

## Tri-*n*-butylphosphate Solvent System: Mechanism of Solvolytic & Substitution Reactions in Tri-*n*-butylphosphate

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Tri-*n*-butylphosphate (TBP) forms solvates with chlorides of Co(II), Mn(II), Cu(II), Fe(III), Cr(III), Sn(IV), Ti(IV) and Sb(V). The behaviour of these solutes in TBP is explained on the basis of a coordination model involving solvent coordination as an essential step. The equilibria proposed are supported by conductometric and visible, UV and IR spectral evidence. The solvolytic displacement of chloride ion in [(amine)<sub>2</sub>SnCl<sub>4</sub>] complexes (where amine is pyridine, 3- or 4-methylpyridine, isoquinoline or nicotinamide) in TBP is a pseudo-first order reaction. On addition of thionyl chloride to TBP solutions of the complexes, chloride ion replaces amine molecule from the substrate. Thermodynamic parameters support the assignment of S<sub>N</sub><sup>1</sup> mechanism for this reaction.

THE solvent extraction behaviour of tri-*n*-butylphosphate (TBP), an excellent coordinating solvent, has been reviewed by Marcus<sup>1</sup>. Almost all metals have been extracted using pure TBP and TBP diluted with carbon tetrachloride, benzene or cyclohexane. Adducts of Sn(IV) and Ti(IV) chlorides with TBP are reported to be electrolytes<sup>2,3</sup>. Recently, some complexes of TBP with metal ions have been reported<sup>4</sup>. However, there is no evidence regarding ligand substitution in metal complexes in this solvent.

Results of investigations on the behaviour of some metal halides and kinetics of solvolytic and substitution reactions of [(amine)<sub>2</sub>SnCl<sub>4</sub>] complexes in TBP are being reported here. In spite of its high viscosity, dilution of TBP with aqueous or alcoholic diluents is precluded because of the possibility of its hydrolysis to corresponding diesters<sup>3</sup>.

### Materials and Methods

CoCl<sub>2</sub>, MnCl<sub>2</sub>, CuCl<sub>2</sub>, FeCl<sub>3</sub> and CrCl<sub>3</sub> (AR) were rendered anhydrous by refluxing with anhydrous SOCl<sub>2</sub>. SnCl<sub>4</sub>, TiCl<sub>4</sub> and SbCl<sub>5</sub> were purified<sup>5</sup> before use. Pyridine, 2-, 3- and 4-methylpyridines, quinoline and isoquinoline were distilled over solid KOH before use. Nicotinamide and TBP (BDH) were used as such. The adducts of TBP with metal halides and [(amine)<sub>2</sub>SnCl<sub>4</sub>] complexes were prepared by reported methods<sup>5,6</sup>. The instruments, techniques and procedures for conductometric and spectral investigations were the same as reported previously<sup>5-7</sup>. The values of rate constants, energy, enthalpy and entropy of activation and frequency factor were calculated following the theory of Absolute Reaction Rates<sup>8</sup>.

### Results and Discussion

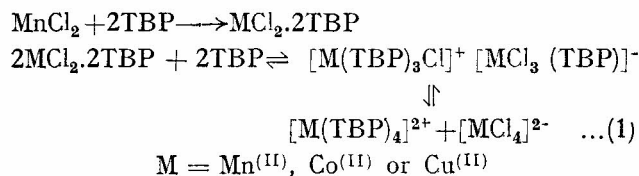
Solution behaviour of some metal halides in triethylphosphate (TEP)<sup>5</sup> and phosphoryl (V) trichloride<sup>9</sup> has already been reported. Structural similarities of TBP to these solvents provide

a basis for coordination model<sup>9</sup> to interpret the present reactions in TBP.

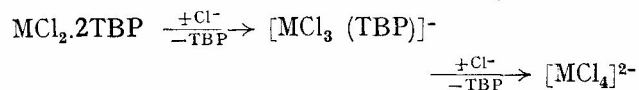
*Reactions of Mn(II), Co(II) and Cu(II) chlorides*—The conductance-composition (plotted as mole ratio of MCl<sub>2</sub>/TBP) curve shows inflection at 1:2 mole ratio indicating formation of adducts of the type MCl<sub>2</sub>.2TBP. Solid adducts of this composition have also been prepared and characterized. These adducts are soluble in TBP and conductance of their solutions indicates their ionic character. Solutions of chlorides of Mn(II), Co(II) and Cu(II) (5.0 × 10<sup>-5</sup> M) in TBP have specific conductance values of 0.85 × 10<sup>-4</sup>, 2.4 × 10<sup>-4</sup> and 3.5 × 10<sup>-4</sup> ohm<sup>-1</sup> cm<sup>-1</sup> respectively. These values register marginal increase on the addition of LiCl (0.5 M solution in TBP). It is inferred that M<sup>2+</sup> (solv.), MCl<sup>+</sup> (solv.), MCl<sup>2-</sup> (solv.) and [MCl<sub>4</sub>]<sup>2-</sup> ions are formed in dilute solutions of MCl<sub>2</sub> in TBP.

Presence of [MCl<sub>4</sub>]<sup>2-</sup> is corroborated by electronic spectra of solutions of metal chlorides (0.5 × 10<sup>-4</sup> M) in TBP. The spectrum of CoCl<sub>2</sub> solution has characteristic maxima<sup>10,11</sup> at 690, 636 (sh.) and 610 nm in the visible region and at 1690, 1775 and 2100 nm in the near IR region. Addition of two moles of lithium chloride has no effect on the spectrum suggesting that the principal absorbing species is [CoCl<sub>4</sub>]<sup>2-</sup>. Characteristic absorption maxima for solutions of (Bu<sub>4</sub>N)<sub>2</sub>[CoCl<sub>4</sub>] in TBP are virtually identical with those for CoCl<sub>2</sub> in TBP. This also supports the formation of [CoCl<sub>4</sub>]<sup>2-</sup>.

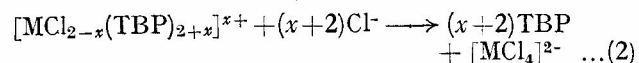
In the case of CuCl<sub>2</sub> solutions, with or without the addition of two moles of lithium chloride, electronic absorption bands are observed at 484 and 426 nm, which are characteristic<sup>12,13</sup> of [CuCl<sub>4</sub>]<sup>2-</sup> ion in solution. Similarly, the spectrum of MnCl<sub>2</sub> solution exhibits a maximum at 420 and a shoulder at 350 nm and is identical with that of [Bu<sub>4</sub>N]<sub>2</sub>[MnCl<sub>4</sub>] in TBP suggesting presence of [MnCl<sub>4</sub>]<sup>2-</sup> ions. Behaviour of chlorides of Co(II), Mn(II) and Cu(II) can thus be interpreted through a coordination model<sup>9</sup> involving the equilibria (1).



The above equilibria are supported by conductometric titrations between  $(\text{C}_2\text{H}_5)_4\text{NCl}$  and metal chlorides in TBP. The curves are characterized by sharp breaks at 1:1 and 2:1 molar ratios and indicate the occurrence of the following reactions:



Participation of chloride ions also involves conversion of cationic metal species to the anionic tetrachlorometallate ion (Eq. 2).

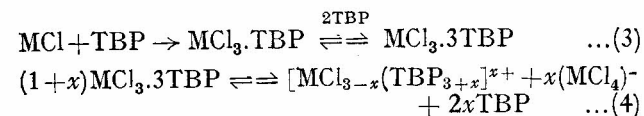


Infrared spectra of the adducts show that  $\nu\text{P}=\text{O}$  frequency of TBP shifts from 1272 to 1210, 1235 and 1224  $\text{cm}^{-1}$  for  $\text{CoCl}_2 \cdot 2\text{TBP}$ ,  $\text{MnCl}_2 \cdot 2\text{TBP}$  and  $\text{CuCl}_2 \cdot 2\text{TBP}$  respectively. The shift observed for TBP is of the same order as for coordination of  $(\text{C}_6\text{H}_5)_3\text{PO}$  and  $(\text{C}_2\text{H}_5\text{O})_3\text{PO}$  (ref. 6). This indicates coordination of TBP through phosphoryl oxygen atom and supports the above mechanistic proposals.

*Reactions of Fe(III) and Cr(III) chlorides* — Although conductivity of pure TBP is very low, addition of small amounts of  $\text{FeCl}_3$  ( $1 \times 10^{-4}\text{M}$ ) or  $\text{CrCl}_3$  ( $1 \times 10^{-5}\text{M}$ ) give conducting solutions. The plot of specific conductance versus molar ratio of metal chloride/TBP at 35° shows sharp inflections at 1:1 and 3:1 mole ratio (TBP: metal chloride). The specific conductance corresponding to 1:1 composition is  $1.2 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$  for  $\text{FeCl}_3$  and  $0.6 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$  for  $\text{CrCl}_3$ .

Solid addition compounds of 1:1 stoichiometry have also been isolated by refluxing the reactants in required ratio in  $\text{CCl}_4$  medium. These compounds are soluble in TBP and the solutions have appreciable conductance. Addition of  $(\text{C}_2\text{H}_5)_4\text{NCl}$  ( $1 \times 10^{-4}\text{M}$ ) to dilute solutions of  $\text{FeCl}_3$  or  $\text{CrCl}_3$  increases conductance only marginally. It is, therefore, inferred that TBP solutions of metal chlorides have ions which exist prior to the addition of tetraethylammonium chloride.

Behaviour of  $\text{FeCl}_3$  or  $\text{CrCl}_3$  in TBP may be explained through the formation of a donor-acceptor complex (Eq. 3) and replacement of chloride ion by TBP in a solvolytic reaction (Eq. 4) on the basis of capacity of Fe(III) and Cr(III) to acquire both six and four coordination.

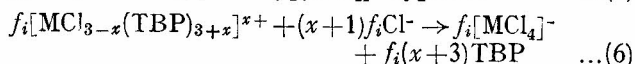


M = Fe(III) or Cr(III)

The existence of  $[\text{FeCl}_4]^-$  in dilute solutions is corroborated by electronic spectrum of  $\text{FeCl}_3$  ( $1 \times 10^{-5}\text{M}$ ) which exhibits maxima<sup>9</sup> at 662, 410 and

352 nm in the visible region. General shape of the curve and absorption maxima for solutions of  $(\text{C}_2\text{H}_5)_4\text{N}[\text{FeCl}_4]$  in TBP are identical with those for  $\text{FeCl}_3$  in TBP. Fe(III) and Cr(III) are also known to be extracted by pure TBP and TBP-HCl mixtures as  $\text{MCl}_3 \cdot 3\text{TBP}$  at low concentration of HCl and as  $\text{H}(\text{TBP})_2\text{MCl}_4$  at higher concentrations of  $\text{HCl}^3$ . This supports the proposed solution behaviour of Fe(III) and Cr(III) in TBP.

The conductometric titrations between metal chlorides and  $(\text{C}_2\text{H}_5)_4\text{NCl}$  in TBP exhibit sharp break in the curves at 1:1 molar ratio corresponding to the formation of  $[\text{MCl}_4]^-$ . It appears that in the presence of excess chloride ions, all Fe(III) and Cr(III) species are converted to  $[\text{FeCl}_4]^-$  and  $[\text{CrCl}_4]^-$  in accordance with Eqs. (5) and (6).

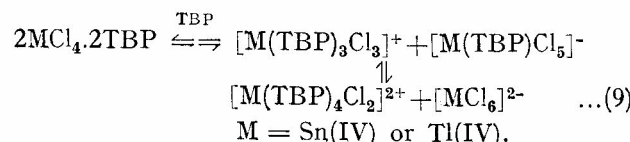
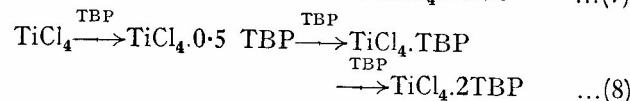
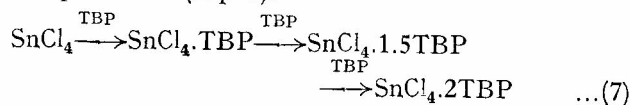


where  $f_i$  is the fraction of total metal chloride present, as the  $i$ th species.

The above solute-solvent interactions are supported by IR spectra of the adducts. There is a large downward shift ( $\Delta\nu\text{P} = 0$  equal to 112 and 90  $\text{cm}^{-1}$  for  $\text{CrCl}_3$  and  $\text{FeCl}_3$  respectively) in phosphoryl oxygen band of TBP together with the corresponding small increase in P-O-C and O-C, absorption bands, suggesting coordination of TBP.

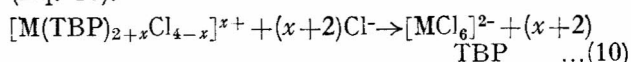
*Reactions of Sn(IV) and Ti(IV) chlorides* — Sn(IV) and Ti(IV) chlorides are miscible with TBP in all proportions. Inflections in the plot of specific conductance versus mole ratio of  $\text{MCl}_4/\text{TBP}$  correspond to the formation of  $\text{SnCl}_4 \cdot \text{TBP}$ ,  $2\text{SnCl}_4 \cdot 3\text{TBP}$  and  $\text{SnCl}_4 \cdot 2\text{TBP}$  and  $2\text{TiCl}_4 \cdot \text{TBP}$ ,  $\text{TiCl}_4 \cdot \text{TBP}$  and  $\text{TiCl}_4 \cdot 2\text{TBP}$ . Identical results have been obtained in excess TBP and the resultant solutions are conducting.

Dilute solutions of  $\text{SnCl}_4$  ( $0.3 \times 10^{-4}\text{M}$ ) and  $\text{TiCl}_4$  ( $1 \times 10^{-4}\text{M}$ ) have specific conductance values of  $1.6 \times 10^{-3}$  and  $8.0 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$  respectively which are much higher than those of the components. Far IR spectra of these solutions show  $\nu\text{Sn-Cl}$  and  $\nu\text{Ti-Cl}$  absorption bands at 318 and 458  $\text{cm}^{-1}$  respectively which are characteristic bands for  $[\text{SnCl}_6]^{2-}$  and  $[\text{TiCl}_6]^{2-}$  ions<sup>5,6</sup>. The formation of  $[\text{MCl}_6]^{2-}$  may be due to the coordination of TBP in such a way that the adducts with metal chlorides, which subsequently ionise through a solvolytic reaction, are produced (Eq. 7).



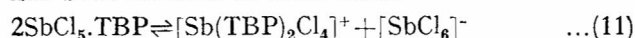
Addition of lithium chloride to dilute solutions of the Lewis acids leads to increased conductance suggesting stronger nucleophilic behaviours of chloride

ion as compared to TBP. This tendency of the chloride ion converts cationic species to  $[\text{MCl}_6]^{2-}$  (Eq. 10).



This is supported by conductance-composition curves for the titration of  $\text{SnCl}_4$  or  $\text{TiCl}_4$  versus chloride ion in TBP. There are two breaks in the curves corresponding to mole ratio of one and two chloride ions per metal chloride.

*Reactions of Sb(V) chloride* — The plot of specific conductance against mole ratio of  $\text{SbCl}_5/\text{TBP}$  at  $35^\circ$  indicates formation of the adduct  $\text{SbCl}_5 \cdot \text{TBP}$  which is soluble in excess TBP. Specific conductance of  $\text{SbCl}_5 (1 \times 10^{-4} \text{M})$  in TBP is very high ( $1.4 \times 10^{-3} \text{ohm}^{-1} \text{cm}^{-1}$ ). This increase in conductance suggests the formation of ionic species due to the formation and subsequent ionization (Eq. 11) of  $\text{SbCl}_5 \cdot \text{TBP}$ , which has been isolated in solid state.



The observed molar conductance of  $\text{SbCl}_5 \cdot \text{TBP}$  in nitrobenzene is in the range  $20\text{--}30 \text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$  for its dilute solutions, which indicates that it is a uni-univalent electrolyte.

The formation of  $[\text{SbCl}_6]^-$  is supported by the far IR spectra of  $\text{SbCl}_5 \cdot \text{TBP}$  and of its solution in TBP. In the spectrum of monosolvate,  $\nu\text{Sb-Cl}$  appears at  $365 \text{cm}^{-1}$  (compared to  $376 \text{cm}^{-1}$  in pure  $\text{SbCl}_5$ )<sup>5</sup>, whereas in the spectra of its solution in TBP,  $\nu\text{Sb-Cl}$  appears at  $346 \text{cm}^{-1}$  which is characteristic for  $[\text{SbCl}_6]^-$  (ref. 5) species.

Electric conductance changes only slightly ( $1.2 \times 10^{-3} \text{ohm}^{-1} \text{cm}^{-1}$ ) when  $\text{LiCl}$  is added to solutions of  $\text{SbCl}_5$  in TBP. In view of the fact that chloride ion is a stronger nucleophile than TBP, reaction (12) is likely to take place in solution.



When  $\text{SbCl}_5$  is titrated conductometrically with  $\text{LiCl}$  (in TBP), the curve shows a break corresponding to  $\text{SbCl}_5 : \text{Cl}^-$  ratio of 1:1. The formation of  $[\text{SbCl}_6]^-$  can be explained according to reaction (13)  $\text{SbCl}_5 \cdot \text{TBP} + \text{Cl}^- \rightarrow [\text{SbCl}_6]^- + \text{TBP}$  ... (13)

$\text{Sn}$ ,  $\text{Ti}$  and  $\text{Sb}$  exist as hexavalent coordinated species in these solutions<sup>14</sup>.

The proposed equilibria are in agreement with the IR spectra of TBP and its mixtures with  $\text{SnCl}_4$ ,  $\text{TiCl}_4$  and  $\text{SbCl}_5$ . The downward shift of  $\nu\text{P} = \text{O}$  of TBP ( $\Delta\nu\text{P} = \text{O}$  is 102, 40 and  $122 \text{cm}^{-1}$  for  $\text{SnCl}_4$ ,  $\text{TiCl}_4$  and  $\text{SbCl}_5$  solvates respectively) and the corresponding small rise in the  $\nu\text{P-O-C}$  and  $\nu\text{O-C}$  suggests coordination through phosphoryl oxygen atom of TBP which supports the coordination model for reactions of the Lewis acids in TBP.

*Nucleophilic substitution reactions of octahedral Sn(IV) complexes in TBP* —  $\text{Sn(IV)}$  chloride forms octahedral complexes with pyridine, 2-, 3- and 4-methylpyridines, quinoline, isoquinoline and nicotinamide. X-ray analysis<sup>15</sup>, Mössbauer<sup>16</sup> and IR spectral investigations<sup>14</sup> on these complexes indicate that amine molecules are in *trans* position.

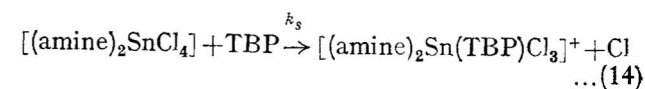
Kinetics of solvolytic and substitution reactions of  $[(\text{C}_5\text{H}_5\text{N})_2\text{SnCl}_4]$  in triethylphosphate (TEP) have

already been reported<sup>6</sup>. Since TBP is isostructural with TEP except that it has much larger molecular volume, kinetics of these reactions in this solvent is expected to follow a similar pattern.

Assuming that ion-pair formation is negligible, conductance values of the solutions measured after a considerable time interval are considered to be proportional to concentrations of the ions formed. To substantiate this assumption, conductance of solution after infinite time is plotted against square-root of the concentration of the complex. The plot obtained is linear with a slope of less than unity in the range  $0.2\text{--}0.8 \text{mM}$ . But at higher concentrations, there is a departure from this behaviour indicating considerable ion-pairing. Therefore, the reactions have been studied at extremely low concentrations of the complex for which activity coefficients are assumed to be unity.

Though base strengths of 2-methylpyridine (5.97) and quinoline (4.80) are of the same order as that of pyridine (5.18) and isoquinoline (5.46), the behaviour of their octahedral tin complexes in TBP is strikingly different. Solutions of  $[(2\text{-CH}_3\text{py})_2\text{SnCl}_4]$  (A) and  $[(\text{C}_9\text{H}_7\text{N})_2\text{SnCl}_4]$  (B) immediately attain  $\Lambda_M$  value equal to that for uni-univalent electrolytes [ $(\text{C}_2\text{H}_5)_4\text{NCl}$  in TBP has  $\Lambda_M$  equal to  $3.5 \text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ ]. However, for the complexes with pyridine, 3- and 4-methylpyridines, isoquinoline and nicotinamide, conductance increases slowly with time. Thus, complexes (A) and (B) instantaneously ionize to yield chloride ion and stable cations  $[(2\text{-CH}_3\text{py})_2\text{SnCl}_3]^+$  and  $[(\text{C}_9\text{H}_7\text{N})_2\text{SnCl}_3]^+$  respectively. In IR spectra of solutions of (A) and (B) in TBP. The phosphoryl frequency of TBP at  $1272 \text{cm}^{-1}$  is lowered to  $1170 \text{cm}^{-1}$  (broad band) along with a band at  $1272 \text{cm}^{-1}$  with markedly reduced intensity. However, there is no absorption band around  $480 \text{cm}^{-1}$  in the far IR region characteristic of Sn-O band. Therefore, it is assumed that the coordination of TBP to tin does not occur. Although some solvation of cationic species is not unlikely, steric factors, which are responsible for cleavage of Sn-Cl bond in solution, may restrain the cations from taking up TBP molecule into the coordination sphere of tin. Displacement of amine molecule in preference to chloride ion is unlikely because this reaction will not result in any ion formation.

The conductance of dilute solutions of  $[(\text{amine})_2\text{SnCl}_4]$  (amine = pyridine, 3- or 4-methylpyridine, isoquinoline and nicotinamide) in TBP increases exponentially with time. Values of molar conductance after infinite time,  $\Lambda_{M\infty}$ , determined for two separate runs for each complex, correspond to the value for a uni-univalent electrolyte in TBP. This suggests solvolytic reaction where chloride ion is replaced by a molecule of TBP (Eq. 14).



$\Lambda_{M\infty}$  values indicate that ionization of amine molecule in preference to or simultaneously with chloride ion is improbable. This is also supported by the fact that addition of amine to the solution of its complex in TBP does not affect the rate.

TABLE 1 — FIRST ORDER RATE CONSTANTS (SEC<sup>-1</sup>) FOR SOLVOLYTIC DISPLACEMENT OF CHLORIDE ION IN THE COMPLEXES [(AMINE)<sub>2</sub>SnCl<sub>4</sub>] IN TRI-*n*-BUTYLPHOSPHATE

(30° ± 0.1°)		(35° ± 0.1°)		(40° ± 0.1°)		(45° ± 0.1°)		Δ <i>H</i> * kcal/mole	Δ <i>S</i> * (EU)
[C]mM	10 <sup>5</sup> × <i>k</i> <sub>s</sub>	[C]mM	10 <sup>5</sup> × <i>k</i> <sub>s</sub>	[C]mM	10 <sup>5</sup> × <i>k</i> <sub>s</sub>	[C]mM	10 <sup>5</sup> × <i>k</i> <sub>s</sub>		
[Py <sub>2</sub> SnCl <sub>4</sub> ]									
0.5972	12.4	0.5272	27.3	0.9310	66.0	1.123	131.7	29.8	15.5
0.5054	14.3	0.7630	26.0	1.054	54.7	1.123	110.9		
[(3-CH <sub>3</sub> py) <sub>2</sub> SnCl <sub>4</sub> ]									
1.052	17.6	1.161	39.1	1.097	88.5	0.7175	181.2	28.2	17.3
0.8975	18.4	0.7175	43.7	1.300	74.2	0.9823	168.4		
[(4-CH <sub>3</sub> py) <sub>2</sub> SnCl <sub>4</sub> ]									
0.6046	29.6	0.7850	48.3	1.119	65.6	0.8590	142.7	21.3	5.2
0.7833	23.7	0.8590	39.9	1.075	78.0	0.6046	163.2		
[(iso-C <sub>5</sub> H <sub>7</sub> N) <sub>2</sub> SnCl <sub>4</sub> ]									
0.6550	15.3	0.5400	33.9	0.6670	83.4	0.5400	156.3	31.4	27.1
0.6265	16.2	0.5495	36.1	0.6363	105.5	0.6363	141.3		
[(C <sub>5</sub> H <sub>4</sub> NCONH <sub>2</sub> ) <sub>2</sub> SnCl <sub>4</sub> ]									
0.5145	21.5	0.8029	41.3	0.7900	73.9	0.5937	120.3	22.9	0.2
0.5159	18.6	0.8213	40.3	0.5200	91.5	0.2576	131.6		

The first order plot of  $\log \frac{\Lambda_{M_t}}{\Lambda_{M_\infty} - \Lambda_{M_t}}$  against time *t* (in sec), where  $\Lambda_{M_\infty}$  is molar conductance at any finite time *t* and  $\Lambda_{M_t}$  is the value for complete ionization after 48 hr, is linear passing through origin. The values of specific rate constant, *k*<sub>s</sub>, calculated from slopes of these plots at four different temperatures, are summarized in Table 1. Solvolytic displacement of chloride ion in the substrate may be due to mass effect of the solvent.

The magnitude of the first order rate constants depends upon the [complex]. The solvolytic reaction following first order kinetics may follow either a dissociation mechanism or a displacement mechanism involving solvent TBP as the attacking nucleophile. The reaction probably corresponds to a bimolecular process (and hence S<sub>N</sub>2 mechanism) but gives first order kinetics because the concentration of one of the reactants (the solvent) is overwhelmingly large and is thus almost constant during the reaction. This is therefore, a pseudo-first order reaction proceeding via a displacement mechanism. The observed variation of Δ*S*\* from ~0 to +27 e.u. for different compounds conform to S<sub>N</sub>2 solvolysis.

On the basis of experimental observations, rate equation (15) is postulated:

$$\text{Rate} = k_s [\text{complex}]$$

where rate varies linearly with [complex].

These proposals are supported by IR spectra of mixtures of [(amine)<sub>2</sub>SnCl<sub>4</sub>] and TBP. In the spectrum of (amine)<sub>2</sub>SnCl<sub>4</sub> when it is freshly mixed with TBP, positions of ν<sub>P</sub> = 0 and ν<sub>Sn-Cl</sub> remain unchanged indicating that TBP is not coordinated to tin. However, spectrum recorded 48 hr after their mixing shows that halogen displacement takes place. Formation of [(amine)<sub>2</sub>Sn(TBP)Cl<sub>3</sub>]<sup>+</sup> in solutions is indicated by the following:

(i) A marked decrease in the ν<sub>P</sub> = O of TBP from 1272 to a band around 1152 cm<sup>-1</sup>. The shift observed

in this system is of the same magnitude as that for [(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>SnCl<sub>4</sub>]-TEP system where [(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>Sn(TEP)Cl<sub>3</sub>]<sup>+</sup> is formed as a result of solvolytic reaction<sup>6</sup>.

(ii) ν<sub>C-H</sub> observed at 3005 cm<sup>-1</sup> in pyridines, shifts to a lower value in the region 2945-2960 cm<sup>-1</sup>. Bands of pyridine at 1583, 1572, 1483 and 1439 cm<sup>-1</sup> due to ν<sub>C</sub> ... C and ν<sub>C</sub> ... N are shifted to higher spectral region. Amine ring vibrations at 1220 and 995 cm<sup>-1</sup> shift to 1258 and 1016 cm<sup>-1</sup> respectively. C-H out-of-plane bending modes at 748 and 705 cm<sup>-1</sup> in pyridine occur at lower region in the spectrum of complex-TBP system. Amine ring vibration at 600 cm<sup>-1</sup> due to in-plane bending is shifted to 620-640 cm<sup>-1</sup> in these spectra. This indicates the presence of pyridines in the cationic species.

(iii) Appearance of a new absorption band in the range 450-485 cm<sup>-1</sup> along with a broad band at 530 cm<sup>-1</sup> assigned to ν<sub>Sn-O</sub> (ref. 6).

(iv) The ν<sub>Sn-Cl</sub> (ref. 6) of the complexes present around 335 cm<sup>-1</sup> shifts to the region 308-315 cm<sup>-1</sup> along with a weak band around 238 cm<sup>-1</sup>.

The steric, electromeric, conjugative and inductive effects of the amine molecules influence the rate of solvolytic reaction. The conjugative electron displacement effect is not significantly involved in methylpyridines<sup>18</sup>. Therefore, only steric and +*I* effect of methyl groups present at different positions in pyridine nucleus are considered. A perusal of Table 1 indicates that rate of displacement of chloride ion increases with increase in basicity of amine. However, there is no linear relationship. Observed order of reactivity for the amine complexes; 4-CH<sub>3</sub>py > 3-CH<sub>3</sub>py > py is consistent with theoretical deductions that +*I* effect of methyl group at different positions promotes unimolecular reaction through electron release towards the metal atom. But, the complex (A) with 2-CH<sub>3</sub>py is kinetically labile. This suggests the presence of contribution due to steric effects. The intensity of the

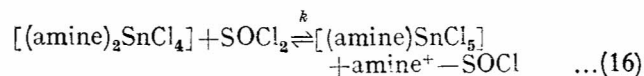
inductive effect of methyl group is small (because the  $pK_a$  values of amines differ by a factor of twenty, corresponding changes in the rates are not very large) and its direction is such that it enhances steric effects which appear to control the solvolytic reaction. Similar conclusions<sup>17,18</sup> have been drawn about methyl substituents attached to influencing amino ligands for solvolytic equation of complexes of the type *cis*-[Co(en)<sub>2</sub>(amine)Cl]<sup>2+</sup> in non-aqueous solvents.

A comparison of rates of displacement of chloride ion in the complexes [(nicotinamide)<sub>2</sub>SnCl<sub>4</sub>] and [(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>SnCl<sub>4</sub>] shows that the rate is faster for nicotinamide complex. The rate of this reaction for [(iso-C<sub>9</sub>H<sub>7</sub>N)<sub>2</sub>SnCl<sub>4</sub>] is greater with respect to pyridine complex. Nicotinamide and isoquinoline are stronger bases compared with pyridine and their complexes suffer from greater steric strain than the pyridine complex. Therefore, enhanced rates of solvolytic displacement of chloride ion may be ascribed to the steric effects.

The rate constants are temperature dependent and follow the Arrhenius equation  $k_s = Ae^{-(E_a/RT)}$ . Average  $k_s$  values have been used to evaluate frequency factor ( $A$ ), enthalpy and entropy of activation given in Table 1. Magnitude of  $A$  is the same as expected for unimolecular reactions<sup>9</sup>. However, less significant positive  $\Delta S^*$  values for 4-CH<sub>3</sub>py and nicotinamide complexes may be due to some bond formation in the transition state.

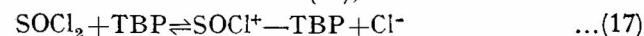
Addition of chloride ion to TBP solutions of the complexes appears to change the course of reaction. Solvolytic displacement of chloride ion is now less significant because the overall reaction is insensitive to the [Cl<sup>-</sup>] added to it. IR spectra of TBP solutions of complexes in the presence of SOCl<sub>2</sub> shows that  $\nu_P = O$  does not shift and there is no Sn-O absorption band in the range 475-525 cm<sup>-1</sup>. Therefore, TBP appears to act only as a medium.

$\Delta M$  of dilute solutions of the complexes in TBP in the presence of SOCl<sub>2</sub> increases with time and  $\Delta_\infty$  approaches maximum value corresponding to a 1:1 electrolyte in TBP. This indicates the occurrence of substitution reaction (16).

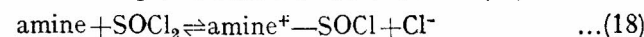


amine = py, 3- and 4-methylpyridines, isoquinoline and nicotinamide

Besides the reaction (17),



an electrophilic substitution reaction (18)



also furnishes chloride ions in the system<sup>6</sup>.

In the substitution reaction, chloride ion replaces amine molecule from the substrate [(amine)<sub>2</sub>SnCl<sub>4</sub>]. The rate is independent of [Cl<sup>-</sup>] but depends on [complex] (reaction has been studied for different complex to SOCl<sub>2</sub> mole ratios). It is, therefore, inferred that in the overall dissociation reaction, heterolysis of amine molecule is a slow process followed by immediate combination of chloride ion

TABLE 2 — FIRST ORDER RATE CONSTANTS AND  $\Delta G^*$  VALUES FOR THE AMINE SUBSTITUTION REACTION IN TBP AT (35+0.1°)

Complex	[C]mM	$10^5 \times k$ (sec <sup>-1</sup> )	[C]mM	$10^5 \times k$ (sec <sup>-1</sup> )	$\Delta G^*$ (kcal/mole)
[(Py) <sub>2</sub> SnCl <sub>4</sub> ]	0.6450	23.0	0.8720	20.0	23.23
[(3-CH <sub>3</sub> Py) <sub>2</sub> SnCl <sub>4</sub> ]	0.6380	24.6	0.9625	22.5	23.15
[(4-CH <sub>3</sub> Py) <sub>2</sub> SnCl <sub>4</sub> ]	0.6710	43.7	0.6710	40.6	22.79
[(iso-C <sub>9</sub> H <sub>7</sub> N) <sub>2</sub> SnCl <sub>4</sub> ]	0.6170	19.5	0.5977	21.8	23.29
[(C <sub>5</sub> H <sub>4</sub> NCONH <sub>2</sub> ) <sub>2</sub> SnCl <sub>4</sub> ]	0.8620	23.0	0.6270	26.3	23.06

to form [(amine)SnCl<sub>5</sub>]<sup>-</sup> which appears to be quite stable towards further substitution in TBP medium.

The decreasing order of reactivity for substitution reaction (Table 2) for various amine complexes is; 4-CH<sub>3</sub>py > nicotinamide > isoquinoline > 3-CH<sub>3</sub>py > py. The observed order of reactivity suggests that besides steric effects inductive effects of the amine molecules also contribute to the variation in the rates of reaction.

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