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Exchange Processes in Diselenium and Selenium–Sulfur Dihalides, Se_2X_2 and $SeSX_2$ (X = Br, Cl). A ^{77}Se 2D-EXSY Study

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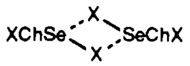
The application of two-dimensional NMR exchange spectroscopy (2D-EXSY) to the study of ^{77}Se exchange kinetics in mixtures of S_2Cl_2 and Se_2Br_2, which contain disulfur, diselenium, and selenium sulfur dihalides, shows that ^{77}Se magnetization transfer takes place predominantly by an exchange process, in which only SeX bonds are broken. Direct exchange via mechanisms, involving ChX radicals, four-chalcogen center transition states and mono- and trichalcogen dihalide species are not consistent with the cross peaks observed in the 2D spectra. Magnetization transfer by means of a bimolecular halogen-bridged intermediate



$$\mathrm{XChSe}\underset{\mathrm{X}}{\overset{\mathrm{X}}{\diamond}}\mathrm{SeChX}$$

or by an ionic process, involving Se–X bonds, are both consistent with the pattern of cross peaks observed. However, the addition of tetraethylammonium chloride to the S_2Cl_2/Se_2Br_2 mixture causes the eight-signal spectrum to collapse to three broad signals, which favors an interpretation in terms of an ionic exchange mechanism. The three broad signals are assigned to BrSSeX, ClSSeX, and SeSe dihalides each undergoing rapid ionic exchange, involving SeX bonds.

Introduction

Disulfur and diselenium dihalides, S_2X_2 and Se_2X_2 (X = F, Cl, Br) have been extensively studied.[1] Both chain and trigonal pyramidal structures are known for the fluorides,[2] and chain structures, for the chlorides and bromides.[3] The ^{77}Se NMR spectra of the Se_2X_2 (X = Cl, Br)[4] indicate that disproportionation to SeX_2 and higher homologues, Se_nX_2 (n = 3, 4), takes place in these liquids and mixtures of Se_2Cl_2 and Se_2Br_2 form mixed selenium dihalides, SeBrCl and Se_2BrCl. Recently, the first structural characterization of mixed sulfur selenium dihalides, $SeSX_2$ (X = Br, Cl), has been reported[5-7] in mixtures of S_2Cl_2 and Se_2X_2 (X = Br, Cl). The NMR spectra of these mixtures indicate, by the resonance line widths, different relaxation rates, suggesting differing relaxation mechanisms or possible differing rates of selenium exchange.

In order to gain information on halogen and chalcogen exchange in simple chalcogen chain molecules, we have studied S_2Cl_2 mixtures with Se_2X_2 (X = Br, Cl) by two-dimensional NMR methods.[8] The technique used, 2D-EXSY, is a powerful tool for studying multisite exchange processes and, to our knowledge, has never been applied to ^{77}Se systems. Selenium-77 NMR has been used extensively in recent structural studies on sulfur selenium rings[9,10] and selenium halides.[4-7,11]

Experimental Section

Selenium tetrachloride was prepared by standard methods[12] and stored in sealed ampoules before use. Bromine (J. T. Baker) was distilled from phosphorus pentoxide before use. Selenium (BDH) was used directly. Diselenium dichloride was prepared[4] by mixing stoichiometric amounts of selenium and selenium tetrachloride, according to

$$3Se + SeCl_4 = 2Se_2Cl_2 \tag{1a}$$

Diselenium dibromide was prepared similarly from elemental selenium and bromine, according to

$$2Se + Br_2 = Se_2Br_2 \tag{1b}$$

In this case, reactants were cooled in dry ice before mixing and allowed to react, holding the temperature below 0 °C in order to prevent Br_2 loss. The mixtures of S_2Cl_2 (BDH Reagent) and Se_2Cl_2 or Se_2Br_2 were made up directly in 8-mm NMR tubes, run through eight freeze–pump–thaw cycles, and then sealed. Tetraethylammonium chloride, Et_4NCl (Aldrich), was dried by heating at 100 °C under vacuum overnight. All transfers and manipulations were carried out in a drybox.

NMR spectra were run using 8-mm tubes contained in 10-mm tubes with D_2O as lock in the interannular space. All spectra were measured at a temperature of 21 °C on a Varian XL-300(7T) spectrometer operating at a selenium resonance frequency of 57.28 MHz. Typical measurement conditions were a spectral width of 150 ppm, a 40° pulse angle, an acquisition time of 1 s, and no relaxation delay between scans. An exponential line broadening of 2 Hz was applied before Fourier transformation. The quantitative spectra were obtained using a 90° pulse width and a relaxation delay of $5T_1$. Spectra were referenced to an external saturated solution of selenous acid in H_2O, by sample replacement. This reference signal is 1300.0 ppm less shielded than the signal of neat dimethyl selenium at 20 °C.[13] Spin lattice relaxation times were measured using the FIRFT method[14] and were calculated using the three parameter exponential curve-fitting routine in the Varian software (Version 6.1c).

The ^{77}Se 2D-EXSY homonuclear exchange spectra were measured at 20 °C. The standard Varian NOESY pulse sequence[15] was used to perform the experiments (software version 6.1c). A spectral window of

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Table I. Signal Designations, Chemical Shifts[a] (δ), Relative Peak Intensities[b] (I_{rel}), Spin–Lattice Relaxation Times (T_1 and Half-Height Line Widths ($W_{1/2}$) for the ^{77}Se NMR Spectra of Mixtures Se_2Cl_2/S_2Cl_2 and Se_2Br_2/S_2Cl_2

mixture	compd	peak no.	δ^a (ppm)	I_{rel}^b	T_1 (s)	$W_{1/2}$ (Hz)
Se_2Cl_2/S_2Cl_2	ClSeSCl	2	1295.0	17	2.71 ± 0.03	21
	ClSeSeCl	4	1282.0	100	2.84 ± 0.02	35
	$SeCl_2$	9	1737.6	13	2.63 ± 0.31	174
	Se_3Cl_2	10	1277.4			
Se_2Br_2/S_2Cl_2	ClSeSBr	1	1309.3	15	1.92 ± 0.09	37
	ClSeSCl	2	1294.6	21	2.02 ± 0.07	33
	ClSeSeBr	3[c]	1287.4	133	2.17 ± 0.02	140
	ClSeSeCl	4	1281.9	100	2.18 ± 0.02	134
	BrSeSBr	5	1219.3	19	2.01 ± 0.07	37
	BrSeSCl	6	1202.4	21	2.05 ± 0.06	28
	BrSeSeBr	7	1183.2	238	2.16 ± 0.01	147
	ClSeSeBr	8[c]	1176.9	124	2.19 ± 0.02	147

[a] $\delta(Me_2Se)$ = 0.0. [b] Referred to ClSeSeCl intensity as 100. [c] Peak number 3 is due to Se bound to Cl, and peak number 8, to Se bound to Br.

10 400 Hz was used, enough to enclose the signals of interest only. The acquisition time was 49 ms, and a relaxation delay of 6 s was used between transients. A total of 48 accumulations were made for each of the 64 t_1 increments in blocks of 16 scans, with two steady-state scans for each block. Mixing times, t_m, were chosen to cover the range 0.001–0.25 s. The F_1 dimension was zero-filled to 1024 points and a sine–bell weighting function was applied prior to Fourier transformation.

Attempts were made to integrate the peak volumes using the standard Varian software, but it was obvious that greater precision would be obtained by integration of the individual slices of the 2D spectrum. Overlapping peaks were deconvoluted, assuming Lorentzian line shape and using a least-squares fit to the experimental line shape. The longitudinal relaxation times are long relative to the residence times for exchange, and their effect on the spectral intensities in the 2D-EXSY experiments were ignored for the range of mixing times studied in this work. While the 2D-EXSY spectra of the S_2Cl_2/Se_2Br_2 mixtures produced well-defined cross peaks, the spectra of the S_2Cl_2/Se_2Cl_2 mixture gave strong dispersive wings on the auto peaks, which obscured the cross peaks.

The deconvolution of the three broad signals in the spectrum of the 0.12:11.7:11.5 molar ratio mixture of Et_4NCl, S_2Cl_2, and Se_2Br_2 was accomplished using Gaussian–Lorentzian curves (80% Gaussian: 20% Lorentzian) with the chemical shifts of the signal maxima fixed. The least-mean-square deviation from the experimental curve was used as the criterion for the best fit.

Results and Discussion

The 1D spectrum of a 1:1 molar ratio mixture of Se_2Br_2 and S_2Cl_2 consists of eight strong signals, due to all seven of the possible selenium-containing dichalcogen dihalides which can be formed,[5] and some weak signals, due to monochalcogen and trichalcogen dihalides,[6] which make up less than 1.5% of the total spectral intensity. The spectrum of a 1:1 molar ratio mixture of Se_2Cl_2 and S_2Cl_2 consists of three strong signals due to Se_2Cl_2, $SeCl_2$, and $SeSCl_2$ and some weak signals due to Se_3Cl_2 and the other three chalcogen selenium sulfur dichlorides.[5,6] The chemical shifts of the major species, their numerical designation, peak intensities, spin–lattice relaxation times, and half-height line widths are listed in Table I. The dichalcogen dihalides are liquids of low viscosity and at room temperature, the NMR spectra are expected to lie in the region of extreme narrowing, where $T_1 = T_2$. Judging from the relaxation times listed in Table I, half-height line widths of less than 1 Hz would be expected. In both mixtures the line widths, $w_{1/2}$, range from 21 to 174 Hz with those of the diselenium dihalides 2–5 times greater than those of the selenium sulfur dihalides. In the tri- and tetraselenium dihalides, the greater line width of the α-Se signal, relative to the β-Se signal, has been attributed to scalar coupling to the quadrupole relaxed near-neighbor Cl or Br ($I = {}^3/_2$ for ^{35}Cl, ^{37}Cl, ^{79}Br, and ^{81}Br).[11] If this were correct, then the ^{77}Se signal line width for Se_2X_2 and XSeSX would be expected to be comparable. Alternatively, the difference in resonance line widths might also be accounted for by chemical exchange processes, involving SeX bond breaking, which would affect the α-Se signal more than that of the β-Se. Such a chemical exchange process would also be consistent with the increased signal breadth observed when the spectra are measured at temperatures above the ambient. Such exchange processes are readily studied by 2D-EXSY NMR.[8]

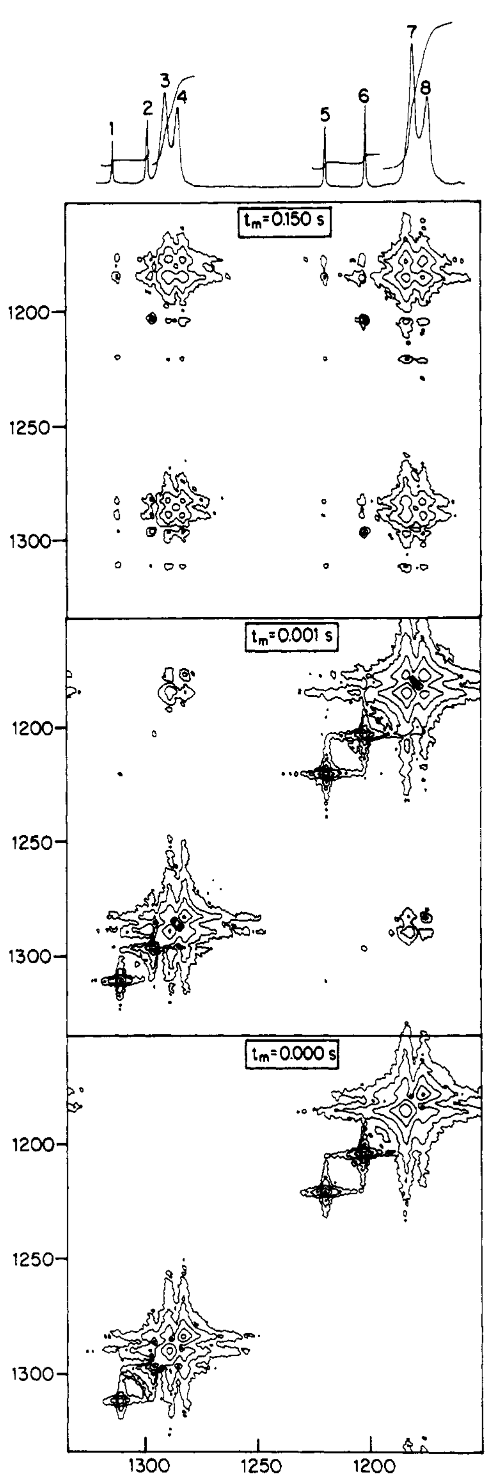

Figure 1. 2D-EXSY ^{77}Se NMR spectra at different mixing times (t_m = 0.000, 0.001, and 0.150 s) and the 1D NMR spectrum of a 1:1 molar ratio mixture of S_2Cl_2/Se_2Br_2.

The 2D-EXSY spectra of a 1:1 molar ratio mixture of S_2Cl_2 and Se_2Br_2 at 0.00, 0.001, and 0.150 s mixing times, t_m, are shown in Figure 1. The trace of the normal 1D spectrum is represented by the diagonal running from the bottom left to top right of each

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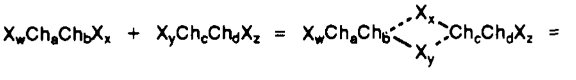
2D spectrum. It is apparent that even at zero mixing time, or more precisely the residual time for decay of the $\pi/2$ labeling pulse and rise of the $\pi/2$ acquisition pulse,[8] magnetization transfer by exchange takes place between Se_2Cl_2 and Se_2BrCl and between Se_2Br_2 and Se_2BrCl, that is between peaks 3 and 4 and peaks 7 and 8. This exchange rate is above the upper limit of that which can be measured by this technique. At $t_m = 0.001$ s, six further exchanges become apparent, 1–5, 2–6, 3–7, 3–8, 4–7, and 4–8. The 3–8 and 4–7 cross peaks represent indirect processes as subsequent analysis will show. Finally at $t_m = 0.150$ s, additional cross peaks for 1–2, 1–3, 1–4, 1–7, 1–8, 2–3, 2–4, 2–7, 2–8, 3–5, 3–6, 4–5, 4–6, 5–7, 5–8, 6–7, and 6–8 exchanges are observed. These all represent indirect cross peaks and, in accord with this, all exhibit an induction period before their appearance.

The exchanges which occur at $t_m = 0.001$ s can be accounted for only by Se–X bond breaking and not by chalcogen–chalcogen bond breaking and therefore, free radical mechanisms with XCh radicals and mechanisms with four or higher membered chalcogen ring transition states are not involved.

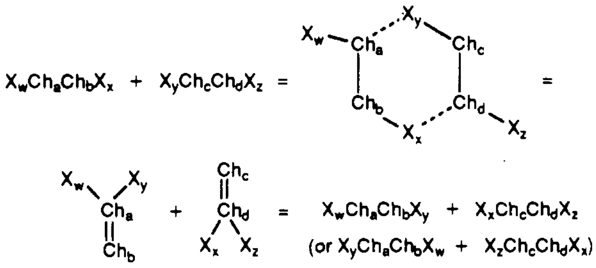
Exchange may take place by the bimolecular halogen transfer mechanism



$$X_wCh_aCh_bX_x + X_yCh_cCh_dX_z = X_wCh_aCh_b{\genfrac{}{}{0pt}{}{X_x}{X_y}}Ch_cCh_dX_z = X_wCh_aCh_bX_y + X_xCh_cCh_dX_z \quad (2)$$

If all chalcogen–halogen bonds were broken in this way, then all possible cross peaks between XSeSX species, as a group, and XSeSeX species, as a separate group, would be observed but magnetization transfer between XSeSX and XSeSeX species would not be. Direct cross peaks between diselenium and selenium sulfur species, 1–3 and 5–7, for instance, and between species where sulfur-halogen bonds are broken, 1–2 and 5–6, for instance, are not observed, indicating that Se–S and S–X bonds are retained, at least in the rapid direct exchange process. The direct cross peaks, which will arise by this mechanism, are 1–5, 2–6, 3–4, 3–7, 4–8, and 7–8, which account for six of the eight cross peaks observed for $t_m = 0.001$ s.

Another possible ^{77}Se exchange mechanism, which involves six-membered halogen-bridged rings, like those observed in the crystal structure of β-Se_2Br_2 and Se_2Cl_2[3]


(3)

is not acceptable, since it is not microscopically reversible and implies that exchange could equally well take place directly via just the trigonal pyramidal intermediate. Significant contributions from $Ch{=}ChX_2$ intermediates would result in the appearance of 3–8 and 1–6 cross peaks, which are not observed.

Magnetization transfer may also take place by an ionic mechanism, initiated by the dissociation

$$XChChX = Ch_2X^+ + X^- \quad (4)$$

followed by electrophilic or nucleophilic attack on another Ch_2X_2 molecule. This mechanism would give the same cross peaks as those predicted for the bimolecular halogen transfer mechanism (2), if SeSe, SeS, SBr, and SCl bonds remained intact and only SeX bonds underwent ionic reaction. This mechanism would account for six (1–5, 2–6, 3–4, 3–7, 4–8, and 7–8) of the eight cross peaks observed for $t_m = 0.001$ s. The cross peaks 3–8 and 4–7 probably arise from two-step processes, since simultaneous exchange of both halides is unlikely. Moreover, the one-step exchange for the diselenium dihalides is extremely rapid and is observable even at zero mixing time (cross peaks 3–4 and 7–8). The second halide exchange for diselenium species would take place within the mixing time required for single halide exchange in selenium sulfur species. The appearance in Figure 1, at $t_m = 0.0$ s, of cross peaks 3–4 and 7–8 and the absence of cross peaks 3–7 and 4–8, although all four peaks involve halide exchanges between diselenium species and should be equivalent in volume (3–4 = 4–8 and 3–7 = 7–8), is due to overlap of the 3–4 and 7–8 peaks with the strong diagonal signals. No such overlap with any strong signals occurs with the isolated 3–7 and 4–8 peaks, although they are apparently stronger, as expected, than the indirect two halide 3–8 and 4–7 exchange peaks as shown in Figure 1 ($t_m = 0.001$ s). The 3–7 and 4–8 peaks are observable at zero mixing time with considerable increase in baseline noise, if the base plateau of the EXSY spectrum is lowered. No other simple mechanistic reason can be found for the difference in volume of the 3–4 and 7–8 peaks, compared to the 3–7 and 4–8 peaks at $t_m = 0.0$ s.

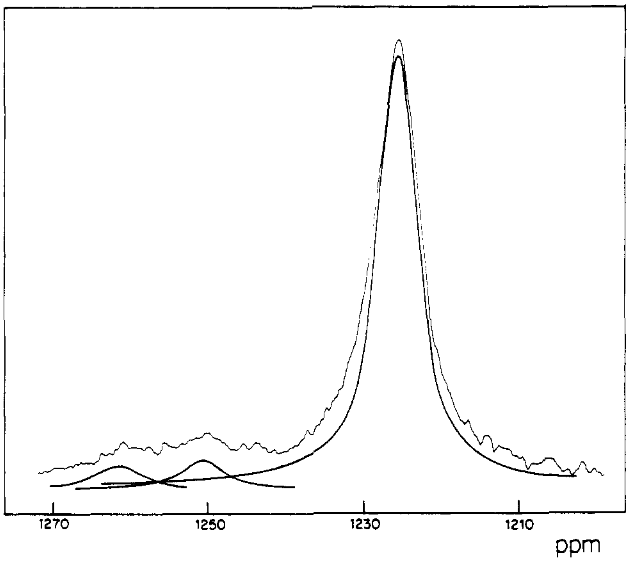


Figure 2. ^{77}Se NMR spectrum of a 0.12:11.7:11.5 molar ratio mixture of Et_4NCl, S_2Cl_2, and Se_2Br_2.

On the basis of the cross peak pattern observed, it is not possible to differentiate between the bimolecular halogen transfer mechanism (2) and the ionic dissociation mechanism (4). However, the ionic mechanism should exhibit a dependence of magnetization transfer rate on halide ion concentration. Addition of anhydrous Et_4NCl to a mixture of S_2Cl_2/Se_2Br_2 ($Et_4NCl/S_2Cl_2/Se_2Br_2$ molar ratio of 0.12:11.7:11.5) causes the eight-line spectrum (Figure 1) to collapse to the spectrum shown in Figure 2 with a strong broad signal at $\delta = 1226.8$ ppm and weaker poorly defined broad peaks at $\delta = 1251.7$ and 1262.3 ppm, which suggests that magnetization transfer in these solutions occurs by halide ion exchange. These broad signals may be assigned respectively to XSeSeX, ClSSeX and BrSSeX species, undergoing rapid halide (X^-) exchange. The average chemical shift of all of the Se_2X_2 compounds, assuming rapid exchange, may be calculated from the relative atom fractions[6] and chemical shifts of the constituent Se_2X_2 species (Se_2Cl_2, Se_2Br_2, and Se_2BrCl). Similarily, the average chemical shift for the ClSSeX and BrSSeX species (X = Br, Cl) may be calculated. All of these average chemical shifts and those observed are listed in Table II. The close agreement between the calculated and observed chemical shifts supports the assignment of the broad peaks in Figure 2 to Se_2X_2, ClSSeX, and BrSSeX species. In addition, a comparison of peak intensities, calculated from atom fractions,[6] with those, obtained by deconvolution of the spectrum in Figure 2, shows good agreement, as

Table II. Observed and Calculated Chemical Shifts and Itensities of Signals in a 0.12:11.7:11.5 Molar Mixture of Et_4NCl, S_2Cl_2, and Se_2Br_2

obsd chem shift (ppm)	calcd[a] chem shift (ppm)	rel obsd intens	rel[b] obsd intens	compd
1226.8	1221.8	0.90	0.89	XSeSeX
1251.7	1248.5	0.055	0.063	ClSSeX
1262.3	1259.0	0.050	0.051	BrSSeX

[a] Calculated from the relative concentration[6] weighted average of the chemical shifts of the constituent XSeSeX, ClSSeX, and BrSSeX species. $\delta(Me_2Se) = 0.0$. [b] Calculated from Gaussian/Lorentzian curve resolution.

shown in Table II, and provides further support for the assignment. It is again evident from these results that SeX bonds undergo rapid exchange, while SX, SeS, and SeSe (and, no doubt, SS) bonds remain intact.

Thus, magnetization transfer in S_2Cl_2/Se_2Br_2 mixtures very probably takes place by an ionic exchange mechanism, involving SeX bonds. The ionic exchange mechanism is supported by other observations. Lundkvist[17] has shown that the electrical conductivity of Se/Cl_2 mixtures is due to "Se^+" and "Cl^-" charge carriers, and electrical conductivity studies on reactions and equilibria in S_2Cl_2,[18] a related species, are accounted for by the self-dissociation

$$S_2Cl_2 = S_2Cl^+ + Cl^- \tag{5}$$

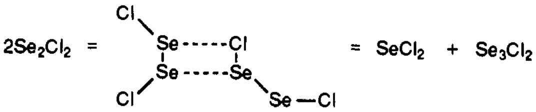
Thus, free ions, which facilitate the magnetization transfer, can exist in these mixtures. It is not possible, however, to exclude entirely some contribution to the magnetization transfer by halogen exchange (reaction 2) in S_2Cl_2/Se_2Br_2 mixtures. A related exchange study of $SnCl_4/SnBr_4$ mixtures, using ^{119}Sn NMR, has been interpreted in terms of halogen transfer[19] although halide exchange was not considered as an alternative interpretation.[8]

Cross peaks, which arise from the replacement of an SBr bond by an SCl bond (1–2, for instance) do not occur, except at very long mixing times (Figure 1, $t_m = 0.150$ s). These cross peaks may arise from S–X or Se–S bond breaking. Other cross peaks, which arise at long mixing times, require Se–S bond breaking (1–3, for example). A likely indirect pathway, which would account for this type of exchange, involves ChX_2 and Ch_3X_2 species. It is known that Se_2X_2 compounds take part in disproportionation equilibria[4,11]

$$2Se_2X_2 = SeX_2 + Se_3X_2 \tag{6}$$

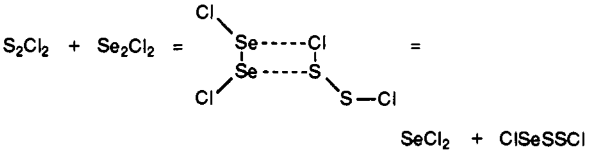
$$3Se_2X_2 = 2SeX_2 + Se_4X_2 \tag{7}$$

Similar equilibria involving mixed three and four chalcogen dihalides[6] could account for the exchanges observed at long mixing times. Unfortunately, it was not possible to test this possibility by a 2D-EXSY experiment because the cross peaks involving $SeCl_2$, Se_3Cl_2, and Se_4Cl_2 were not sufficiently strong to be differentiated from the overlap of the dispersive wings of the diagonal peaks. However, it is apparent from the half-height line width of the $SeCl_2$ resonance (Table I) that a rapid exchange involving this species is taking place. The exchange between Se_nCl_2 (n = 1, 2, 3) species would involve breaking of Se–Se bonds.



(8)

Magnetization transfer between Se_2X_2 and $SeSX_2$ species could take place via mechanisms like (8), involving a three-chalcogen–one-halogen four-square transition state.



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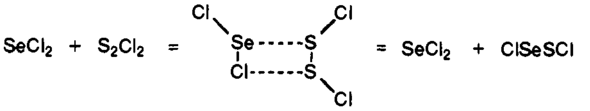

(10)

Weak signals arising from Se_2SCl_2 and SeS_2Cl_2 species are observed in the 1D spectrum.[6] This mechanism accounts for the induction period before the appearance of the 5–7 (Figure 3) and 2–4 cross peaks in the spectrum of the S_2Cl_2/Se_2Br_2 mixture. However, it is possible that the 1–2 cross peak arises from direct S–X exchange. The weak intensity of this cross peak and the absence of the 5–6 cross peak over the range of mixing times studied does not permit an absolute distinction between direct and indirect exchange, but indirect exchange by mechanisms like (9) and (10) is more likely.

The unidirectional pseudo-first-order rate constants, R_{ij}, for a particular cross peak, may be determined by using the initial rate approximation[20]

$$I_{ij}(t_m) = t_m R_{ij} M_i^0 \tag{11}$$

where $I_{ij}(t_m)$ ($=I_{ji}(t_m)$) is the integrated volume of the cross peak at mixing time, t_m, and M_i^0 is the net magnetization at site i when $t_m = 0$. A plot of $I_{ij}(t_m)/M_i^0$ against t_m gives slope R_{ij}, which represents the pseudo-first-order exchange rate constant. For this system the overall rates consist of contributions from several processes. For instance, the rate constant for magnetization transfer from Se_2Cl_2 to the Se bound to Cl in ClSeSeBr, 4 → 8 exchange, may proceed by several routes: (a) Se_2Cl_2 dissociation

$$Se_2Cl_2 = Se_2Cl^+ + Cl^- \tag{12}$$

and subsequent reaction of Se_2Cl^+ with Br^-, produced by ionic dissociation of other species with Se–Br bonds

$$Se_2Cl^+ + Br^- = Se_2ClBr \tag{13}$$

(b) attack by Br^- from other Se–Br species on Se_2Cl_2, followed by anion dissociation

$$Br^- + Se_2Cl_2 = Se_2Cl_2Br^- \tag{14}$$

$$Se_2Cl_2Br^- = Se_2ClBr + Cl^- \tag{15}$$

and (c) attack by Se_2Cl^+ from dissociation of Se_2Cl_2 on other Se–Br species

$$Se_2Cl^+ + BrSeChX = Se_2ClBr + SeChX^+ \tag{16}$$

Magnetization transfer via indirect mechanisms like those shown in (8), (9) and (10) will not contribute significantly to the initial rates. Figure 3 shows plots of $I_{ij}(t_m)/M_i^0$ vs. t_m for direct cross peaks 1 → 5, 2 → 6, 3 → 7, and 4 → 8 and, as examples, indirect cross peaks 1 → 7 and 5 → 7. From the limiting slopes, the

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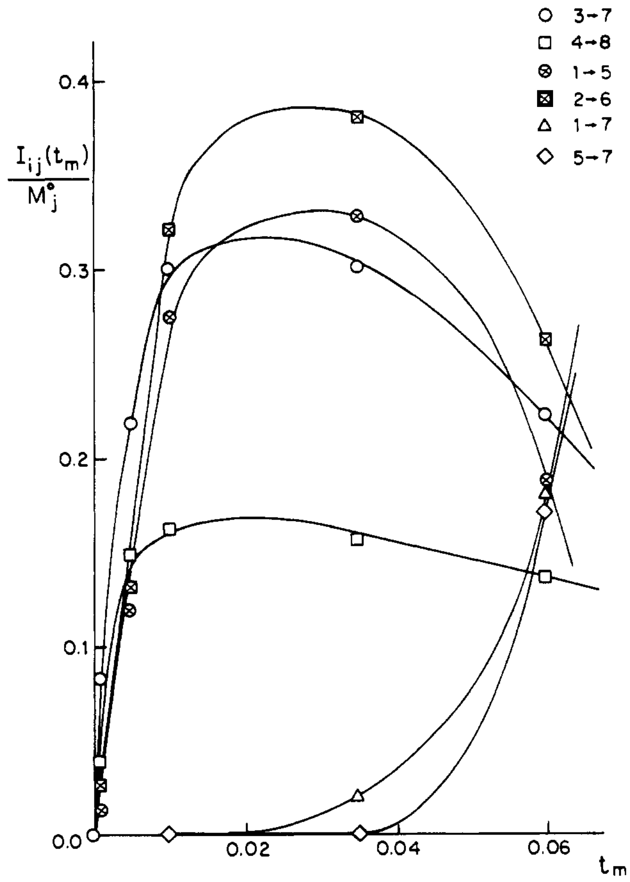

Figure 3. Plot of $I_{ij}(t_m)/M_i^0$ against t_m for direct cross peaks 1 → 5, 2 → 6, 3 → 7, and 4 → 8 for the determination of unidirectional pseudo-first-order rate constants for magnetization transfer, and, for the indirect cross peaks 1 → 7 and 5 → 7, showing the induction period.

pseudo-first-order rate constants of direct magnetization transfer, R_{ij}, may be determined, and these are listed in Table III for both the forward and reverse exchanges. An induction period is apparent for the indirect cross peaks 1 → 7 and 5 → 7. For the 3 → 7 and 4 → 8 cross peaks, these initial rates must be regarded as minima, since the 8 → 7 and 4 → 3 peaks, which are equivalent to the 3 → 7 and 4 → 8 peaks, are observed even at zero mixing time, indicating that the rate of magnetization transfer is much faster than those given in Table III.

Table III. Unidirectional Pseudo-First-Order Rate Constants, R_{ij}, for Cross Peaks 1-5, 2-6, 3-7, and 4-8.

species		Rate constants (s^{-1})[a]	
i	*j*	$10^{-1}R_{i\to j}$	$10^{-1}R_{j\to i}$
1 (BrSSeCl)	5 (BrSSeBr)	2	1
2 (ClSSeCl)	6 (ClSSeBr)	3	2
3 (BrSeSeCl)	7 (BrSeSeBr)	>8	>5
4 (ClSeSeCl)	8 (ClSeSeBr)	>4	>4

[a] The precision on these rate constants is estimated to be ±25%.

In spite of the large number of processes that may contribute to these rate constants, some general statements can be made. In general, the unidirectional pseudo-first-order rate constants for replacement of Cl by Br are larger than those for replacement of Br by Cl, which is a reflection of the greater number of Se–Br than Se–Cl bonds in the mixture (S is preferentially bonded to Cl[6]) and the higher resultant concentration of Br^- (or BrSeChX) compared to Cl^- (or ClSeChX), rather than a result of the relative weakness of the Se–Cl compared to Se–Br bond. It is also noteworthy that the rate constants in Table III for diselenium species are larger than those for sulfur–selenium species. This is what would be expected on the basis of the relative electropositivity of an XSSe group compared to an XSeSe group. Related to this observation is the generally more rapid exchange of SeX bonds, compared to SX bonds. The selenium–halogen bond is expected to undergo ionic dissociation more readily than the sulfur–halogen bond on the basis of the ionic character of the bonds (Se–X > S–X) and the relative magnitudes of the bond dissociation energies (D(SeCl) = 243 kJ mol^{-1}; D(SCl) = 272 kJ mol^{-1} [21]). Furthermore, the electrical conductivity of S_2Cl_2 (1.3×10^{-10} Ω^{-1} cm^{-1} [22]) is less than that of Se_2Cl_2 (2×10^{-7} Ω^{-1} cm^{-1} [23]), indicating a greater degree of ionic dissociation in Se_2Cl_2 compared to S_2Cl_2.

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