Preparation and Properties of Dimethylselenium Difluoride

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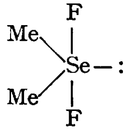
EMELÉUS and HEAL suggested that the higher organochalcogen fluorides were unstable.[1] Sheppard however has demonstrated the stability of organosulphur tri- and penta-fluorides.[2] In a further study of methylselenium halides,[3] we have found more evidence for the stability of organochalcogen fluorides. We have synthesized the first reported example of a diorganoselenium difluoride, dimethylselenium difluoride, Me_2SeF_2. This compound was prepared from the reaction of dimethylselenide with silver(II) fluoride in 1,1,2-trichloro-1,2,2-trifluoroethane. Satisfactory C, H, Se, and F analyses were obtained.

Although previously reported organoselenium dihalides have been found to be solids at ambient temperature, Me_2SeF_2 is a liquid freezing at 11·2—11·4° which distils slowly under reduced pressure (0·01 mm.) at 25°. When exposed to moist air, $MeSeF_2$ rapidly forms a white solid which reacts slowly with glass. The liquid possesses moderate thermal stability, but decomposes above 120°. Usually, alkylselenium halides are less thermally stable than the corresponding aryl derivatives. Thus, diarylselenium difluorides, when they are synthesized, should exhibit even better thermal stability.

The ^{1}H n.m.r. spectrum of pure Me_2SeF_2 at 100 MHz and 30°, showed δ-3·13 (t, J_{HF} 9·0 c./sec.) with tetramethylsilane as internal reference. The triplet starts to collapse at about 50°. These data indicate that rapid intermolecular fluorine exchange does not occur at ambient temperature. In contrast, ^{19}F n.m.r. data for SeF_4 in propane showed that fluorine exchange could not be completely eliminated at −200°.[4]



The structure of Me_2SeF_2 is probably trigonal bipyramidal as shown. This is consistent with the n.m.r. data which indicate the presence of two equivalent fluorines, and with *X*-ray data on diorganoselenium dichlorides and dibromides.[5]

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