

On the Nature of Triphenylselenonium Chloride

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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, $[(C_6H_5)_3Se]^+[Cl.Lewis\ acid]^-$.

PEACH¹ has recently reported the formation of compounds containing cations like $(RSCl_2)^+$ and $(R_2SCl)^+$ in liquid hydrogen chloride. The existence of the cation $(R_3S)^+$ has been known since long. While Wynne and coworkers²⁻⁴ have reported the existence of the corresponding chloro-organoselenium cations $(MeSeCl_2)^+$, $(Me_2SeCl)^+$ and $(Me_3Se)^+$, a survey of literature reveals that there is no information on the formation of $(R_nSeCl_{3-n})^+$ cation where R is an aromatic group. Recently the stabilization and characterization of $(C_6H_5)_2SeCl^+$, monochlorodiphenylselenonium ion has been reported by Paul and Bhasin⁵. In the present paper the formation and characterization of triphenylselenonium cation $(Ph_3Se)^+$ are reported.

Materials and Methods

Triphenylselenonium chloride was prepared from diphenylselenium dichloride⁶ employing Friedel-Crafts reaction. The dihydrate, $(C_6H_5)_3SeCl \cdot 2H_2O$, 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^{7,8}.

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 Malhotra⁹.

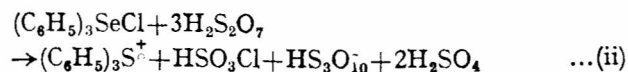
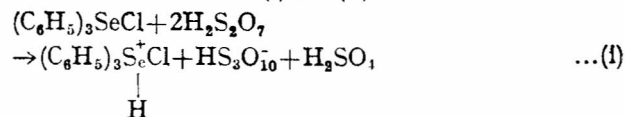
Infrared spectra of the adducts were scanned on Perkin-Elmer 337 and 521 double beam grating spectrophotometers. Viscous liquids or the emulsion of the solid complexes were pressed between silver chloride plates. In some cases their IR spectra were studied by preparing potassium bromide pellets. All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

Selenium was estimated by modified Arne Fredga's method⁹.

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 conductance¹⁰. 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^{11,12} 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).



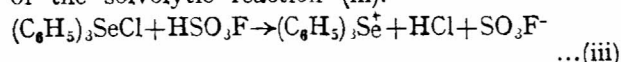
Eq. (i) is ruled out on the basis of depression in freezing point curve. The observed value of ν is 3 whereas the Eq. (ii) requires ν value of 2. In addition the conductance data is comparable with that of potassium chloride suggesting the validity of Eq. (ii).

TABLE 1 — COMPLEXES OF TRIPHENYLSELENIUM CHLORIDE WITH LEWIS ACIDS

Lewis acid	Stoichiometric composition	Physical state, colour and m.p. (°C)	$\Lambda_M^{25^\circ}$ (ohm ⁻¹ cm ² mole ⁻¹)*	Se (%)		Cl (%)	
				Found	Reqd	Found	Reqd
BCl ₃	(C ₆ H ₅) ₃ SeCl·BCl ₃	White solid, 104-5	25.86	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 ₃	(C ₆ H ₅) ₃ SeCl·SO ₃	Colourless viscous liquid	—	18.40	18.58	8.15	8.35
SeO ₃	(C ₆ H ₅) ₃ SeCl·SeO ₃	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

*Molar conductance was determined in nitrobenzene.

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



Hydrochloric acid behaves as a non-electrolyte in fluorosulphuric acid. The conductance of triphenylselenium chloride is comparable with that of potassium fluorosulphate in fluorosulphuric acid. Thus it is clear that it behaves as a chloride ion donor.

X-ray study¹³ has revealed that the orthorhombic crystals of (C₆H₅)₃SeCl possess the space group Pna-C_{2v} (ref. 9) with four molecules of triphenylselenium chloride in a unit cell. Beg and Shaikh¹⁴ have elucidated the structure of triphenylselenium chloride on the basis of IR* and UV spectra particularly regarding the manner of orientation of the rings but no attempt has been made to study the (Se-C) and (Se-Cl) frequencies.

Recently Wynne and George³ have assigned (Se-C) and (Se-Cl) frequencies in organo-selenium compounds. A comparison of the infrared spectra of diphenylselenide and diphenylselenium dihalide are of assistance in interpreting the IR spectra of triphenylselenium chloride. On analogy, the bands at 472 and 484 are assigned to symmetric and antisymmetric (Se-C) stretching frequencies. The band appearing at 328 is assigned to (C-Se-C) deformation mode.

Further evidence of the ionic nature of triphenylselenium chloride is obtained from a study of its complexes with the Lewis acids, viz. SbCl₅, SO₃, SeO₃, BCl₃, AlCl₃, PCl₅, SnCl₄, GeCl₄ and TiCl₄. The general properties of these moisture-sensitive compounds are given in Table 1.

The higher phenyl modes are not being reported in all the complexes except that of sulphur trioxide and selenium trioxide as they virtually remain unchanged from the parent compound.

In the boron trichloride adduct only one band of sharp intensity at 690 is observed whereas at 480 in the case of aluminium trichloride adduct. The band appearing at 690 in the case of boron trichloride adduct could be easily assigned to BCl₄ species

as the characteristic absorption band of BCl₄⁻ in KBCl₄ and C₆H₅NHBCl₄ occur at 660 and 690 cm⁻¹ (ref. 15). The band at 660 was not considered as triphenylselenium chloride itself absorbs very strongly at 660 due to skeletal vibration. The new band at 480 in the aluminium trichloride adduct is assigned to AlCl₄⁻ species¹⁶.

Six intense bands at 532, 560, 585, 1047, 1275 and 1150 confirm the presence of chlorosulphate group¹⁷ (C_{3v}) 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 SeO₃Cl⁻ (chloroselenate) group¹⁸.

The assignments of the observed bands at 330 in the case of titanium tetrachloride adduct and at 323 in tin tetrachloride adduct are in agreement with those of related hexahalo species (MX₆²⁻) as these are in the regions where the characteristic absorption bands arising from [TiCl₆]²⁻ and [SnCl₆]²⁻ species occur^{19,20}. No assignment could be made to [GeCl₆]²⁻ species as the (Se-C) vibration in the adduct of germanium tetrachloride overlapped with the characteristic absorption of [GeCl₆]²⁻ species²⁰. 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 [SbCl₆]⁻ and [PCl₆] respectively²⁰.

In all the complexes the (Se-C) vibrations are lowered by about 15 cm⁻¹ as compared with that of triphenylselenium 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.

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*IR ν_{max} throughout the paper in cm⁻¹.

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