

ANTIMONY(V) AS ACCEPTORS

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Abstract

Lewis acidity of antimony(V) pentahalides and their organo substituted derivatives is well known. SbX₅ acts as a strong acceptor towards halide ion as compared to antimony trihalide due to presence of two more electronegative halogen atoms in antimony pentahalide makes it better acceptor. Hexacoordinated organoantimony(V) complexes including chelating ligands are also known and hexacoordination and heptacoordination environment have been suggested for such compounds. The substitution of hydrocarbon groups bound to antimony by trifluoromethyl or pentafluorophenyl groups enhances the Lewis acidity of antimony facilitating the formation of neutral adducts. Such properties have mainly been investigated with organoantimoy(V) halides. As expected successive replacement of an organic group by halogen atom increases acceptor strength of antimony(V) compounds.

Key words

Antimony(V); hexacoordinate; heptacoordinate; chelate; trifluoromethyl

Introduction

Lewis acidity of antimony(V) pentahalides with a variety of Lewis bases which may be oxygen donors (Ph₃PO, R₂SO, Cl₂SO), sulphur donors (R₂S, RSH), nitrogen donors (C₅H₅N, R₃N) and chlorine donors (NOCl, TeCl₄, Me₃SbCl₂) has been reported and the majority of the adducts conform 1:1 stoichiometry (Abel *et al.* 1969). SbX₅ act as acceptor towards halide ion forming the complex of the type M[SbX₆] [M = alkali metal, R₄N⁺], in which antimony moiety acts as anion. Substitution

of one or two chlorine atom(s) by phenyl group(s) in SbCl₃ still leaves the molecules with acceptor properties. Substitution of three chlorine atoms by organic group also leaves the molecules with some acceptor properties provided that the substituted group should be strongly electronegative for e.g. (CF₃)₃SbCl₂ and (C₆F₅)₃SbCl₂ which form weak complexes with pyridine (Dale *et al.*, 1957). Given below is summary of the complex forming tendency of antimony in its pentavalent state containing (mainly halide, X) and organic groups R (R = CH₃, C₆H₅, CF, *p*-XC₆H₄; X = CH₃, Cl, Br etc.).

Neutral complexes of organoantimony(V) compounds

Mono and dialkyl antimony(V) halides, RSbX_4 and R_2SbX_3 are thermally unstable and decompose even at room temperature as such few studies have been made with these compounds (Poller, 1979). However, Nishii *et al.* have succeeded in stabilizing these compounds by substituting X atom with a chelating group or by adding an oxygen donor molecule and have studied the structure of resulting alkylantimony compounds (Nishii *et al.*, 1969) together with those of corresponding aryl-antimony derivatives (Nishii *et al.*, 1973). For example, for monomethyl antimony adducts, $\text{CH}_3\text{SbCl}_4 \cdot \text{L}$ (L = PyO or 4-CH₃PyO) in solution two isomeric forms (Fig. 1) and (Fig. 2) were suggested to be in equilibrium from the solvent dependent PMR spectra. And for dimethylantimony adducts, $(\text{CH}_3)_2\text{SbCl}_3 \cdot \text{L}$ (L = DMSO, HMPA, TPPO or PyO) in solution, an octahedral structure with *trans*-methyl configuration (Fig. 3) was suggested.

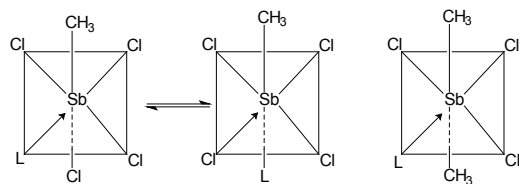
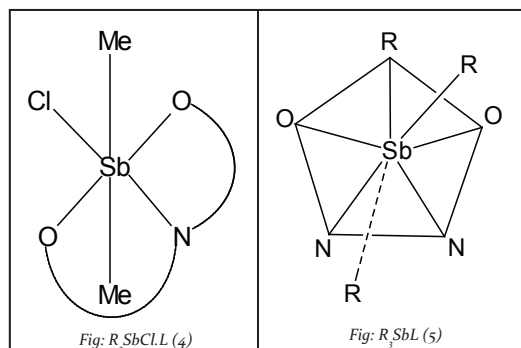


Fig: *cis*-(CH_3)₂ $\text{SbCl}_3 \cdot \text{L}$ adduct (1) Fig: *trans*-(CH_3)₂ $\text{SbCl}_3 \cdot \text{L}$ adduct (2) Fig: *trans*-(CH_3)₂ $\text{SbCl}_3 \cdot \text{L}$ (3)

Hexacoordinated organoantimony(V) complexes including chelating ligands such as acetylacetonate (Meinema *et al.*, 1972) and oxinate (Meinema *et al.*, 1969) are also known. Organoantimony(V) compounds, $\text{R}_n\text{SbX}_{5-n}$ (n = 2 and 3) also form complexes with Schiff bases (Saxena *et al.*, 1990). Hexacoordination and also heptacoordination environment have been suggested for organoantimony(V) compounds of type $\text{R}_2\text{SbCl}_3 \cdot \text{L}$ (L = tridentate ligand with ONO donor system) and R_3SbL (L = dibasic tetradentate ligand with ONNO donor system) suggesting figure (4) and (5) respectively (Saxena *et al.*, 1990).



Gopinathan have also reported chelated organoantimony complexes of the types Ph_3SbL_2 , LSbCl_4 (L = Salicylaldehyde, hydroxyquinoline, etc.).

The substitution of hydrocarbon group(s) bound to antimony by trifluoromethyl or pentafluorophenyl group(s) enhances the Lewis acid character of antimony facilitating the formation of neutral molecular adducts with oxygen, nitrogen and sulphur donor Lewis bases, for *e.g.*, $(\text{CF}_3)_3\text{SbCl}_2 \cdot \text{Py}$ (Trotman-Dickenson, 1973).

It is well established that Lewis acidity of the $\text{R}_n\text{SbX}_{5-n}$ derivatives in their reactions with various ligands as demonstrated by IR and NMR spectra increases with decreasing value of n. (Wardell, 1982). Such properties have mainly been investigated with organoantimony(V) halides (Okawara & Matsumura, 1976). As expected successive replacement of an organic group by halogen results in increasing the acceptor strength of the antimony(V) compounds. Thus Popov and Kondratenko have established the Lewis acidity sequences, as $\text{RSbX}_4 > \text{R}_2\text{SbX}_3 > \text{R}_3\text{SbX}_2$ with neutral monodentate oxygen donor *viz.* DMSO molecular adducts of the type $\text{RSbCl}_4 \cdot \text{DMSO}$ and $\text{R}_2\text{SbCl}_3 \cdot \text{DMSO}$ are readily isolated and their structure is established (Dale *et al.*, 1957). Such complexes have octahedral environment around antimony. Schiff base complexes of diorganoantimony(V) chlorides are also well known (Dibianca *et al.*, 1973).

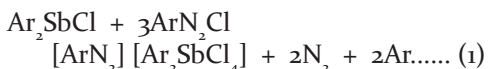
Anionic complexes of organoantimony(V) halides

Apart from neutral and chelated complexes of organoantimony(V) compounds R_nSbCl_{5-n} ($n = 1$ to 4), substantial work has reported on organoantimonates isolated in combination of bulkier cations. The anions $[R_nSbX_{6-n}]^{-1}$ ($n = 1$ to 3) correspond to hexahalogenoantimonates, $[SbX_6]^{-1}$ ($X = F, Cl$ or Br) (Fisher & Norman, 1994 and Hall & Sowerby, 1988) as well as to the mixed species, $[SbCl_nF_{6-n}]^{-1}$ ($n = 1$ to 5) and $[SbCl_5Br]^{-1}$ obtained as solid salts of suitable cations (Bentley *et al.*, 1972). The synthesis and spectral data of some compounds containing hexacoordinate organoantimony(V) anions of the type $[ArSbX_5]^{-1}$ ($X = Cl, Br$ or F) have been reported (Bertazzi *et al.*, 1975).

Dialkylantimony(V) derivatives are considered to be thermally unstable. Only dimethyl antimony trihalides, Me_2SbX_3 ($X = Cl, Br$) have been isolated and were found to undergo a gradual decomposition at room temperature into Me_2SbX and MeX . These alkyl compounds can be made thermally stable by complexing with halide (Beattie *et al.*, 1973) to form anion of the type $[Me_2SbCl_4]^{-}$ and also with Lewis base (Meinema & Noltes, 1974) and mono-, bi- or tridentate ligands (Meinema & Noltes, 1974).

Diarylantimony trichloride forms anions of the type $[Ar_2SbCl_4]^{-1}$ with amine hydrochloride (Doak *et al.*, 1952) and diazonium chloride. These decompose in the range 74° - $170^{\circ}C$ and it is claimed that decomposition temperature are sufficiently reproducible for characterization purposes. Campbell and White (1958), however, isolated and reported melting points for several unsymmetrical pyridinium tetrachlorodiarylantimonates (V), $[C_5H_5N] [p-EtO_2CC_6H_4SbArCl_4]$ ($Ar = p$ -tolyl, p -cyclohexylphenyl, 1-naphthyl or 3-diphenyl). The diazonium tetrachlorodiarylantimonates(V), $[ArN_2] [Ar_2SbCl_4]$ have also been obtained by the reaction between diarylchlorostibine and an aryldiazonium tetrachloroferrate (III) or an aryldiazonium

chloride.



This reaction is in contradiction of an earlier work which indicates the formation of expected diazonium salts, $[ArN_2]$, $[Ar_2SbCl_2]$. Reutov and coworkers were unable to obtain such compounds under a variety of reaction conditions and they doubt if these substances are capable of existence.

Apart from synthesis of tetrachlorodiarylantimonate(V), $[Ar_2SbCl_4]^{-1}$, Bertazzi *et al.* (Bertazzi *et al.* 1974) during their studies on the formation and structure of organoantimony(V) complexes succeeded in the preparation of mixed chlorohalogeno and mixed chloropseudohalogeno diphenyl antimonate(V) of the type $[M(i)][Ph_2SbCl_3X]$ (Where $M(i) = Me_4N$, $X = Cl, Br, N_3$ or $M(i) = Ph_4As$, $X = NCS$). Subsequently, the same authors reported diphenylantimonates(V) of the type $[Ph_4As] [Ph_2SbX_4]$ ($X = F, Cl, Br, N_3, NCS, X_4 = Cl_3Br, Cl_3N_3$) (Bertazzi 1976).

Meinema *et al.* (1977) have synthesized trichlorodiorganoantimony(V) compounds. R_2SbX_3 in which the antimony atom is a part of a hetrocyclic ring and converted to the same compound into the corresponding tetramethylammonium tetrachlorodiorganoantimonates $[Me_4N] [cis-R_2SbCl_4]$ which are hexacoordinated antimony(V) species in which Sb-Cl bonds are forced into *cis*-position as shown below.

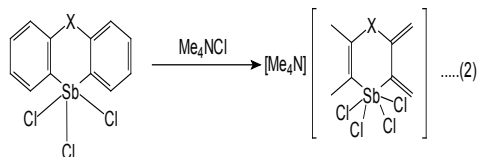


Fig: R_2SbX_3 (16)

Fig: $[Me_4N] [cis-R_2SbCl_4]$ (17)

($X = O^-, CH_2^-, -CH_2CH_2^-$)

Beattie *et al.* (1973) proposed the structure of

hexacoordinated diorganoantimony(V) anion in the complex $[\text{Me}_4\text{N}][\text{Me}_2\text{SbCl}_4]$ by IR and Raman spectra from which an octahedral structure with trans organic groups has been deduced. Later on Bertazzi *et al.* (1976) established a similar structure for analogous $[\text{Ph}_2\text{SbX}_4]$ and $[\text{Ph}_2\text{SbCl}_3\text{X}]^-$ species (X = halogen or pseudohalogen) by Raman and Vibrational spectra.

A number of diarylantimonates(V) anionic complexes have been prepared and isolated with tetraalkylammonium, tetraphenylphosphonium and stibonium cations. Solution phase and spectroscopic studies were made to elucidate their structures.

The existence of the anionic complexes in the series of R_3SbX_2 could only be demonstrated, only when $\text{R} = \text{CF}_3$, for *e.g.*, $[\text{C}_5\text{H}_5\text{N}][\text{R}_3\text{SbCl}_3]$, $[\text{NO}][\text{R}_3\text{SbCl}_3]$ and $[\text{H}][\text{R}_3\text{Sb}(\text{OH})_3]$.

Cationic complexes of organoantimony(V) compounds

In sharp contrast to well documented neutral and anionic complexes of $\text{R}_n\text{SbCl}_{5-n}$ ($n = 1$ to 4), reports on the isolation of cations of the type $[\text{R}_3\text{SbL}_2]^{+2}$, $[\text{R}_2\text{SbL}_3]^{+3}$, $[\text{RSbL}_4]^{+4}$ are rather limited (L = Neutral O, N, S, donor) (Wardell, 1982). The existence of complex cations of the type $[\text{R}_3\text{SbL}_2]^{+2}$, $[\text{R}_3\text{SbL-L}]$ and $[\text{R}_2\text{SbL}_3]^{+3}$ isolated in combination of bulkier anions *viz.*, BF_4^- , BPh_4^- , ClO_4^- etc. has been demonstrated by Goel & Prasad (1973) and later on by Premraj *et al.* (1992^a) and Premraj *et al.* (1992^b). In addition to these, cationic complexes of the types $[(\text{R}_3\text{SbL}_2)_2\text{O}][\text{ClO}_4]_2$ and $[\text{Ph}_3\text{Sb}(\text{H}_2\text{O})_2\text{O}(\text{ClO}_4)_2]$ are also known containing penta-coordinate cations (Goel & Prasad, 1972). Only recently hexacoordinate complex cations of the type $[\text{R}_2\text{SbL}_3(\text{OCIO}_4)]$ $[\text{ClO}_4]_2$ have been synthesised by Singhal and coworkers. However, reports on $[\text{R}_2\text{SbL}_3][\text{Y}]_3$ where Y is BF_4^- , BPh_4^- or PF_6^- are still lacking.

Conclusion

Complex formation tendency of antimony plays important role as result of this voluminous amount of work done on organo derivatives of antimony(V) such as anionic, cationic complexes and molecular adducts. However, a perusal of literature reveals that complex forming tendency of antimony(V) halides is yet to be accomplished.

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