SELENIUM CHLORIDE AND BROMIDE EQUILIBRIA IN APROTIC SOLVENTS; A ⁷⁷Se NMR STUDY

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Abstract—The ⁷⁷Se NMR spectra of solutions with stoichiometries near those for SeX₂ and Se₂X₂ (X = Br, Cl) formation in aprotic solvents of varying basicity have been recorded. Chemical shifts for SeCl₄, SeX₂, Se₂X₂, Se₃X₂ and Se₄X₂ are reported. The constants for the equilibria,

 $2SeBr_{2} \Longrightarrow Se_{2}Br_{2} + Br_{2}$ $3SeCl_{2} \Longrightarrow SeCl_{4} + Se_{2}Cl_{2}$ $2Se_{2}X_{2} \Longrightarrow SeX_{2} + Se_{3}X_{2}$ $3Se_{2}X_{2} \Longrightarrow 2SeX_{2} + Se_{4}X_{2}$

have been determined in various solvents from NMR spectra and chemical analysis. The position of the equilibria is very sensitive to solvent donor strength, with the selenium halide of stronger Lewis acidity favoured in the more basic solvent. Selenium bromide chloride, Se_2BrCl , has been shown to exist in equilibrium with Se_2Br_2 and Se_2Cl_2 in dichloromethane.

The oxidation state +2 is uncommon for selenium and none of the dihalides are known as pure compounds. The presence of selenium dichloride and dibromide in solution in non-aqueous solvents^{1,2} and in the gas phase^{3,4} has been demonstrated. It has recently been shown that pure liquid diselenium dichloride and dibromide disproportionate to a small extent and contain equilibrium concentrations of the selenium dihalide and polyselenium dihalides.⁵ Selenium(II) is known in chloroand bromoselenate(II) compounds⁶ where it is apparently stabilized by halo coordination. Selenium(II) has been shown to be in equilibrium with selenium(IV) and Se_2X_2 in aqueous HCl and HBr also.^{7,8} Stabilization by solvent coordination may also occur and have an important influence on the selenium dihalide concentration in solution. This present study was carried out, to determine the influence of solvent on the equilibrium distribution of selenium, diselenium and polyselenium dichlorides and dibromides in solution.

Few ⁷⁷Se NMR studies of inorganic selenium

compounds have been made⁹ and this study relies principally on this technique.

EXPERIMENTAL

Elemental selenium (99.999, Aldrich) was used directly. Selenium tetrachloride was prepared from chlorine and selenium.¹⁰ Bromine (Fisher reagent) was distilled from phosphorus pentoxide before use. Dimethylformamide (DMF) (Fisher certified) and pyridine (py) (BDH assured) were dried over, and distilled from Dreirite. Carbon tetrachloride (Fisher certified), dichloromethane (Fisher certified) and acetonitrile (BDH assured) were dried over and distilled from phosphorus pentoxide. Solutions of the desired stoichiometry were made up by weight from selenium and SeCl₄ or selenium and Br₂ and the solvent, using a balance accurate to ± 2 mg. In a typical experiment 82 mg of selenium were combined with 228 mg of SeCl₄ in 3.993 g of acetonitrile to yield a solution of SeCl_x composition with x = 2.00 + 0.003, where $c(\text{SeCl}_2) = 0.41 \pm 0.01 \text{ M}$. The solution volume was considered to be that of the solvent alone. All solutions were made up in a dry box. In several cases

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an initial precipitate of red selenium was produced, which dissolved to yield clear yellow-brown coloured solutions.

Analyses for chloride and selenium were carried out, respectively, by Volhard and gravimetric methods.¹¹ For the pyridine mixture of 2:1 Cl/Se mole ratio, containing the insoluble SeCl₄ adduct (see below), dilution in aqueous acid (1 in 10) resulted in disproportionation to elemental selenium and selenate(IV). After gravimetric analysis for the precipitated selenium, the supernatant was analysed for chloride.

The bis(pyridine) adduct of $SeCl_4$, $SeCl_4 \cdot 2py$, was prepared by shaking $SeCl_4$ and dry pyridine (1:50 mol ratio) together for 12 h and filtering out the yellow product in a dry atmosphere. The product was very difficult to filter and free of solvent. Found: Se, 36.3; Cl, 20.0. Calc.: Se, 37.4; Cl, 20.8%.

Raman spectra were recorded using equipment described earlier.² ⁷⁷Se NMR spectra were recorded in 10 mm tubes, using a Varian FT300 spectrometer operating at 57.28 MHz. All shifts are reported with respect to the reference shift of saturated aqueous selenous acid solution at 20°C. The chemical shifts were determined by sample replacement and are accurate to ± 0.7 ppm. The shift of saturated selenous acid is at 1282 ppm with respect to dimethyl selenium.¹²

RESULTS AND DISCUSSION

Selenium chlorides

Selenium tetrachloride exhibits a broad range of solubility in aprotic solvents. Saturation molarities at $20(\pm 1)^{\circ}$ C have been determined for several solvents and these are CCl_4 : insoluble; CH_2Cl_2 : 1.36×10⁻³; CH_3CN : 2.05×10⁻²; py: 5.82×10^{-2} ; DMF : >1.15. The solubility increases with the donor strength of the solvent, reflecting the Lewis acidic nature of $SeCl_4$. In the case of CCl_4 , CH₂Cl₂ and CH₃CN, the insoluble phase is pure SeCl₄ as shown by the Raman spectrum, which has characteristic strong bands at 387, 340 and 97 cm⁻¹.¹³ However, in the case of pyridine the insoluble phase is a yellow adduct, $SeCl_4 \cdot 2py$, with Raman bands at 119 (6), 149 (7), 247 (9) and 279 (10) cm⁻¹ (intensities in parentheses). In CH₂Cl₂ and CH₃CN solutions, even at such low concentrations, Raman bands corresponding to SeCl₄ species are observed,^{2,14} but the ⁷⁷Se NMR signal could only be observed for the DMF solution, as given in Table 1 (solution No. 1). The signal observed at 153.7 ppm, which is 25 ppm to low field of that reported by Birchall et al.9 for SeCl₄ in DMF, is broad (width at half-height = 3.4 ppm). The earlier measurement was carried out with a saturated solution, using broad-line techniques, which may account for the difference between the two results. Because of low solubility and signal breadth, the SeCl₄ shift could not be detected in CH₂Cl₂, CH₃CN and py. SeCl₄, which is known to be monomeric in CH₃CN,¹⁵ is expected to give a broad NMR signal due to coupling to the 4 Cl's (I = 3/2 for both ³⁵Cl and ³⁷Cl), which will be quadrupole relaxed, and due to intramolecular chlorine exchange via a Berry mechanism. Intermolecular exchange may also occur. Similar processes causing broadening will occur with SeCl₄ in other solvents.

When elemental selenium is added to a saturated solution of $SeCl_4$ in CH_3CN , CH_2Cl_2 or CCl_4 , there is reaction to give lower selenium chlorides :

$$\operatorname{SeCl}_4 + \operatorname{Se} \Longrightarrow 2\operatorname{SeCl}_2$$
 (1)

$$\operatorname{SeCl}_4 + \operatorname{3Se} \Longrightarrow \operatorname{2Se}_2\operatorname{Cl}_2.$$
 (2)

After sufficient selenium has been added all of the SeCl₄ reacts and the solution becomes saturated with respect to elemental selenium. The Raman spectra¹⁴ of the Se/SeCl₄ solutions saturated with SeCl₄ exhibit peaks characteristic of SeCl₂ (417, 397 and 164 cm^{-1} ² and those, saturated with selenium, peaks characteristic of Se_2Cl_2 (373 and 131 cm⁻¹).² The ⁷⁷Se NMR spectra of Se/SeCl₄ solutions saturated with SeCl₄, consist of two signals as given in Table 2 (solutions Nos 2, 4, 6). The weaker signal to highest field has a chemical shift corresponding to that of $Se_2Cl_2^{5,9}$ and that at lowest field arises from SeCl₂.⁵ The chemical shifts of these two compounds in Se₂Cl₂ as solvent⁵ are given for comparison (No. 9). The UV-vis spectra of CH₃CN solutions of 2:1 Cl/Se stoichiometry have been interpreted in terms of the equilibrium,

$$3\text{SeCl}_2 \xrightarrow{K(\text{SeCl}_2)} \text{Se}_2\text{Cl}_2 + \text{SeCl}_4.$$
(3)

The ⁷⁷Se NMR spectra of the solutions in CH₃CN and CH₂Cl₂ may be interpreted similarly. The equilibrium constant at $20(\pm 1)^{\circ}$ C may be calculated from the saturation concentration for SeCl₄ in each solvent, the ratio of the concentrations of Se₂Cl₂ and SeCl₂ calculated from NMR signal intensities and from the stoichiometric concentration of elemental selenium dissolved, c_{Se} (Table 1), which is related to the Se₂Cl₂ and SeCl₂ concentrations by,

$$c_{\rm Se} = \frac{[{\rm SeCl}_2]}{2} + \frac{3[{\rm Se}_2{\rm Cl}_2]}{2}.$$
 (4)

The calculated values of $K(SeCl_2)$ are given in Table 2. The ⁷⁷Se NMR signals for pyridine were too weak for observation but chemical analysis for

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		Storemonieuy	SeC14	SeCl ₂	Se ₂ Cl ₂	Selemum chlorides Se ₃ Cl ₂ β α	$c_{\rm s} = c_{\rm s} C C C_{\rm s} C C C C C C C C C C C C C C C C C C $
DMF	1	1.15 M SeCl4	153.7				
CH ³ CN	0 N	$c_{se} = 0.20 \text{ M}$; SeCl ₄ saturated $c_{seCl_4} = 0.97 \text{ M}$; Se saturated		470.5 (117) 464.2 (32)	8.3 (14) 5.1 (1520)	— 11.0 (7), —3.3 (12)	11
CH ₂ Cl ₂	4 s	$c_{se} = 0.25 \text{ M}$; SeCl ₄ saturated $c_{seCl} = 0.14 \text{ M}$; Se saturated		459.7 (103.4) 458.1 (16.5)	-23.1 (47.1) -23.8 (1170)	-10.3 (3.9), -30.6 (4.4)	— — 356.5 (1.5). — 374.9 (2.1)
cCl4	8 7 9	$c_{sec1} = 0.10 \text{ M}$; SeCl ₄ saturated $c_{sec1} = 0.20 \text{ M}$; Se saturated $c_{sec1} = 2.2 \text{ M}$; Se saturated		445.5 (63.5) 444.4 438.2 (11.4)	-47.1 (37.5) -47.5 -30.4 (3114)	-23.2 (7.6)39.2 (11.0)	- 353 (2.4) 373 (7.1) 391 (2.7)
Se ₂ Cl ₂ ^b	6	Liquid Se ₂ Cl ₂ containing 3.34 weight % Se	I	425.4 (6.6)	-9.74 (736)	- 10.3 (12)	-365.5 (14)
				SeBr ₂	Se ₂ Br ₂	Selenium bromides Se ₃ Br ₂ α β	α Se ₄ Br ₂ β
CH ₃ CN	10 11 12	$c_{s_{2}Br_{2}} = 1.23 M$ $c_{s_{6}Br_{2}} = 2.34 M$ $c_{s_{6}Br_{4}} = 1.11 M$			- 110.3 - 108.0 (40.2) - 110.5 (trace, broad)		
CH ₂ Cl ₂ ^e	13	$c_{s_{s_2}s_{r_2}} = 1.02 M$ $c_{s_{s_c}} = 0.34 M$		173.9 (15.6)	- 132.5 (2020)	-150.4 (28), -168.2(14)	- 372.0 (10), - 381.8 (10)
${\rm Se}_2{\rm Br}_2^b$	14	Liquid Se ₂ Br ₂		164.4 (4)	-110.9 (163)	-132.2 (5), -143.9(2)	- 360.7 (1), - 372.7 (2)
				Se ₂ Cl ₂	Diselenium bron Se ₂ Br ₂	nide chloride Se ₂ BrCl	
CH ₂ Cl ₂	15	$c_{\rm Se_2Cl_2} = 1.6 M$ $c_{\rm Se_3Br_3} = 1.5 M$		-22.1 (64)	-128.5 (50.5)	-13.6 (50.5)	-137.5 (48)
Se ₂ Cl ₂ /Se ₂ Br ₂	16	0.92: 1.00 : 0.21 mol ratio Se ₂ Br ₂ /Se ₂ Cl ₂ /Se		-9.11 (152)	-110.9 (164)	- 12.7 (166)	- 115.1 (140)

Selenium chloride and bromide equilibria

Table 1. ⁷⁷Se NMR chemical shifts (ppm)^a of selenium chlorides, bromides and bromide chloride

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^b From Ref. 5. ^c An additional signal was observed at -133.2(24).

Solvent	Donor number	Dielectric constant (25°C)	$\frac{K(\text{SeCl}_2)^a}{(\text{dm}^3 \text{ mol}^{-1})}$	$K(\text{Se}_2\text{Cl}_2)^h$	$K'(\operatorname{Se}_2\operatorname{Cl}_2)^c$
CCl ₄	0	2.24	0	2.9×10^{-5}	8.4 × 10 ⁻⁸
CH ₂ Cl ₂	0	9.08	3.7×10^{-3}	1.3×10^{-4}	1.2×10^{-6}
$Se_{2}Cl_{2}^{d}$				4×10^{-4}	3×10^{-6}
CH ₃ CN	14.3	36.7	0.024	5.4×10^{-4}	
ру	33.1	12.3	663		

Table 2. Disproportionation equilibria for SeCl₂ and Se₂Cl₂ at $20(\pm 1)^{\circ}$ C in aprotic solvents

^a Equilibrium (3).

^b Equilibrium (5).

^c Equilibrium (6).

^d Reference 5.

selenium and chlorine in the supernatant over $SeCl_4 \cdot 2py$ to which elemental selenium had been added ($c_{Se} = 0.204$ M) gave [SeCl_2] = 0.0090 M and [Se_2Cl_2] = 0.0083 M. The equilibrium constant, $K(SeCl_2)$, in pyridine, is given in Table 2. The value of $K(SeCl_2)$ for the CCl₄ solution is also given in Table 2 for comparison.

Solutions of SeCl₄ saturated with Se give the ⁷⁷Se NMR spectra shown in Fig. 1 and listed in Table 1 (Nos 3, 5, 7 and 8). In these solutions the low field shift due to SeCl₂ is now much weaker in intensity than that due to Se_2Cl_2 . However, in addition to these peaks, there are several peaks to higher field, which may be assigned to Se_nCl_2 species (n = 3, 4). These signals have also been observed in solutions of selenium in Se₂Cl₂⁵ and there is Raman spectroscopic evidence for Se_nCl₂ species in Se/Se₂Cl₂ mixtures.^{5,17} The strongest ⁷⁷Se signals, and the only ones observed in this work, will arise from Se_nCl_2 species with one ⁷⁷Se in the chain. For Se_3Cl_2 (ClSe^{α}Se^{β}Se^{α}Cl), two chemical shifts, from α - and β selenium atoms, of relative intensity 2:1, respectively, are expected. For Se_4Cl_2 (ClSe^{α}Se^{β}Se^{β}Se^{α}Cl), two chemical shifts of equal intensity are expected. The two weak chemical shifts which bracket the Se_2Cl_2 shift may be assigned to Se_3Cl_2 on the basis of their 2:1 intensity ratio with the α -selenium shift lying to high field of the Se₂Cl₂ shift in all cases. The chemical shifts of Se₃Cl₂ lie close to that of Se_2Cl_2 in pure Se_2Cl_2 also⁵ and these shifts have been listed in Table 1 for comparison. The chemical shifts for Se₄Cl₂ lie to high field of those of Se₃Cl₂.⁵ These are not observed for CH₃CN solutions but for CH₂Cl₂, a pair of weak signals of equal intensity at -356.5 and -374.9 ppm are observed. The lowest field signal of these two, while of the same intensity as that at -374.9 ppm, is the broader of the two and is therefore assigned to the α -selenium, which is expected to be broader due to greater coupling to the spin 3/2 chlorine nuclei, which undergo quadrupole relaxation.

In CCl₄, three signals, -353.0, -372.7 and -391.0 ppm are observed in the Se₄Cl₂ region of the spectrum. The low intensity of these signals precludes a definite interpretation, but it is not possible to assign the peaks in terms of the overlapping spectra of Se₄Cl₂ and Se₅Cl₂ (three signals of 2:2:1 relative intensity). The spectra of Se₄Br₂ in liquid Se₂Br₂, containing dissolved selenium, has a similar appearance and that of Se₄Cl₂ in liquid Se₂Cl₂ consists of a single broad peak.⁵ The spectrum in CCl₄ may be accounted for by the presence of the chain form of Se₄Cl₂ and some other isomer, or higher homologue, undergoing rapid intramolecular exchange.

As in the case of pure Se_2Cl_2 ,⁵ disproportionation equilibria of the type,

$$2\operatorname{Se}_{2}\operatorname{Cl}_{2} \xrightarrow{K(\operatorname{Se}_{2}\operatorname{Cl}_{2})} \operatorname{SeCl}_{2} + \operatorname{Se}_{3}\operatorname{Cl}_{2}$$
(5)

$$3Se_2Cl_2 \xrightarrow{K'(Se_2Cl_2)} 2SeCl_2 + Se_4Cl_2$$
(6)

take place in these solutions. From the relative intensities of the signals, $K(\text{Se}_2\text{Cl}_2)$ and $K'(\text{Se}_2\text{Cl}_2)$ may be determined and these are given in Table 2 along with the equilibrium constants determined for liquid Se_2Cl_2 .⁵

Selenium bromides

Selenium tetrabromide is known as a crystalline solid but in the gas phase or when dissolved in



Fig. 1. ⁷⁷Se NMR spectra of solutions of selenium chlorides, bromides and bromide chlorides in aprotic solvents.

aprotic solvents at 25°C, it dissociates according to,

$$\operatorname{SeBr}_{4} \Longrightarrow \operatorname{SeBr}_{2} + \operatorname{Br}_{2}. \tag{7}$$

The SeBr₂ dissociates further to Se_2Br_2 :^{1,2,18}

$$2\operatorname{SeBr}_{2} \xrightarrow{K(\operatorname{SeBr}_{2})} \operatorname{Se}_{2}\operatorname{Br}_{2} + \operatorname{Br}_{2}.$$
(8)

The chemical shifts for selenium bromide solutions are given in Table 1. The spectrum of a solution with a 1:4 atomic ratio of Se/Br (No. 12) in CH₃CN consists of a strong signal at 194.7 ppm and a very weak signal at -110.5 ppm, which is near to the reported shift for pure Se₂Br₂^{5.9} and Se₂Br₂ in CH₃CN. The strong, low field signal is assigned to SeBr₂. For a solution in acetonitrile of 1:2 Se/Br atomic ratio (No. 11), the same two chemical shifts are observed but the Se₂Br₂ signal has become stronger, compared to that of SeBr₂, reflecting a shift of equilibrium (8) to the right due to a decrease in Br_2 concentration. The equilibrium constant, $K(SeBr_2)$, for equilibrium (8) was determined from the signal intensities of solution No. 11 and this is given in Table 3. There is excellent agreement between the value calculated here and that for the CH_3CN solution determined from UV-vis spectrophotometry.² The spectrum of a solution of Se_2Br_2 in acetonitrile (No. 10) had only one signal. No signals for Se_3Br_2 of Se_4Br_2 were observed due to the small number of transients collected.

The ⁷⁷Se NMR spectrum of a solution of a 1.17:1.00 Se/Br atomic ratio in CH₂Cl₂ is shown in Fig. 1 and the chemical shifts and intensities are given in Table 1 (No. 13). In addition to signals for SeBr₂ and Se₂Br₂, at 173.9 and -132.5 ppm, respectively, there are two sets of two signals each to high field of the Se₂Br₂ signal, which may be

Solvent	Donor number	Dielectric constant (25°C)	$K(SeBr_2)^a$	$K(\mathrm{Se}_{2}\mathrm{Br}_{2})^{b}$	$K'(\operatorname{Se}_2\operatorname{Br}_2)^c$
CCl ₄	0	2.24	0.0252 ^d		
CH_2CL_2	0	9.08		2.2×10^{-4}	1.2×10^{-6}
CH ₃ CN	14.3	36.7	0.14 0.014 ^e	—	
Se_2Br_2				1.1×10^{-3}	1.7×10^{-6}

Table 3. Disproportionation equilibria for $SeBr_2$ and Se_2Br_2 at $20(\pm 1)^{\circ}C$ in aprotic solvents

^a Equilibrium (8).

^b Equilibrium (9).

^c Equilibrium (10).

^d Reference 1.

^e Spectrophotometric determination.²

clearly assigned to Se_3Br_2 and Se_4Br_2 on the basis of their relative intensities. The assignment of the α - and β -selenium signals for Se_3Br_2 is readily made on the basis of signal intensity and width at halfheight and, for Se_4Br_2 on the basis of width at halfheight alone. There is an additional weak signal at -133.2 ppm, which may be due to an isotope shift in Se_2Br_2 , although the shift is large compared to that observed in other compounds.¹⁹ The signals are all assigned in Table 1. The spectra show that the diseleniumdibromide disproportionates in CH_2Cl_2 in an analogous manner to diselenium dichloride :

$$2\operatorname{Se}_{2}\operatorname{Br}_{2} \xrightarrow{K(\operatorname{Se}_{2}\operatorname{Br}_{2})} \operatorname{SeBr}_{2} + \operatorname{Se}_{3}\operatorname{Br}_{2}$$
(9)

$$3\operatorname{Se}_{2}\operatorname{Br}_{2} \xrightarrow{K'(\operatorname{Se}_{2}\operatorname{Br}_{2})} 2\operatorname{Se}\operatorname{Br}_{2} + \operatorname{Se}_{4}\operatorname{Br}_{2}.$$
 (10)

From the signal intensities of solution No. 13, $K(Se_2Br_2)$ and $K'(Se_2Br_2)$ have been determined and these are listed in Table 3 along with analogous constants for disproportionation in pure Se₂Br₂.⁵

Diselenium bromide chloride

The ⁷⁷Se NMR spectrum of a 0.92:1.00:0.21Se₂Br₂/Se₂Cl₂/Se mol ratio mixture dissolved in CH₂Cl₂ is shown in Fig. 1 and the chemical shifts are listed in Table 1. Four signals are observed corresponding to the chemical shifts of pure Se₂Cl₂ and Se₂Br₂ in CH₂Cl₂ at -22.1 and -128.5 ppm, respectively, and, to ⁷⁷Se α to chlorine and bromine in Se₂BrCl, respectively, at -13.6 and -137.5 ppm. No signals were observed for any triselenium compound in this routine spectrum. The spectrum shows that the following equilibrium is established,

$$\operatorname{Se}_{2}\operatorname{Br}_{2} + \operatorname{Se}_{2}\operatorname{Cl}_{2} \stackrel{K_{d}}{=} 2\operatorname{Se}_{2}\operatorname{Br}\operatorname{Cl}.$$
 (11)

This equilibrium occurs in mixtures of liquid Se_2Cl_2 and Se_2Br_2 also.⁵ The equilibrium constant, K_d , calculated from the intensities listed in Table 1, is 3.0.

CONCLUSIONS

For the selenium dihalide compounds in general, the chemical shifts for ⁷⁷Se move to higher field with increasing chain length. For the dialkyl polyselenides, the change in shift is in the opposite sense.¹⁹ Since chlorine and bromine are more electronegative than selenium while carbon is of equivalent or lower electronegativity,²⁰ it appears that these trends are due to changing shielding effects arising from greater withdrawal of electrons from the selenium by chlorine and bromine than by carbon. The chemical shift of SeCl₄ in DMF lies to high field of that of SeCl₂, which is in the opposite direction of that expected on the basis of electron shielding. Birchall et al.9 have noted that ⁷⁷Se resonance of selenium(VI) compounds lies in general to high field of those of the selenium(IV) compounds.

The change in chemical shift with changing solvent is much greater than that which can be accounted for by bulk susceptibility changes and must arise from solute-solvent interactions. For each of the $\text{Se}_n X_2$ species (n = 1, 2, 3) in aprotic solvents at comparable concentrations, the shift is to low field with increasing solvent donor strength.

Tables 2 and 3 list the values of the various disproportionation constants, $K(SeX_2)$, $K(Se_2X_2)$ and $K'(Se_2X_2)$, determined for selenium bromides and chlorides, as well as the dielectric constants and donor numbers for the different solvents.²¹ In all cases, except for $K(SeBr_2)$, the disproportionation is favoured by greater solvent donor strength. The dielectric constant appears to play a less important role as shown by a comparison of the CH_3CN and pyridine values for $K(SeCl_2)$ in Table 2. This is expected for these equilibria where no ions are involved. The Lewis acidity of the selenium halides is expected to follow the order,

$$\operatorname{SeX}_{4} > \operatorname{SeX}_{2} > \operatorname{Se}_{2} X_{2}.$$
(12)

Thus, in pyridine, the Lewis acid base adduct formation is so favourable for $SeCl_4$ that, in spite of the weak interaction of Se_2Cl_2 with pyridine, $SeCl_2$ disproportionates extensively. Similarly, the relatively strong Lewis acidities of $SeCl_2$ and $SeBr_2$ favour the disproportionation of Se_2Cl_2 and Se_2Br_2 in more strongly donating solvents. Ultimately one of the disproportionation products is elemental selenium, which is insoluble in the solvents studied. The addition of Cl^- or Br^- to their respective selenium halides will promote disproportionation of the lower halides in some cases as well:⁶

$$\operatorname{Se_2Cl_2+Cl^-}_{\operatorname{CH,CN}} \operatorname{Se^0+SeCl_3^-}_{\operatorname{CH,CN}} (13)$$

$$2\operatorname{SeCl}_{3}^{-} \xrightarrow{\operatorname{SeCl}_{3}} \operatorname{SeCl}_{6}^{2-} + \operatorname{Se}^{0}.$$
(14)

In the vapour phase where there is no Lewis acidbase stabilization, $SeCl_2$ disproportionates to a very small extent.¹⁶ No doubt in CCl_4 , $K(SeCl_2)$ has a small value also and not, as shown in Table 2, zero, which is a result of the immeasurably small solubility of $SeCl_4$ in this solvent.

Selenium dibromide dissociates to Se_2Br_2 and Br_2 , according to eq. (8). The dissociation constant in CCl_4^1 is greater than that in CH_3CN (Table 3). This may also be accounted for by the strong solvent–SeBr₂ interaction in the stronger donor solvent, CH_3CN . Apparently the Lewis acid–base interaction of the solvent with either of the two products of dissociation is weaker than that with SeBr₂. The Br⁻ ion acts to stabilize selenium(II) as well,⁶ and halo coordination even permits the stabilization of bromoselenate(IV) anions,²² while SeBr₄ is unstable.

The previous ⁷⁷Se NMR study by Birchall *et al.*⁹ concluded that no Se₂BrCl was formed in a mixture of Se₂Cl₂ and Se₂Br₂. Recently it has been shown, however, that Se₂BrCl is formed.⁵ The present

study shows that Se_2BrCl is also formed in CH_2Cl_2 . The equilibrium constants for Se_2BrCl formation, eq. (11), are both 3.0 in the two media, indicating that a small change in the polarity of the solvent has little effect on equilibrium (11).

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