^-$ in MeCN–dmso mixed solvent at 25 °C *

% dmso	0.00(70),	25(53),	50(38),	75(20),	100(17)

* $[Cl^-] : [I^-] = 4 : 1$ in each run. The percentage replacement of iodide is given in parentheses.

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[7] M. F. Guest, I. H. Hillier, and V. R. Saunders, *J.C.S. Faraday II*, 1972, 114.

[8] D. S. Urch, *J. Chem. Soc.* (*A*), 1969, 3026.

[9] D. Shadwick, D. C. Frost, F. G. Herring, A. Katrib, C. A. McDowell, and R. A. N. McLean, *Canad. J. Chem.*, 1973, **51**, 1893.

[10] D. Shadwick, A. B. Conford, D. C. Frost, F. G. Herring, A. Katrib, C. A. McDowell, and R. A. N. McLean, *Electron Spectroscopy*, 1972, 453.

[11] D. Kivelson, *J. Chem. Phys.*, 1954, **22**, 904.

[12] D. C. Frost, F. G. Herring, A. Katrib, R. A. N. McLean, J. E. Drake, and P. C. Westwood, *Chem. Phys. Letters*, 1971, **10**, 347; *Canad. J. Chem.*, 1971, **49**, 4033.

[13] D. C. Frost, A. Katrib, C. A. McDowell, and R. A. N. McLean, *J. Mass Spectrometry Ion Phys.*, 1971, **7**, 485.

[14] J. H. D. Eland and C. J. Danby, *Internat. J. Mass Spectrometry Ion Phys.*, 1971, 111.

[15] M. Jonathan, D. J. Smith, and K. J. Ross, *Chem. Phys. Letters*, 1971, **9**, 217.

[16] E. Buncel, and H. W. Leung, *J.C.S. Chem. Comm.*, 1975, 19.