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The Mechanism of Fluorine Exchange in Diorganoselenium Difluorides

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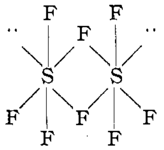
The discovery of a preparative route to diorganoselenium difluorides has made available a new class of compounds which are amenable to fluorine exchange studies *via* both ^1H and ^{19}F nuclear magnetic resonance spectroscopy. We have determined the temperature dependence of the ^1H nmr spectrum of dimethyl-, diethyl-, and diisopropylselenium difluoride and the ^{19}F nmr spectrum of diisopropylselenium difluoride. An increase in the rate of fluorine exchange with increasing bulk of the alkyl group has been found. In addition, the F-exchange rate in the three diorganoselenium difluorides investigated was independent of concentration over the concentration range studied (0.74 *m* in 1,1,2,2-tetrachloroethane to neat liquid diorganoselenium difluoride). These results and other considerations suggest that the rate-determining step for the fluorine-exchange process in R_2SeF_2 molecules is mainly heterolytic Se–F bond breaking, *i.e.*, a *dissociative* process: $R_2SeF_2 \rightarrow R_2SeF^+ + F^-$. This is in contrast with SF_4 and SeF_4 where exchange appears to occur principally *via* a second-order associative mechanism.

There have been a number of studies on compounds of the main group elements which undergo fluorine exchange but in relatively few instances has the mechanism of the exchange process been clearly indicated. Pentacoordinate phosphorus derivatives[1-3] have received much attention, and investigations of SF_4[4] and certain of its derivatives have been reported. The ^{19}F nmr spectra of SF_4 (−80°) and RSF_3 compounds (−40°)[4,5] revealed separate peaks due to axial and equatorial fluorines. Coalescence to a single peak occurred at higher temperatures with the coalescence temperature being concentration dependent. It was therefore suggested that the exchange process could be second order and that a fluorine-bridged intermediate (shown below for SF_4) might be involved.



These studies did not completely rule out the possibility that the exchange process was first or higher than second order.

The discovery of a preparative route to diorganoselenium difluorides has made available a new class of compounds which are amenable to fluorine-exchange studies *via* both ^1H and ^{19}F nmr.[6] Although the rate of fluorine exchange in these compounds is sensitive to the presence of small quantities of water, we find that compounds of high purity displaying reproducible nmr spectral data may be obtained by careful high-vacuum distillation and sample storage over NaF. We report below our results concerning the temperature dependence of the proton nmr spectra of dimethyl-, diethyl-, and diisopropylselenium difluoride and the ^{19}F nmr spectrum of diisopropylselenium difluoride.

Results

For $(CH_3)_2SeF_2$ the triplet[7] observed in the ^1H nmr spectrum at ambient temperature coalesces to a broad peak at *ca.* 120°. The triplet gradually coalesced due to decomposition if samples were held at 90°, while at temperatures >90° the collapse was rapid. The coalescence temperature given above is therefore an extrapolated value.

A coalescence temperature of 42° was observed for the methylene protons in diethylselenium difluoride. Above this temperature the expected quartet appeared, but at lower temperatures (*ca.* 0°) the anticipated 12-line spectrum could not be resolved due to viscosity line broadening in the neat liquid. However, in methylene chloride at −30° the expected 12-line spectrum was resolved ($J(^1H_{CH_2}–^{19}F) = 10.5$ Hz). An identical coalescence temperature (+42°) was observed for 1.26 (Figure 1) and 0.74 *m* solutions of $(C_2H_5)_2SeF_2$ in 1,1,2,2-tetrachloroethane.

The methine protons in $(i\text{-}C_3H_7)_2SeF_2$ appear as a broad septet at 34°. On cooling, the peaks broaden markedly but coalescence is not observed above the melting point (−8 ± 1°). A methylene chloride solution (2.0 *m*) behaved similarly but on cooling to −22° coalescence was observed. Further cooling produced a poorly resolved nine-line spectrum (−60°) as $J(^1H_{CH_3}–^1H_{CH}) \approx J(^{19}F–^1H_{CH})$. The sample froze at lower temperatures. The ^{19}F nmr spectrum of this solution exhibited a single peak at room temperature which broadened on cooling, the coalescence temperature being close to that observed in the proton nmr spectrum. At −60° the expected triplet ($J(^{19}F–^1H_{CH}) = \sim 7$ Hz) was barely resolved (Figure 2), along with satellites due to $^{77}Se–^{19}F$ coupling ($J^{77}Se–^{19}F = 642.1$ Hz). Viscosity line broadening was a problem again below −50°.

We studied the effect of certain added impurities on the fluorine exchange rate of diorganoselenium difluorides. Addition of the soluble fluoride (PPN)F[8] or insoluble NaF did not affect the exchange rate. Like certain previous investigators,[9] we found the presence of NaF beneficial, presumably because it removed traces of HF.

Addition of small amounts of BF_3, $(CH_3)_2SeF_2 \cdot BF_3$,[10] or H_2O to $(CH_3)_2SeF_2$ caused a drastic increase in the rate of fluorine exchange as noted by the com-

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[1] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964).

[2] A. H. Cowley and M. W. Taylor, *J. Amer. Chem. Soc.*, **91**, 1934 (1969).

[3] G. M. Whitesides and H. L. Mitchell, *ibid.*, **91**, 5384 (1969).

[4] E. L. Muetterties and W. D. Phillips, *ibid.*, **81**, 1084 (1959).

[5] W. A. Sheppard, *ibid.*, **84**, 3058 (1962).

[6] K. J. Wynne, *Inorg. Chem.*, **9**, 299 (1970).

[7] Unless otherwise noted nmr parameters have been given in Table II of ref 6.

[8] (PPN)F is bis(triphenylphosphiniminium) fluoride kindly provided by Professor John K. Ruff.

[9] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

[10] Details for the preparation of this compound which we believed to be $[(CH_3)_2SeF^+][BF_4^-]$ will appear separately.

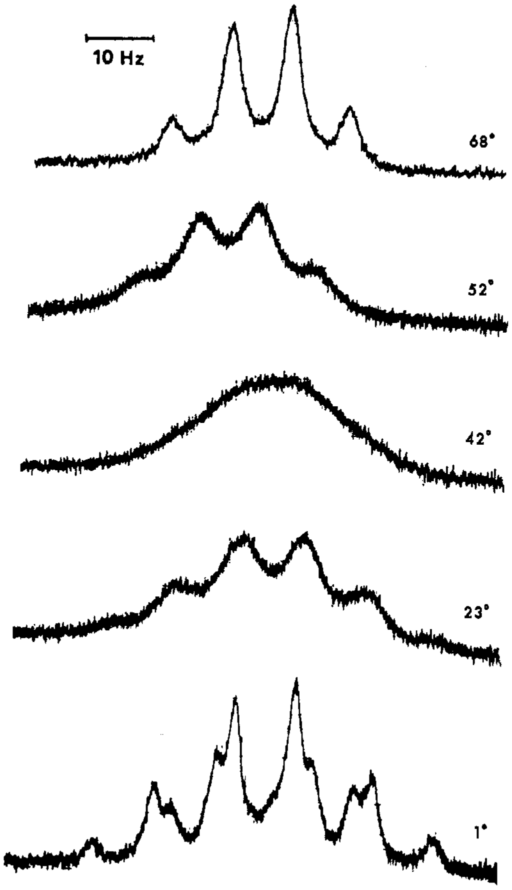


Figure 1.—The ^1H nmr spectrum of the methylene protons in $(C_2H_5)_2SeF_2$ *vs.* temperature (1.26 *m*, $CHCl_2CHCl_2$).

Figure 2.—The ^{19}F nmr spectrum of $(i\text{-}C_3H_7)_2SeF_2$ at −60° and 57.6 MHz (2.0 *m*, CH_2Cl).

plete collapse of the proton nmr triplet. Samples of diorganoselenium difluorides which had been briefly exposed to moisture showed coalescence temperatures lowered by 20–60°. Solvent addition thereupon raised the coalescence temperature.

Discussion

The rate of fluorine exchange in the diorganoselenium difluorides investigated increased in the order $(CH_3)_2SeF_2 < (C_2H_5)_2SeF_2 < (i\text{-}C_3H_7)_2SeF_2$, with respective coalescence temperatures being ~120, 42, and −22°. The increase in the rate of exchange, as evidenced by decreasing coalescence temperature, with increasing bulk of the alkyl group is consistent with the exchange being a first-order process. This trend weighs heavily against a bimolecular intermediate in the rate-determining step for the exchange process in R_2SeF_2 molecules. Furthermore, a molecular model suggests that the bulk of two isopropyl groups offers considerable steric hindrance to the formation of a dimer. Therefore a trend in exchange rates opposite that observed would be expected if the rate-determining step in the exchange process involved a bimolecular intermediate.

Additional evidence concerning the mechanism of fluorine exchange may be inferred from the lack of concentration dependence of the fluorine exchange rate. The coalescence temperature for $(C_2H_5)_2SeF_2$ (neat liquid) was identical with that of 1.26 and 0.74 *m* solutions in 1,1,2,2-tetrachloroethane. By comparison of pure liquid and solution spectra at a given temperature it was also ascertained that neither $(CH_3)_2SeF_2$ in $CHCl_2CHCl_2$ nor $(i\text{-}C_3H_7)_2SeF_2$ in CH_2Cl_2 displayed concentration-dependent fluorine exchange rates.

The fact that added fluorine caused no spectral changes also strongly militates against an associative mechanism being operative in the rate-determining step of the exchange process. In other words the observation that the nmr spectra are independent of added fluoride suggests that R_2SeF_2 molecules have negligible acceptor power. Thus the absence of exchange rate concentration dependence, the increased exchange rate with increasing organo group bulk, and the independence of the rate of exchange on fluoride concentration provide strong evidence that the rate-determining step in fluorine exchange is a first-order dissociative process

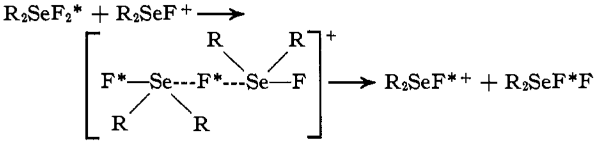
$$R_2SeF_2 \longrightarrow R_2SeF^+ + F^- \qquad (1)$$

The increased rate with increasing bulk of the organo group may be correlated with the increasing electron-releasing character of the bulkier groups and concomitant increase in the ionic character of the Se–F bonds. This is consonant with ^{19}F chemical shift data.[6]

After Se–F bond breaking occurs, ion recombination may take place (eq 2). Alternatively the R_2SeF^+ ion

$$ReSeF^+ + F^-(soln) \longrightarrow R_2SeF_2 \qquad (2)$$

formed *via* eq 1 could interact with an R_2SeF_2 molecule *via* a bimolecular process leading to intermolecular fluorine scrambling (eq 3). No information is available to ascertain which of these mechanisms might be most important in the pure compounds or their solutions.



$$R_2SeF_2{}^* + R_2SeF^+ \longrightarrow \left[\begin{matrix} & R & & R & \\ F^*\text{—}Se & \cdots F^* \cdots & Se\text{—}F \\ R & & R & & \end{matrix}\right]^+ \longrightarrow R_2SeF^{*+} + R_2SeF^*F \qquad (3)$$

A marked increase in the rate of exchange in all samples was observed upon addition of HF (from hydrolysis). A similar increase was seen upon addition of BF_3 or $(CH_3)_2SeF_2 \cdot BF_3$ to dimethylselenium difluoride. We believe the addition of Lewis acids to R_2SeF_2 compounds increases the concentration of R_2SeF^+ (eq 4), as ample precedent has been set for

$$ReSeF_2 + A \longrightarrow R_2SeF^+ + AF^- \qquad (4)$$

halide ion transfer in related systems.[11] The cation so produced may effect rapid intermolecular fluorine exchange *via* the second-order self-regenerative "chain" process indicated by eq 3. With a single bridging fluorine the structure of the $Se_2F_3(CH_3)_4^+$ ion could be similar to the well-established isoelectronic $Sb_2F_7^-$ species.[12] That the rate of fluorine exchange is dependent on the concentration of BF_3 or $(CH_3)_2SeF_2 \cdot BF_3$ added is consonant with the second-order process described by eq 3.

The ionic exchange process for R_2SeF_2 molecules is in sharp contrast with the associative mechanism suggested for SF_4 and SeF_4 by Muetterties and Phillips.[4] Their view is nonetheless supported by spectroscopic studies[13,14] on SF_4 and SeF_4 and indirectly by an X-ray determination of the crystal structure of TeF_4[15] which has shown the presence of endless chains containing square-pyramidal TeF_5 units. Only limited structural data are available on diorganochalcogen difluorides[6] but crystal structures of $(CH_3)_2SeCl_2$[16] and related compounds[17] have shown little intermolecular interaction to occur in the solid state. This supports our hypothesis concerning the mechanism of fluorine exchange and is consistent with our view on structure and bonding in these systems.[18]

A comparison of fluorine chemical shifts and infrared stretching frequencies shows that Se–F bonds are weaker and more ionic in diorganoselenium difluorides than the corresponding bonds in SeF_4.[6] Perhaps this is also reflected in the $^{77}Se-^{19}F$ coupling constants which are notably low in diorganoselenium difluorides compared with other typical Se–F compounds.[19] Replacement of F by CH_3 should also simultaneously lower the acceptor power of Se. Evidently ionic character in Se–F bonds has increased and acceptor power of Se has decreased sufficiently that a dissociative rate-determining step is energetically favored relative to an associative one. Klanberg and Muetterties[20] reasoned along similar lines from results on a study of the isoelectronic $R_xSiF_{5-x}^-$ ions ($x = 0, 1, 2$). Although their evidence was not strong, these workers preferred an associative exchange process for SiF_5^- but suggested that a dissociative exchange mechanism was operative for $CH_3SiF_4^-$.

An activation energy of 4 kcal has been calculated for the exchange process in SF_4.[4] This value probably sets an upper limit for E_a in SeF_4 assuming that the mechanism of the exchange process is the same. In contrast we have obtained an E_a for fluorine exchange in $(CH_3)_2SeF_2$ of $\sim$10 kcal.[21] Thus, although the Se–F bonds are apparently stronger in SeF_4 than in R_2SeF_2 the activation energy for fluorine exchange in the former is lower thereby supporting a different mechanism for exchange in the respective molecules.

Finally, we draw attention again to the unusual observation that the rate-determining step in the exchange process is unaffected by the presence of added fluoride. Diorganoselenium difluorides are the first reported class of compounds in which the rate-determining step in fluorine exchange is apparently a first-order dissociative process which is not affected by the presence of F^-.

Experimental Section

Samples were triply distilled, the first distillation being carried out in a glass apparatus. In the second the sample was distilled from anhydrous NaF into a Kel-F waxed trap while final distillation from NaF utilized a Kel-F waxed flask and a high-density polyethylene trap attached to the vacuum line with Swage-Lock fittings. All distillations were carried out at *ca.* 10^{-5} Torr. Samples were transferred to Teflon nmr cells (NMR Specialities) in a dry nitrogen atmosphere.

The samples were analytically pure before even the first distillation but because of the sensitivity of the nmr spectra to impurities which would catalyze the exchange process, only samples which displayed the same coalescence temperatures before and after the addition of NaF were utilized. This procedure proved to be the key in obtaining reproducibly high coalescence temperatures which we took to be a measure of high sample purity.

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