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On the High Stability of Hypervalent X-Se-X Bonds Superior to Dipolar I-X Bonds Formed in the Reaction of I_2 with Selenides and Cl_2 or Br_2

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The Formation of a hypervalent X-Se-X bond in a TB, together with a non-polar I-I bond in an MC, was superior to that of a couple of dipolar I-X bonds in MC's (RSeXX'R': R, R' = Me or Ph; X, X' = Cl, Br, or I). The stability of the X-Se-X bonds depended much more on the difference of their elecrtonegativities than that of the I-X bonds: MC's of IX of selenides were formed in solution when X was only Br or I.

We have been interested in the structure of halogen adducts of selenides, trigonal bipyramidal adducts (TB's) or molecular complexes (MC's),[1)] which depends on their electronegativity:[2,3)] TB's contain highly polar hypervalent bonds, $X^{\delta -}$-$Se^{\delta +}$-$X^{\delta -}$, which become more stable as the difference of their electronegativities increases,[2,3)] similarly to the case of the dipolar $X^{\delta -}$-$Y^{\delta +}$ bonds.[4)]

Knobler and McCullough have shown that the structure of the ICl adduct of 1-oxa-4-selenane is MC based on X-ray crystallography.[5)] This result might be taken as evidence for the MC structure of ICl adducts of selenides, but there are several points to be considered before concluding in that way, since the examples that yield MC's in the reaction of selenides with IX in solutions are too few in the literature. However, we have encountered that the addition of ICl to a selenoanisole solution did not give its ICl adduct, which might form just after the mixing, but a mixture of the chlorine and the iodine adducts, based on NMR. This finding led us to investigate the relative stability of these adducts shown in Eq. 1 (X = Cl, Br) in solution.

$$RSeX_2R' + RSeR' + nI_2 \rightleftharpoons RSeX_2R' + RSeI_2R' + (n-1)I_2 \qquad (1)$$

Table 1 shows the results of the reactions. An ^1H NMR spectrum of a 1:1 mixture of MeSeMe (<u>1a</u>) and $MeSeCl_2Me$ (<u>1b</u>) in $CDCl_3$ contained two sharp singlets at δ 2.00 and 3.64, showing that the chlorine migration from <u>1b</u> to

Table 1. NMR Data of the Mixtures of a Selenide and Its Chlorine or Bromine Adduct with or without Iodine[a,b]

Compound[c]	1a·nI_2,1b	1a·nI_2,1c	Calcd δ_{av}[d]	(α')	2a·nI_2,2b	2a·nI_2,2c	Calcd δ_{av}[d]	(α')
n = 0.0	2.00, 3.64	2.00, 3.63			2.35, 3.90	2.35, 3.90		
	(≦ 1) (≦ 1)	(5.2) (5.2)			(≦ 1) (≦ 1)	(12) (13)		
	av. 2.82	av. 2.82	2.82		av. 3.13	av. 3.13	3.13	
0.5					2.60, 3.90			
					av. 3.25	3.01	3.22	(0.353)
1.0	2.50, 3.64				2.72, 3.90[e]			
	(4.7) (3.5)				(5.2) (5.0)			
	av. 3.08	3.02	3.07	(0.887)	av. 3.32	2.99	3.29	(0.598)
		(20)				(≦ 1)		
1.5					2.80, 3.90			
					av. 3.35	2.99	3.33	(0.783)

a) ^1H chemical shifts (ppm) from TMS in $CDCl_3$. b) Half-value widths (Hz) at n = 0 and 1.0 are given in parentheses. c) RSeR' : MeSeMe (1a); PhSeMe (2a), $RSeX_2R'$: X = Cl (1b, 2b); Br (1c, 2c); I (1d, 2d) = (1a + I_2, 2a + I_2). d) The calculated δ_{av}'s for chlorine adducts are the same as those for the bromine adducts since the δ_{TB}'s for the chlorine and bromine adducts are almost equal. e) The same spectrum was recorded for the ICl adduct of 2a.

1a is much slower than the NMR time scale (60 MHz, 27 °C, and 6.2×10^{-2} M for each). Addition of equimolar iodine to the solution caused downfield shift for the methyl protons of 1a, due to the formation of $\mathrm{MeSeI_2Me}$ (1d). Though the chemical shift and the relative intensity of 1b were not changed within the experimental errors, in addition of $\mathrm{I_2}$, the signals of 1b and 1d became broader, which shows that the amount of 1b was not decreased but the chlorine migration was accelerated by the addition of $\mathrm{I_2}$.

Since $\mathrm{RSeI_2R'}$ (MC) is in a rapid equilibrium with its components1b) (Eq. 2), the observed shift (δ_{obsd}) and the average value (δ_{av}) are given by Eqs. 3 and 4, respectively, if the reaction follows Eq. 1. The calculated δ_{av}, with known or estimated K,1b α', δ_F (for free selenides), δ_{MC},1b) δ_{TB},1b) and the concentrations, are also shown in Table 1. The δ_{av}

$$\underset{a\alpha'}{\mathrm{RSeI_2R'}} \overset{K}{\rightleftharpoons} \underset{a-a\alpha'}{\mathrm{RSeR'}} + \underset{b-a\alpha'}{\mathrm{I_2}} \tag{2}$$

$$\alpha' = \{(a+b+K) - \sqrt{(a+b+K)^2 - 4ab}\}/2a$$

$$\delta_{obsd} = \alpha'\delta_{MC} + (1-\alpha')\delta_F \tag{3}$$

$$\delta_{av} = (\delta_{TB} + \delta_{obsd})/2 = (\delta_{TB} + \delta_F)/2 + \alpha'(\delta_{MC} - \delta_F)/2 \tag{4}$$

$$\mathrm{RSeX_2R'}\ (\mathrm{TB}) + \mathrm{RSeI_2R'}\ (\mathrm{MC}) \rightleftharpoons 2\ \mathrm{RSeIXR'}\ (\mathrm{MC}) \tag{5}$$

for 1b and 1d was calculated to be 3.07, which is almost the same as that observed. Thus the reaction must follow Eq. 1 or the equilibrium lies so far to the left in Eq. 5 (X = Cl). These results show that the hypervalent Cl-Se-Cl bond, together with the MC of an I-I bond, is more stable than the two MC's of I-Cl bonds. The stability of the hypervalent bond in 2b was also shown with a mixture of PhSeMe (2a), $\mathrm{PhSeCl_2Me}$ (2b), and $\mathrm{I_2}$.

Figure 1 shows the plots of the observed and the calculated δ_{av}'s for 2a and 2b vs. $\mathrm{I_2}$ concentrations. The coincidence of the two plots was very good, which exhibits that this reaction also obeys Eq. 1, with the negligible formation of PhSeIClMe (2e). Since ΔH values for MC formation would not be very large and the values for MC formation with $\mathrm{I_2}$ may not be larger than those with ICl,1-3) the hypervalent Cl-Se-Cl bond, together with a non-polar I-I bond, must be more stable than two dipolar I-Cl bonds.

After establishing the favorable formation of the Cl-Se-Cl bond, similar reactions (Eq. 1) with X = Br were examined. Though the ^{1}H NMR spectrum of a mixture of 1a and $\mathrm{MeSeBr_2Me}$ (1c) or 2a and $\mathrm{PhSeBr_2Me}$ (2c) gave two singlets similarly to the case of X = Cl, they were not so sharp. The rate of the bromine migration must be comparable to the NMR time scale. The two signals coalesced to one as iodine was added to the solution.

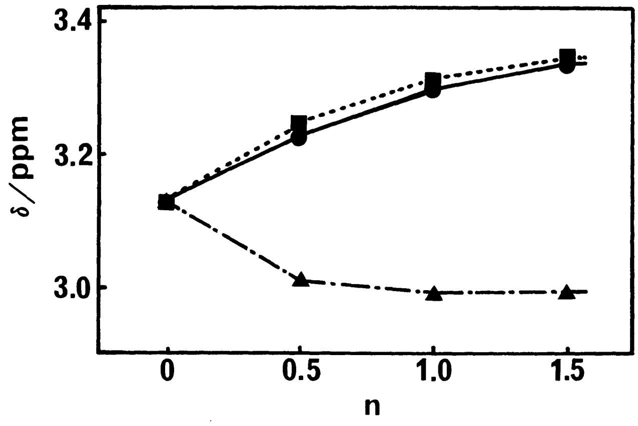

Fig. 1. Plots of δ_{av} vs. I_2 concentrations for the reaction (Eq. 1) of selenoanisoles, of which concentrations are 6.2×10^{-2} mol dm^{-3} (■, ▲, and ● stand for X = Cl, Br, and the calculated values, respectively).

In the case of 1c with 1d, the hypervalent Br-Se-Br bond, together with an I-I bond, is more stable than two I-Br bonds, since the observed δ_{av} was close to that observed for 1b and 1d, and to the calculated value; the reason why the former is slightly smaller (upfield) than the latter becomes apparent, if one goes to 2c with 2d.

The observed δ_{av} for 2c and 2a moved upfield as iodine was added to the mixture (Table 1). The data were also plotted in Figure 1, which are very different from those of 2b with 2d and of the calculated ones. Since the addition of I_2 to 2a does form 2d resulting in the downfield shift for the methyl protons (Eq. 3), the upfield shift must be brought by a species other than 2d. It must be an MC of IBr (2f) formed in the reaction of 2c with I_2. The observed chemical shift (n = 1.0) can be explained by assuming that the contents of 2a, 2c, 2d, and 2f are comparable, if the chemical shift and the K value of 2f were not very different from those of 2d, compared with those of 2c. These results show that the stability of the hypervalent Br-Se-Br bond is comparable to that of the dipolar I-Br bond in this case.

The ^{13}C NMR data of 1, 2, and diphenyl selenides (3) also support the above results, though the hypervalent bonds of 3 are less stable.

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