Weak Complexes of Sulphur and Selenium. Part IV.[1] Complex of Selenium Dioxide and Seleninyl Dichloride with Halide Ions

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The formation of 1 : 1 complexes between SeO_2 and $SeOCl_2$ and Cl^-, Br^-, and I^- ions is reported. The stability constants and nature of the complexes are correlated with those of SO_2 and $SOCl_2$ and the role of dimethyl sulphoxide as solvent is discussed.

THE tendency of SeO_2 to form complexes was reported by Carnevali[2] who studied the formation of $R_4NCl{\cdot}SeO_2$ (R = alkyl) adducts. No work has been reported on the nature of such species which is the aim of the present study.

EXPERIMENTAL

Following recent investigations[1,3,4] of weak charge-transfer complexes, we report the new species $SeO_2{\cdot}X^-$ and $SeOCl_2{\cdot}X^-$ (X = Cl, Br, or I). Both SeO_2 and $SeOCl_2$ presented some difficulty in the choice of suitable solvent. Acetonitrile, nitromethane, tetrahydrofuran, and *NN*-dimethylformamide were not suitable either for solubility (particularly for SeO_2) or for oxidising reactions (for I^-). Dimethyl sulphoxide (dmso) solutions were more stable and were used for this study, spectra being recorded on fresh solutions only (Table 1). The absorbance peaks were obtained in the presence of R_4NX and KX (R = alkyl; X = halide), indicating that they correspond to new complexes between the selenium compound and the halide ligand.

TABLE 1

Absorption peaks (nm) of $SeO_2{\cdot}X^-$ and $SeOCl_2{\cdot}X^-$ in dmso

X / Complex		Cl	Br	I
$SeO_2{\cdot}X^-$	260	312	334	380
$SeOCl_2{\cdot}X^-$	260	310	330	370

Stoicheiometry of the Complexes.—Job's[5] method was adopted. Table 2 gives data for the $SeO_2{\cdot}I^-$ species for which equimolar solutions of SeO_2 and iodide were used.

TABLE 2

Stoicheiometry of $SeO_2{\cdot}I^-$ species in dmso by Job's method. $[SeO_2] = 4 \times 10^{-2}$M and $[I^-] = 4 \times 10^{-2}$M

Solution	(1)	(2)	(3)	(4)	(5)
Volume of SeO_2 (cm^3)	2.0	1.5	1.25	1.0	0.5
Volume of I^- (cm^3)	0.5	1.0	1.25	1.5	2.0
Volume of dmso (cm^3)	2.5	2.5	2.5	2.5	2.5
Mol fraction of I^-, x_I	0.2	0.4	0.5	0.6	0.8
$D_{obs.}$	0.080	0.125	0.133	0.125	0.080

A maximum absorbance at $x_I = 0.5$ suggests that the species is a 1 : 1 complex. Similar results were obtained for all the other species. For $SeOCl_2{\cdot}I^-$ the observed peak changed with time and was unusually high, indicating a reaction (possibly oxidation of I^- by $SeOCl_2$), and the data for $SeOCl_2{\cdot}I^-$ were thus abandoned.

RESULTS AND DISCUSSION

(a) *Evaluation of Stability Constants.*—The selenium species are formed between a polar compound and a halide ion which permits only the use of polar solvents such as dmso. In all spectroscopic runs the halide ion (*i.e.* the donor ligand) was in excess of the selenium compound (*i.e.* the acceptor) and in the ratio $[X^-] : [Se] = 1.3 : 16$. This ensured the formation of one

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[1] Part III, S. B. Salama and S. Wasif, *J.C.S. Dalton*, 1975, 151.

[2] F. Carnevali, *Atti. Acad. naz. Lincei*, 1908, **5**, 11, 17, 385.

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

[4] S. B. Salama and Saad Wasif, *J.C.S. Dalton*, 1973, 2148.

[5] P. Job, *Ann. Chim.*, 1928, **10**, 113.

species only which was a 1 : 1 complex and it makes the correlation of stability constants significant.

The evaluation of the stability constants of the species from spectral data was as outlined before [1,3,6,7] and in nearly all cases a graphical K value was supplemented by one calculated from an equation such as that in Table 3. Table 3 gives a typical example of the calculation of K for $SeO_2{\cdot}Br^-$, Table 4 detailed data for the other species studied, Table 5 a summary of K data at 25 °C together with those for $SO_2{\cdot}X^-$ and $SOCl_2{\cdot}X^-$, and Table 6 the thermodynamic constants for formation of $SeO_2{\cdot}X^-$ and $SeOCl_2{\cdot}X^-$. All chemicals used were of AnalaR quality except dmso which was twice distilled. Mixtures were prepared immediately before the spectra were recorded on a Unicam SP 700 machine. The cell compartment was thermostatted to ±0.01 °C and matched silica cells were used. Data processing was as outlined before.[6,7]

TABLE 3

Stability constants of $SeO_2{\cdot}Br^-$ in dmso at 25, 35, and 45 °C [a]

Solution	(1)	(2)	(3)	(4)
$10^3[Br^-]/mol\ l^{-1}$	4.27	8.53	12.8	14.9
$10^3[SeO_2]/mol\ l^{-1}$	3.08	3.08	3.08	3.08
$D_{obs.}$ at 25 °C	0.26	0.48	0.68	0.76
35 °C	0.29	0.51	0.71	0.83
45 °C	0.34	0.615	0.84	0.96
$10^3/(\varepsilon_a - \varepsilon_A)$ at 25 °C [b]	13.38	6.83	4.73	4.23
35 °C [b]	11.84	6.41	4.52	3.86
45 °C [b]	9.88	5.24	3.80	3.31
$10^4[DA]/mol\ l^{-1}$ at 25 °C	1.49	2.92	4.23	4.73
$K/l\ mol^{-1}$	12.4	12.7	12.9	12.6
$10^4[DA]/mol\ l^{-1}$ at 35 °C	1.69	3.12	4.42	5.20
$K/l\ mol^{-1}$	14.2	13.7	13.6	14.1
$10^4[DA]/mol\ l^{-1}$ at 45 °C	2.025	3.81	5.27	6.04
$K/l\ mol^{-1}$	17.3	17.3	16.8	17.1

$\varepsilon_{DA} = 1\,548$, $\varepsilon_A = 9.75\ l\ mol^{-1}\ cm^{-1}$ at 334 nm

[a] Calculated from the equations $1(\varepsilon_a - \varepsilon_A) = \{K[Br^-](\varepsilon_{DA} - \varepsilon_A)\}^{-1} + (\varepsilon_{DA} - \varepsilon_A)^{-1}$ and $K = [DA]/[D][A]$, where [A], [D], and [DA] are the concentration of the acceptor, donor, and complex at equilibrium. [b] Values of K from the graphical method [3,4,6,7] are 12.3, 13.4, and 16.3 l mol⁻¹ at 25, 35, and 45 °C respectively.

(b) *Correlations between the Stability Constants of the Complexes.*—The data in Table 5 show that the order of stability constants for $SeO_2{\cdot}X^-$ is $Cl^- > Br^- > I^-$ and for $SeOCl_2{\cdot}X^-$ it is $Cl^- < Br^-$ (the stability constant for $SeOCl_2{\cdot}I^-$ was not obtainable due to possible reaction.) The same order was also noted for $SO_2{\cdot}X^-$ and $SOCl_2{\cdot}X^-$ in dmso.[1] In order to explain this order we should remember that both sulphur and selenium have *d* orbitals that act as acceptors for the halide ligands, resulting in formation of the complex species. The difference in the order of stability constants suggests that the factors responsible for the observed behaviour are related to differences in the bonding properties of the acceptors, the nature of the donors, and the role of dmso as a solvent.

TABLE 4

Stability constants in dmso at different temperatures *

Solution	(1)	(2)	(3)	(4)
(a) $SeO_2{\cdot}Cl^-$				
$10^3[Cl^-]/mol\ l^{-1}$	1.22	2.45	3.67	4.28
$10^4[SeO_2]/mol\ l^{-1}$	9.37	9.37	9.37	9.37
$D_{obs.}$ (25 °C)	0.135	0.24	0.335	0.375
(45 °C)	0.155	0.26	0.36	0.41
$K/l\ mol^{-1}$ at 25 °C	31.3	32.8	32.8	32.5 (31.5)
45 °C	37.6	36.0	35.8	35.8 (35.0)
$\varepsilon_{DA} = 3\,157$, $\varepsilon_A = 32.0\ l\ mol^{-1}\ cm^{-1}$ at 312 nm				
(b) $SeO_2{\cdot}I^-$				
$10^2[I^-]/mol\ l^{-1}$	1.307	2.614	3.921	4.575
$10^3[SeO_2]/mol\ l^{-1}$	7.532	7.532	7.532	7.532
$D_{obs.}$ (25 °C)	0.28	0.55	0.75	0.835
(35 °C)	0.335	0.63	0.845	0.92
(45 °C)	0.405	0.70	0.905	1.025
$K/l\ mol^{-1}$ at 25 °C	8.3	9.0	8.9	8.8 (8.5)
35 °C	10.2	10.8	10.5	10.1 (10.0)
45 °C	12.9	12.4	12.5	11.9 (11.6)
$\varepsilon_{DA} = 400\ l\ mol^{-1}\ cm^{-1}$ at 312 nm				
(c) $SeOCl_2{\cdot}Cl^-$				
$10^3[Cl^-]/mol\ l^{-1}$	8.1	16.2	24.3	32.4
$10^3[SeOCl_2]/mol\ l^{-1}$	5.1	5.1	5.1	5.1
$D_{obs.}$ (15 °C)	0.32	0.46	0.58	0.73
(25 °C)	0.41	0.58	0.73	0.88
(35 °C)	0.48	0.72	0.82	1.02
$K/l\ mol^{-1}$ at 15 °C	7.42	7.91	7.88	8.73 (6.6)
25 °C	13.2	12.0	11.8	12.1 (10.2)
35 °C	17.6	17.5	14.4	16.0 (14.0)
$\varepsilon_{DA} = 540$, $\varepsilon_A = 40\ l\ mol^{-1}\ cm^{-1}$ at 310 nm				
(d) $SeOCl_2{\cdot}Br$				
$10^3[Br^-]/mol\ l^{-1}$	5.92	11.84	17.76	23.68
$10^3[SeOCl_2]/mol\ l^{-1}$	1.31	1.31	1.31	1.31
$D_{obs.}$ (15 °C)		0.27	0.30	0.36
(25 °C)		0.30	0.36	0.41
(35 °C)		0.34	0.40	0.47
$K/l\ mol^{-1}$ at 15 °C		25.5	22.1	24.8 (17.5)
25 °C		33.4	33.4	34.2 (24.1)
35 °C		42.7	46.0	46.5 (31.1)
$\varepsilon_{DA} = 607$, $\varepsilon_A = 107.2\ l\ mol^{-1}\ cm^{-1}$ at 330 nm				

TABLE 5

Summary of stability constant data (l mol⁻¹) in dmso at 25 °C

Complex \ X	Cl^-	Br^-	I^-
$SeO_2{\cdot}X^-$	32 ± 0.4	13 ± 0.2	9 ± 0.2
$SO_2{\cdot}X^-$	26 ± 0.5	21 ± 0.4	12 ± 0.1
$SeOCl_2{\cdot}X^-$	12 ± 0.4	31 ± 4	
$SOCl_2{\cdot}X^-$	18 ± 0.5	21 ± 0.4	35 ± 0.7

TABLE 6

Thermodynamic constants of $SeO_2{\cdot}X^-$ and $SeOCl_2{\cdot}X^-$ *

Complex	$\frac{-\Delta G^\ominus}{kcal\ mol^{-1}}$	$\frac{-\Delta H^\ominus}{kcal\ mol^{-1}}$	$\frac{-\Delta S^\ominus}{cal\ K^{-1}\ mol^{-1}}$
$SeO_2{\cdot}I^-$	1.27	−2.92	14
$SeO_2{\cdot}Br^-$	1.49	2.67	14
$SeO_2{\cdot}Cl^-$	2.05	0.99	10
$SeOCl_2{\cdot}Br^-$	1.87	−5.10	−23
$SeOCl_2{\cdot}Cl^-$	1.38	−5.80	−24

* 1 cal = 4.184 J.

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The reversed order of stabilities for SeO_2X^- and $SO_2{\cdot}X^-$ from that for $SeOCl_2{\cdot}X^-$ and $SOCl_2{\cdot}X^-$ leads one to assume that the *d* orbitals of sulphur and selenium must be involved to different extents in the bonding of SeO_2 and SO_2 molecules than they are in $SOCl_2$ and $SeOCl_2$. In SO_2 and $SOCl_2$, *d*-orbital participation is different because in the former the orbital used is $(2p{-}3d)_\pi$ while in $SOCl_2$ the orbitals used are $(3p{-}3d)_\pi$ or σ with greater overlap. Estimates of *d*-orbital participation in SO_2 have been made by Guest *et al.*[8] from quantum-mechanical calculations and by Urch [9] from *X*-ray fluorescence spectroscopy. Chadwick and other workers [10–16] studied a number of sulphur–oxygen molecules by photoelectron spectroscopy and found that the S–O bond order is different in SO_2 and $SOCl_2$. It is thus possible that *d*-orbital overlap is different in SO_2 and $SOCl_2$.

No similar studies have been made for SeO_2 and $SeOCl_2$, but by comparison of the stability-constant data for $SeO_2{\cdot}X^-$ and $SeOCl_2{\cdot}X^-$ with those of $SO_2{\cdot}X^-$ and $SOCl_2{\cdot}X^-$ it is not unreasonable to assume that the *d* orbitals have a different degree of overlap in SeO_2 from that of $SeOCl_2$. For $SeO_2{\cdot}X^-$, the chloride species is the most stable and the iodide is the least. Here, like $SO_2{\cdot}X^-$,[6] back bonding is expected to be the principal stabilising factor. The Cl^- ion, being a hard base, whereas I^- is a soft polarisable base, favours this situation resulting in $SO_2{\cdot}Cl^-$ and $SeO_2{\cdot}Cl^-$ being the most stable species despite the strong solvating property of dmso towards Cl^- ligands.

The reversed order for $SeOCl_2{\cdot}X^-$ and $SOCl_2{\cdot}X^-$ where the chloride species is the least stable suggests that the *d* orbitals in $SOCl_2$ and $SeOCl_2$ are more involved in the bonding than they are in SeO_2 or SO_2. This makes the *d* orbitals of $SOCl_2$ and $SeOCl_2$ less available for back bonding (which stabilises the halide complex species) and thus results in lower stability constants for $SeOCl_2{\cdot}Cl^-$ or $SOCl_2{\cdot}Cl^-$. In this situation dmso becomes more effective in lowering the stability constants of the $SeOCl_2{\cdot}Cl^-$ or $SOCl_2{\cdot}Cl^-$ species due to its greater solvating power towards Cl^- than Br^- or I^-, *d* orbitals being more readily available than those of the acceptors used.

This shows that although dmso is the principal environment for the complex species $SeO_2{\cdot}X^-$, $SO_2{\cdot}X^-$, $SeOCl_2{\cdot}X^-$, and $SOCl_2{\cdot}X^-$ its effect on their stability is selective. Its effect as solvating agent (or alternatively as a competing acceptor) varied according to the degree of *d*-orbital involvement in each acceptor molecule in internal bonding and their availability to external association with halide ligands which are themselves differently affected by dmso.[1]

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

[4/2226 *Received*, 28*th October*, 1974]

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