On the Nature of Triphenylselenonium Chloride

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Received 23 February 1976; accepted 29 July 1976

On the basis of its molar conductance in organic solvents and a study of its solutions in disulphuric acid and fluorosulphuric acid, triphenylselenonium chloride has been shown to be a chloride ion donor. It forms a number of complexes with strong Lewis acids. Conductance and spectroscopic studies of the complexes formed have been interpreted in terms of the ionic formulation, \([\text{C}_6\text{H}_5\text{Se}^+][\text{C}_1\text{.Lewis acid}]\).

Peach has recently reported the formation of compounds containing cations like (RSCl)+ and (R2SCl)+ in liquid hydrogen chloride. The existence of the cation (R2S)+ has been known since long. While Wynne and coworkers have reported the existence of the corresponding chloroorganoselenium cations (MeSeCl)+, (Me2SeCl)+ and (Me3Se)+, a survey of literature reveals that there is no information on the formation of (R3SeCl)+ cation where R is an aromatic group. Recently the stabilization and characterization of (C6H5)3SeCl, monochlorodiphenylselenonium ion has been reported by Paul and Bhasin. In the present paper the formation and characterization of triphenylselenonium cation (Ph3Se)+ are reported.

Materials and Methods

Triphenylselenonium chloride was prepared from diphenylselenium dichloride employing Friedel-Crafts reaction. The dihydrate, (C6H5)3SeCl.2H2O, thus obtained was dehydrated by heating it at 70° under reduced pressure for 48 hr. It was further purified by recrystallization from methyl ethyl ketone.

The Lewis acids employed were purified by the methods already reported in literature. Nitrobenzene (AR) and dichloromethane (BDH) were kept over molecular sieves and distilled twice before use. Fluorosulphuric acid and disulphuric acid were prepared by the literature procedures.

Preparation of the adducts — The adducts were prepared by mixing the well-cooled solutions of triphenylselenonium chloride and Lewis acids in 1:1 or 1:2 molar ratio in methylene chloride. Addition of carbon tetrachloride resulted in the precipitation of adducts. However, in the case of sulphur trioxide and selenium trioxide the two components were mixed in appropriate amounts in liquid sulphur dioxide at -40°. The resulting mixture so obtained was allowed to stand for 6 hr at -40°. Sulphur dioxide was evaporated slowly at 0° and the resulting viscous liquids washed repeatedly with carbon tetrachloride and dried in vacuo.

Physical measurements — The design of the conductivity cell and the mode of measuring specific conductance in disulphuric acid and fluorosulphuric acid was the same as described by Gillespie and Malhotra.

Infrared spectra of the adducts were scanned on Perkin-Elmer 337 and 521 double beam grating spectrophotometers. Viscous liquids or the emulsion of the solid complexes were pressed between silver chloride plates. In some cases their IR spectra were studied by preparing potassium bromide pellets. All manipulations as far as possible were carried out in a dry box.

Selenium was estimated by modified Arne Fredga's method.

Results and Discussion

The ionic nature of triphenylselenonium chloride is in keeping with its high solubility in the polar solvents like nitromethane, nitrobenzene and acetonitrile. It behaves as a 1:1 electrolyte in these solvents as revealed by its molar conductance. The possibility of the formation of adducts between triphenylselenonium chloride and these non-protonic solvents is ruled out as the addition of carbon tetrachloride or petroleum ether to the solutions result in the separation of pure triphenylselenonium chloride.

The general behaviour of solutes in disulphuric acid and fluorosulphuric acid is already established. Triphenylselenonium chloride readily dissolves in disulphuric acid to give a clear highly conducting solution. The increase in conductance may be due to the reaction (i) or (ii).

\[
\text{(C}_6\text{H}_5\text{)}_3\text{SeCl} + 2\text{H}_2\text{SO}_3 \rightarrow \text{(C}_6\text{H}_5\text{)}_3\text{S}^+ + \text{HSO}_3^- + \text{H}_2\text{SO}_4
\]

Eq. (i) is ruled out on the basis of depression in freezing point curve. The observed value of \(\nu\) is 3 whereas the Eq. (i) requires \(\nu\) value of 2. In addition the conductance data is comparable with that of potassium chloride suggesting the validity of Eq. (ii).
Lewis acid | Stoichiometric composition | Physical state, colour and m.p. (°C) | $\lambda_{max}$ (nmi) | Se (%) | Cl (%) |
---|---|---|---|---|---|
BCl$_3$ | (C$_6$H$_5$)$_3$SeCl.BCl$_3$ | White solid, 104-5 | 25 66 | 17 08 | 17 13 | 30 31 | 30 37 |
SbCl$_5$ | (C$_6$H$_5$)$_3$SeCl.SbCl$_5$ | White solid, 130-31 | 21 23 | 12 18 | 12 26 | 34 18 | 34 62 |
SO$_2$ | (C$_6$H$_5$)$_3$SeCl.SO$_2$ | Colourless viscous liquid | — | 18 40 | 18 58 | 8 15 | 8 35 |
SeO$_4$ | (C$_6$H$_5$)$_3$SeCl.SeO$_4$ | Pale yellow viscous liquid | — | 33 40 | 33 47 | 7 45 | 7 40 |
AlCl$_3$ | (C$_6$H$_5$)$_3$SeCl.AlCl$_3$ | Lemon yellow, 137-38 | 21 44 | 16 50 | 16 56 | 29 31 | 29 77 |
PCl$_5$ | (C$_6$H$_5$)$_3$SeCl.PCl$_5$ | White solid, 119-20 | 20 39 | 14 31 | 14 34 | 38 04 | 38 65 |
SnCl$_4$ | 2(C$_6$H$_5$)$_3$SeCl.SnCl$_4$ | White solid, 127-28 | 42 14 | 16 58 | 16 66 | 23 08 | 23 20 |
GeCl$_4$ | 2(C$_6$H$_5$)$_3$SeCl.GeCl$_4$ | Cream colour, 121-23 | 44 41 | 17 40 | 17 52 | 23 12 | 23 61 |
TiCl$_4$ | 2(C$_6$H$_5$)$_3$SeCl.TiCl$_4$ | Yellow solid, 135-36 | 45 20 | 17 21 | 17 32 | 23 92 | 23 98 |

*IR work throughout the paper in cm$^{-1}$.

The conductance data of triphenylselenonium chloride in fluorosulphuric acid are also indicative of the solvolytic reaction (iii).

$$(C$_6$H$_5$)$_3$SeCl + HSO$_2$F$\rightarrow$(C$_6$H$_5$)$_3$Se$^+$ + HCl + SO$_2$F$^-$  

... (iii) Hydrochloric acid behaves as a non-electrolyte in fluorosulphuric acid. The conductance of triphenylselenonium chloride is comparable with that of potassium fluorosulphate in the case of aluminium trichloride adduct. The new band at 480 in the aluminium trichloride adduct is assigned to AlCl$_3$ species$^{18}$. Six intense bands at 532, 560, 585, 1047, 1275 and 1150 confirm the presence of chlorosulphate group$^{17}$ ([C$_6$]) in the case of sulphur trioxide adduct, and at 500, 570, 690, 850, 990 and 1270 cm$^{-1}$ in the case of selenium trioxide adduct confirm the presence of SeO$_2$Cl$^-$ (chloroselenate) group$^{18}$. The assignments of the observed bands at 330 in the case of titanium tetrachloride adduct and at 325 in tin tetrachloride adduct are in agreement with those of related hexahalo species ([XCl$_6$]$^{2-}$) as these are in the regions where the characteristic absorption bands arising from [TiCl$_4$]$^{2-}$ and [SnCl$_4$]$^{2-}$ species occur$^{19,20}$. No assignment could be made to [GeCl$_4$]$^{2-}$ species as the (Se-C) vibration in the adduct of germanium tetrachloride overlapped with the characteristic absorption of [GeCl$_4$]$^{2-}$ species$^{20}$. The new bands appearing at 342 in the case of antimony pentachloride adduct and at 435 in the case of phosphorus pentachloride adduct are due to the species [SbCl$_5$]$^-$ and [PCl$_5$]$^-$ respectively$^{20}$. In all the complexes the (Se-C) vibrations are lowered by about 15 cm$^{-1}$ as compared with that of triphenylselenonium chloride which shows (Se-C) vibration at 484. The molar conductance values of the complexes in nitrobenzene further support the ionic nature of the complexes.

**References**