354. *Reaction Mechanisms in Organometallic Compounds. Comparative Solvolyses of Organotin and Organosilicon Chlorides.*

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The solvolyses of organotin chlorides R_3SnCl (R = Et, Pr^i, Bu^t, Ph) in ethanol, propan-2-ol, and water–dioxan have been studied. The behaviours of tin and silicon have been compared in solvolysis and hydrolysis of the tri*iso*propyl halides in propan-2-ol.

Alcoholysis and hydrolysis of organotin halides are rapid to positions of equilibrium which depend upon the medium and the nature of the alkyl group. When the latter is *iso*propyl and in propan-2-ol rates are measurable; when it is *tert.*-butyl solvolysis rates are measurable in ethanol and in propan-2-ol but solvolytic equilibrium lies further in favour of the undissociated halide. The solvolysis of tri*iso*propylsilyl chloride in propan-2-ol has an abnormally low steric factor and is catalysed by pyridine; hydrolysis in propan-2-ol is of second order and is not catalysed by pyridine.

Potentiometric, conductivity, and rate data are consistent with a synchronous displacement at tin and silicon in which steric effects are important in determining reactivity.

ALTHOUGH the mechanism of substitution at a saturated carbon atom is now well understood [1] kinetic–mechanistic studies of organosilicon halides are few [2-4] and none exists of organotin halides. Kinetic data on organosilicon halides have been interpreted in terms of (*a*) a quinquecovalent intermediate [2,4] and (*b*) a synchronous mechanism in which bond-making between silicon and the attacking nucleophile is dominant.[3] The balance of evidence on sterically-hindered monochlorosilanes favours the latter. There is no kinetic evidence for an S_N1 substitution at silicon; indeed the only siliconium ion appears to be the optically active sexaco-ordinated ion $(acac)_3Si^+$ (acac = acetylacetone).[5] Silicon halides are much more rapidly solvolysed than are carbon halides of analogous structure, and in chlorides R_3SiCl (R = alkyl) rates of substitution show marked dependence on the steric effectiveness of the alkyl group: only when R is branched (or is a bulky aromatic group) are rates measurable. Previous comparison of triorgano-silicon and -tin compounds [6] indicated than when R is simple rapid reactions are observed, but, whereas ethanolysis and hydrolysis of organosilicon compounds are essentially complete, with organotin compounds an equilibrium is reached.[6-8]

This paper describes the solvolysis of the halides R_3SnCl (R = Et, Pr^i, Bu^t, and Ph) in ethanol, propan-2-ol, and water–dioxan; comparison is made of the *iso*propyl compound with that of silicon.

EXPERIMENTAL

Preparation of Materials.—Triethyltin chloride. Commercial triethyltin hydroxide was treated with hydrochloric acid followed by potassium hydroxide, and filtered to remove diethyltin oxide; the hydroxide was reconverted into the chloride and purified by molecular distillation. The product contained traces of tetraethyltin which were allowed for subsequently.

*Tri*iso*propyltin chloride and di*iso*propyltin dichloride.* Stannic chloride–ether complex (0·063 mole) was alkylated with the stoicheiometric amount of *iso*propyl-lithium for formation of the trialkyl compound (0·189 mole; prepared in ether at –40°); a mixture of tetra*iso*propyltin and the mono- and di-chlorides in approximately equal amounts was obtained. The

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[1] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, ch. 7.

[2] Swain, Esteve, and Jones, *J. Amer. Chem. Soc.*, 1949, **71**, 943.

[3] Hughes, *Quart. Rev.*, 1951, **5**, 245; Allen, Charlton, Eaborn, and Modena, *J.*, 1957, 3668; Allen and Modena, *J.*, 1957, 3671.

[4] Shaffer and Flanigen, *J. Phys. Chem.*, 1957, **61**, 1591.

[5] Dhar, Doron, and Kirschner, *J. Amer. Chem. Soc.*, 1958, **80**, 753.

[6] Dennison, Thesis, London University, 1954.

[7] Rochow and Seyferth, *J. Amer. Chem. Soc.*, 1953, **75**, 2877.

[8] Kraus and Callis, *ibid.*, 1923, **45**, 2624; Kraus and Greer, *ibid.*, p. 2946.

dichloride was isolated by molecular distillation and resublimed *in vacuo* (Found: Cl, 25·0. Calc. for $C_6H_{14}Cl_2Sn$: Cl, 25·7%).

The monochloride was prepared [9] from the tetra-alkyltin, which was obtained by addition of stannic chloride (0·063 mole) to excess of *iso*propylmagnesium bromide (2 mol.) in ether. The ether was distilled off and the residue kept at 100° for 1 hr.; fractionation gave tetra*iso*propyltin (61·2 g.; 61%), b. p. 100·6—101·2°/8 mm. This was treated with stannic bromide (⅓ mol.) at 125—165°. The liquid phase consisted mainly of the monobromide (~90% w/w); unchanged tetra-alkyl and dibromide were removed by the following treatment which depends upon the insolubility of the alkyltin fluorides and the polymeric dialkyltin oxides. The mixture in ether was treated with a 20% w/v solution of potassium fluoride in 60% aqueous ethanol: the precipitated fluorides (Pr^i_3SnF, $Pr^i_2SnF_2$) were filtered off, extracted with ether to remove tetra*iso*propyltin, and then treated with concentrated hydrochloric acid and extracted with ether. The extract was treated with 10% w/v sodium hydroxide; the precipitated oxide $(Pr^i_2SnO)_n$ was filtered off. The filtrate ($Pr^i_3Sn{\cdot}OH$) in ether was converted into the chloride by concentrated hydrochloric acid and subjected to molecular distillation. The product was 99·95% pure.

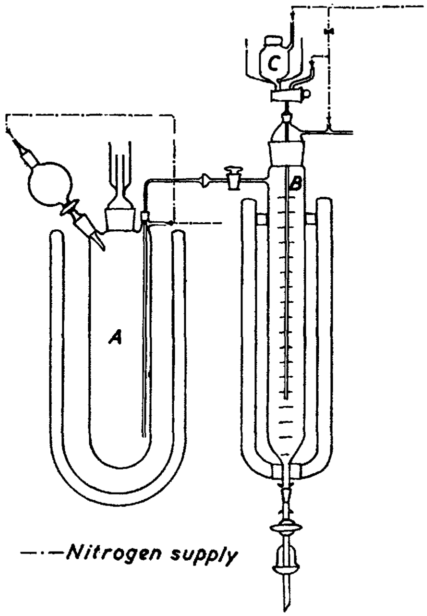

FIG. 1. *Apparatus for the preparation of* tert.-*butyl-lithium in ether at low temperature.*

tert.-*Butyl-lithium.* This was prepared by treatment of excess of lithium sand or wire with *tert.*-butyl chloride in ether at −55° to −60° for 4—4½ hr.

tert.-Butyl-lithium attacks ether; in the controlled alkylation of stannic chloride with ethereal *tert.*-butyl-lithium the concentration of derivative was determined by double titration in which the alkali formed by hydrolysis was titrated before and after coupling of the derivative with benzyl chloride.[10]

tert.-Butyl-lithium was prepared in a 400-ml. vessel kept at −55° to −65° (Fig. 1; *A*). When all the alkyl chloride had been added the temperature was lowered to −80°, and lithium chloride allowed to settle. The clear solution was then transferred by pressure of nitrogen to a 3·5 × 40 cm. tube (*B*) graduated in 10-ml. divisions. Samples of solution were transferred to a small vessel (*C*) by nitrogen pressure and removed for analysis by a 2-ml. hypodermic syringe *via* a vaccine-cap closure. The solution was then added to the calculated quantity of stannic chloride–ether complex.

Di-tert.-*butyltin dichloride and tri*-tert.-*butyltin chloride.*—The alkyl-lithium was added to a suspension of the stannic chloride–ether complex at 0°: addition in reverse order caused

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[9] Kocheskov, *Ber.*, 1933, **66**, 1661; *J. Gen. Chem. Russia*, 1934, **4**, 1359; 1935, **5**, 211.

[10] (*a*) Gilman and Haubein, *J. Amer. Chem. Soc.*, 1944, **66**, 1515; (*b*) Gilman and Clark, *J. Amer. Chem. Soc.*, 1947, **69**, 1499.

formation of coloured reduction products. Variation of the mole ratio $Bu^tLi : SnCl_4$ gave the following results. 3 : 1-*ratio*: Alkylation to the monochloride was incomplete and a product containing 55% of the monochloride was isolated. Molecular distillation followed by centrifugation at −10° enabled half of the dichloride present to be isolated. Attempts to purify the residue by the fluoride–hydroxide method (above) were unsuccessful owing to the partial solubility of the dihydroxide, $Bu^t_2Sn(OH)_2$, in ether. 6 : 1 *ratio*: A viscous liquid was isolated which gave a product containing 93% of monochloride on molecular distillation. 3·3 : 1 *ratio*: A product containing 90% of monochloride was isolated. 3·0 : 1·05 *ratio*: Treatment of the product in ether with potassium hydroxide gave a voluminous white precipitate; with concentrated hydrochloric acid this gave a 44% overall yield of the dichloride, which was purified by sublimation at 0·01 mm. (Found: Cl, 23·2. Calc. for $C_8H_{18}SnCl_2$: Cl, 23·35%).

The monochloride could not be obtained pure and the best sample (93% of monochloride) contained the dichloride as impurity. In solvolyses the effect of the dichloride was examined by separate solvolysis.

Triphenyltin chloride. Eastman Kodak material was recrystallised thrice from ethanol and sublimed *in vacuo* (m. p. 105°, lit., 104—108°). The material was 99% pure, the impurity being tetraphenyltin. Allowance was made for this in electrochemical experiments.

*Tri*iso*propylsilyl chloride.* This was prepared as previously described[10b] (b. p. 75·2—75·5°/7·6 mm., Found: Cl, 18·3. Calc. for $C_9H_{21}SiCl$: Cl, 18·4%).

Ethanol and propanol. Ethanol was dried over calcium oxide and distilled twice from sodium and ethyl phthalate in a baked-out fractionation apparatus: the water content of the product was 0·002—0·004% w/v.

Analytical reagent, peroxide-free propan-2-ol was dried by three methods: (i) distillation from lithium; (ii) a column method with calcium sulphate as the stationary phase; (iii) distillation from magnesium and iodine. Method (i) was satisfactory for the preparation of alcohol with water content about 0·02% w/v. Method (ii) was used with (iii) to obtain the driest samples: after the water concentration had been reduced to 0·02—0·03% w/v by method (ii) the alcohol was refluxed with magnesium powder and iodine for 8 hr. and then fractionated with intermittent take-off. Samples prepared in this way had water contents in the range 0·001—0·002% w/v.

Dioxan. This was purified as described by Vogel.[11]

Determination of Water Concentration.—A method based on Fischer's reagent was used.[12] A " dead-stop " electrometric method located the end-point of the titration: when the rates of titration were kept constant, results having a coefficient of variation of ±2% were obtained for water-content levels from 0·002 to 0·01% w/v.

Conductivity Measurements.—Four cells of conventional design were calibrated:[13] the constants were $0·0790_3$, $0·0208_9$, $0·0395_0$, $0·0438_0$. In two of these provision was made for passing a stream of dry nitrogen through the cell contents to expedite mixing and for adding halide samples to solvent contained in the cell without ingress of atmospheric moisture.

A high precision A.C. bridge with Wagner earth[14] was used for measurements of cell constant and equilibrium. For conductometric runs the Philips GM 4249 direct-reading A.C. bridge was more suitable: it was calibrated with standard resistances, and the accuracy and repeatability were then better than ±1% in the range 10^2—10^7 ohm.

Results of Solvolysis Experiments.—Solvolyses of organotin halides were followed conductometrically and those of tri*iso*propylsilyl chloride conductometrically and titrimetrically.

Organotin halides. Under the following conditions equilibrium values of conductivity were reached too rapidly for rate measurements to be made at 0°: triethyltin chloride in ethanol[6] and in propan-2-ol; tri*iso*propyltin chloride in ethanol; triphenyltin chloride in ethanol–acetone. Even at −80° the rates were not observable by conventional kinetic means. Measurements of conductivity as a function of water concentration in the range 1—25 × 10^{-3}M and extrapolation to zero water concentration showed that the halide conducted in the alcohol independently of residual water in the solvent.[15]

Measurable rate effects were observed with the tri*iso*propyltin compound in propan-2-ol.

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[11] Vogel, " Practical Organic Chemistry," Longmans, 1951, p. 175.

[12] Prince, *Analyst*, 1953, **78**, 607.

[13] Jones and Bradshaw, *J. Amer. Chem. Soc.*, 1933, **55**, 1780.

[14] Luder, *ibid.*, 1940, **62**, 89; Solomons, Thesis, London University, 1956.

[15] Rochow, Hurd, and Lewis, " The Chemistry of Organometallic Compounds," Wiley, 1957, p. 185; Rochow and Thomas, *J. Inorg. and Nuclear Chem.*, 1957, **4**, 205.

The effect (Fig. 2) depends on water concentration and temperature. The initial decrease of cell resistance, although too rapid to give accurate kinetic data, is slower than that observed with triethyltin chloride where a step-wise change of conductivity occurs on addition to the solvent with rapid mixing. The only inorganic compound possibly present in the tri*iso*propyltin chloride is a trace of di*iso*propyltin dichloride. The effect of the dichloride was examined by solvolysis in propan-2-ol: a step-wise change of conductivity was observed when the sample was added to the solvent, followed by a slight drift during several hours which could not account for the effects found with the monochloride.

The specific conductivity of tri*iso*propyltin chloride at concentrations $\sim 10^{-3}$M in ethanol at 0° is of the order of 0·2—0·3 × 10^{-6} ohm^{-1} cm.$^{-1}$: this is 10—15 times larger than the specific conductivity of propan-2-ol solutions under the same conditions. In the same alcohol the specific conductivity of solutions of the triethyl compound is 2—3 times larger than that of the tri*iso*propyl compound.

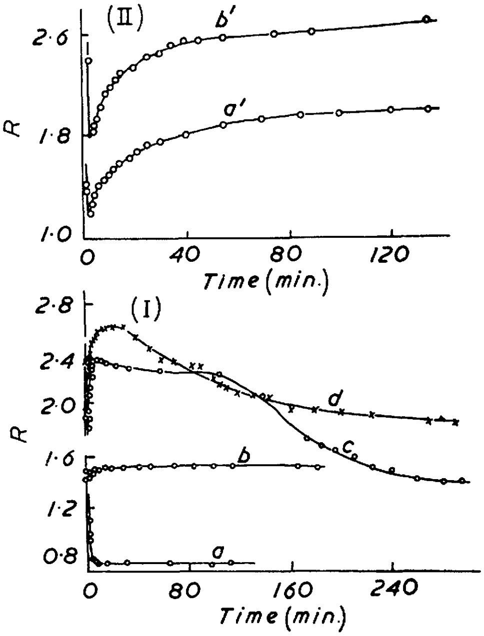


FIG. 2. *Resistance–time curves for solvolysis of tri*iso*propyltin chloride in propan-2-ol–water.*

R is cell resistance (ohm × 10^{-6}). (I) Runs at 0°: (*a*) [Halide] 0·0125M, [H_2O] 0·040M; (*b*) [Halide] 0·0085M, [H_2O] 0·0102M; (*c*) [Halide] 0·0105M, [H_2O] < 0·0004M; (*d*) [Halide] 0·0091M, [H_2O] < 0·0004M. (II) Runs at 25°: [H_2O] in each case <0·0004M; (*a*′) [Halide] 0·0108M; (*b*′) [Halide] 0·0045M.

The equivalent conductivity of ethanol solutions of tri-*tert.*-butyltin chloride at equilibrium was lower than that of tri*iso*propyltin chloride solutions at the same concentration, but the equilibrium value was not attained instantaneously. The slow approach of the conductivity to equilibrium was attributed to the slow solvolysis of the halide by the alcohol since addition of traces of water caused immediate readjustment of the conductivity.

Rate effects in propan-2-ol were similar to those in ethanol except that water reacted at a measurable rate with the halide and the conductivity–time curve was of two parts: the first, shown by the effect of water addition to be due to attack by water, had a first-order constant 40 times as large as that of the second part: the latter was therefore attributed to the solvolysis of the halide. The first-order constants for solvolysis in ethanol and propan-2-ol obtained from the initial phase of the solvolysis are as follows [units are $10^4 k_1$ (in sec.$^{-1}$); R is the percentage of dichloride in the sample of the monochloride used].

Temp.	0°		25°	
R	7	45	7	45
Ethanol	3·4	10	33	46
Propan-2-ol	0·11	—	0·80	—

Solvolysis of di-*tert.*-butyltin dichloride alone gave a step-wise change of conductivity on addition to the solvent: the rate effects observed with the monochloride samples are therefore attributable to the monochloride. The rate is greater in the sample containing the greater dichloride content.

*Tri*iso*propylsilyl chloride.* Solvolysis was examined in propan-2-ol and in propan-2-ol–water. Conductometric data were treated as follows. The rate equation for formation of ions by a first-order process is:

$$k_1t/2{\cdot}303 = \log [(R_0 - R_\infty)/R_0] + \log [R_t/(R_t - R_\infty)]$$

where R_0 = cell resistance at zero time, R_t = cell resistance at time t, and R_∞ = the cell resistance at infinite time. It is assumed that the conductivity of the cell at any time is proportional to the concentration of ions formed at that time. The range of concentration of halide over which this assumption is valid is examined below

It is useful to test whether departure from this equation arises because ions are formed by a second-order process or by a first- + second-order one (*e.g.*, simultaneous alcoholysis by solvent and hydrolysis by small amounts of water present in the solvent). This can be done as follows: if α represents (cell resistance)$^{-1}$ and the subscripts are the same as before, then

$$a/(a - x) = (\alpha_\infty - \alpha_0)/(\alpha_\infty - \alpha_t) \text{ and } (b - x)/b = 1 - [a(\alpha_t - \alpha_0)/b(\alpha_\infty - \alpha_0)],$$

where a, b, and x have their usual significance. The equation for simultaneous first- and second-order reactions is:

$$dx/dt = k_1(a - x) + k_2(a - x)(b - x)$$

therefore
$$d \ln [a/(a - x)]/dt = k_1 + k_2(b - x)$$

and
$$d \ln [(\alpha_\infty - \alpha_0)/(\alpha_\infty - \alpha_t)]/dt = k_1 + k_2b\{1 - [a(\alpha_t - \alpha_0)/b(\alpha_\infty - \alpha_0)]\}$$

Hence a plot of $d(\log [\alpha_\infty - \alpha_t])/dt$ against $[(\alpha_t - \alpha_0)/(\alpha_\infty - \alpha_0)]$ gives a straight line of slope $k_2a/2{\cdot}303$ and intercept $-(k_1 + k_2b)/2{\cdot}303$; given a and b the values of k_1 and k_2 can be found.

Analysis of conductivity–time curves in this way showed that at halide concentrations $\geqslant 2 \times 10^{-3}$M the data did not fit first-, first- + second-, or second-order kinetics: this was probably because proportionality between conductivity and ion concentration breaks down above this concentration. Below this concentration rates agreeing well with those obtained titrimetrically were observed: the assumption of proportionality is then valid.

At similar concentrations in the same solvent the specific conductivity of solutions of tri*iso*propylsilyl chloride was some 100 times larger than that of the corresponding tin compound.

Titrimetric data were analysed in the usual way: first- and second-order constants were derived from appropriate log plots. Runs were followed by removing aliquot parts at known time intervals after the addition of the halide to the alcohol, quenching the sample in dry acetone at −80°, and titrating the hydrochloric acid formed with ethanolic sodium ethoxide to a lacmoid end point. The end point was stable in presence of free halide for 15 minutes after titration.

An example of hydrolysis of tri*iso*propylsilyl chloride in propan-2-ol is as follows; $[k_1]_0$ is the value of the first-order constant at zero time:

$[H_2O]$ (M × 10^3)	18·4	22·25	32·45	37·9	45·4
$[Pr^i_3SiCl]$ (M × 10^3)	16·25	32·25	13·3	10·6	9·65
10^2k_2 (l. mole^{-1} sec.$^{-1}$)	2·57	2·59	2·59	2·57	2·54
$10^4[k_1]_0$ (sec.$^{-1}$)	4·15	5·76	7·78	10·4	12·3

A plot of $[k_1]_0$ against $[H_2O]$ is a straight line giving $k_2 = 2{\cdot}5 \times 10^{-2}$ (l. mole^{-1} sec.$^{-1}$) The value of k_2 obtained from the second-order plots decreased after 60—70% of reaction; addition of pyridine resulted in a plot linear to 75—90% of reaction, k_2 remaining constant.

Alcoholysis by propan-2-ol at 44·6°, 59·1°, and 73·1° gave the following results:

Temp. (°)	44·6	44·6	59·1	73·1	73·1	73·1
[Py]	absent					
$[Pr^i_3SiCl]$ (M × 10^2)	3·21	7·31	7·11	4·43	4·79	5·13
10^5k_1 (sec.$^{-1}$)	1·09	1·11	2·12	3·04	$3{\cdot}04_5$	$3{\cdot}04_5$
[Py]	0·17	0·17	—	3·97	8·60	—
$[Pr^i_3SiCl]$ (M × 10^2)	5·8	5·7	—	3·25	2·40	—
10^5k_1 (sec.$^{-1}$)	1·89	2·02	—	5·82	5·64	—

Addition of pyridine increased the rate by a factor of two. The Arrhenius parameters for the solvolysis in absence of pyridine are E_A 9 kcal./mole and log PZ 1·3. It is evident that the same reaction has an unusually low steric factor.

tert.-*Butyl chloride in propan-2-ol at low concentrations of water.* For comparison with the data on organo-silicon and -tin halides the solvolysis of *tert.*-butyl chloride, which is typically an S_N1 process, was studied at 44·6°, 59·1°, and 73·1° in propan-2-ol containing ~0·02M of water, a sealed tube titrimetric technique being used. The concentration of hydrochloric acid formed during solvolysis goes through a maximum and then decreases with time: the maximum concentration is approximately equivalent to the water concentration. The initial rate as a function of temperature gave log PZ 10, E_A 24 kcal./mole.

Hydrolysis of organotin chlorides in dioxan–water. Tri*iso*propyltin chloride in dioxan–water showed the following behaviour when the water concentration was varied over a wide range; [Halide] 2·00 × 10^{-3}M; κ = specific conductivity (ohm^{-1} cm.$^{-1}$ × 10^{10}); Λ_v = equivalent conductivity (ohm^{-1} cm.^{2} × 10^{3}).

$[H_2O]$ (M) ...	2·13	2·29	2·56	2·97	3·16	3·46	3·78	4·64	5·15	5·53	6·82
κ	1·0	2·03	3·85	8·07	14·6	27·1	51·2	174	316	479	1553
Λ_v	0·052	0·104	0·217	0·425	0·773	1·44	2·74	9·46	17·3	26·4	88·0

At water concentrations less than 2M there was no significant conduction.

At every point the equilibrium conductivity value was reached within the time necessary for complete mixing of the components of the solution.

The effect of variation of R in R_3SnCl was studied in dioxan–water solutions of fixed composition (26% w/w of water): if water is present in large excess over the chloride, the dissociation $R_2SnCl + H_2O \rightleftharpoons R_3SnOH_2^+ + Cl^-$ should obey the dilution law. If the solution is sufficiently dilute and the degree of dissociation is small, activity coefficients tend to unity; if interionic attraction effects are also small the conductivity ratio, Λ_v/Λ_∞, can be used as an approximate measure of the degree of dissociation. Then $K = (\Lambda_v/\Lambda_\infty)^2c/(1 - \Lambda_v/\Lambda_\infty)$ or $c\Lambda_v = K(\Lambda_\infty^2/\Lambda_v) - K\Lambda_\infty$ and a plot of $c\Lambda_v$ (*i.e.*, 10^3 × specific conductivity) against Λ_v^{-1} should be a straight line of slope $K\Lambda_\infty^2$ and intercept $-K\Lambda_\infty$. A preliminary experiment showed that provided the halide concentration was $<1{\cdot}25 \times 10^{-3}$M the simple dilution law held. Conductivity data on triethyl-, tri*iso*propyl-, and triphenyl-tin chlorides at 25° ± 0·01° plotted in this way gave the following results (standard errors are given in parentheses):

R	Et	Pr^i	Ph
Λ_∞	34·7 (±1·9$_5$)	110 (±26)	303 (±91)
10^4K............................	1·12 (±0·13)	0·35$_1$ (±0·017)	0·0025$_3$ (±0·0015)
pK	3·95 (±0·05)	4·45$_5$ (±0·02)	6·60 (±0·26)

Potentiometric Measurements of Equilibria.—The e.m.f. at half-titration with silver nitrate of the halides R_3SnCl (R = Et, Pr^i, Bu^t, Ph) in 80% ethanol enables an estimate of their relative degrees of dissociation to be made. The titration was in acid solution (0·3M-perchloric acid) to suppress the dissociation of the ion $R_3SnOH_2^+$. The cell was made up as follows:

$$\text{Ag} \mid \text{AgCl} \mid R_3\text{SnCl solution} \mid \text{KNO}_3(\text{satd.}) \mid \text{KCl(satd.)} \mid \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$$

Measurements were made at 21° ± 0·1° with approximately 5 × 10^{-3}M-halide solutions.

For this cell, it being assumed that activity coefficients are unity because the solutions are dilute, we may write for its e.m.f., $E = \sum E_i + (\boldsymbol{RT/F}) \ln ([\text{Ag}^+]$, where $\sum E_i$ = the algebraic sum of liquid junction potentials, the potential of the reference electrode relative to hydrogen, and any asymmetry potential of the silver electrode arising from its previous history. The same cell is used for all the halides so that $\sum E_i$ is constant throughout the experiments. If the solubility product of silver chloride is K_s we have

$$E = \sum E_i - (\boldsymbol{RT/F}) \ln ([\text{Cl}^-]/K_s) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Since water is in excess the equilibrium constant for the chloride hydrolysis is $K' = [R_3SnOH_2^+][Cl^-]/[R_3SnCl]$ and eqn. (1) then becomes

$$E = \text{const.} - (\boldsymbol{RT/F}) \ln K'[R_3SnCl]/[R_3SnOH_2^+]$$

At half-titration with silver ion [R_3SnCl] = [$R_3SnOH_2^+$], and if $E_{\frac{1}{2}}$ is then the e.m.f. of the cell the difference between the $E_{\frac{1}{2}}$ values of any pair of halides (I) and (II) is $\Delta E_{\frac{1}{2}} = (\boldsymbol{RT}/\boldsymbol{F}) \ln (K'_{\text{II}}/K'_{\text{I}})$. The $E_{\frac{1}{2}}$ values for the halides R_3SnCl are as follows.

R	Et	Pr^i	Bu^t	Ph
$E_{\frac{1}{2}}$ (v)	0·04	0·06	0·17	0·065
K'_{Et}/K'_{R}	1	2·2	170	27

DISCUSSION

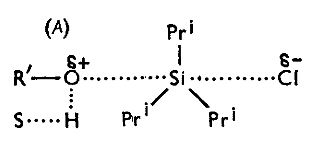
Kinetic Aspects.—Solvolysis of tri*iso*propyltin chloride with propan-2-ol is at a measurable rate: in water–dioxan, and in ethanol, equilibrium is established too rapidly for rate measurement and this is true also of the triethyl and triphenyl compounds in all solvents studied. In propan-2-ol solvolysis of the tri*iso*propyltin compound an unusual periodic change occurs in the observed conductivity which depends upon water concentration and temperature. The effect of water concentration makes it likely that the rapid initial increase in conductivity is caused by attack of water on the chloride. This increase is followed by a gradual decrease which may be due to the formation of another species of lower mobility, *e.g.*, the ion $Pr^i_3SnCl_2^-$, or to an electrochemical effect such as the formation of ion-pairs as the concentration of ions in the solution increases, or to a change in the conduction mechanism of the proton as water is removed from the solution by progressive reaction with chloride. At 0° there is finally another increase of conductivity which does not appear at 25°.

Two facts suggest that a synchronous type of substitution is occurring at tin: (*a*) measurable rates of solvolysis appear at R = Pr^i in the series R_3SnCl with R = Et, Pr^i, Bu^t in propan-2-ol and at R = Bu^t in ethanol; (*b*) solvolytic equilibria lie further in favour of the undissociated halide as the size and electron-releasing power of the alkyl group increase in this series. The converse of (*a*) and (*b*) would apply if solvolysis proceeded through a " stannonium " ion, R_3Sn^+. The solvolyses of *tert.*-butyl chloride in propan-2-ol show that only comparisons of rates in the same solvent are valid mechanistic criteria: thus, although the solvolysis rate (and degree of dissociation) of tri-*tert.*-butyltin chloride is lower in propan-2-ol than in ethanol this cannot be evidence that rearward attack is necessarily occurring at tin because the rate of solvolysis of *tert.*-butyl chloride, which reacts typically by the S_N1 mechanism, is also lower in propan-2-ol than in ethanol. This is an example of a specific solvent effect since the dielectric constants of the two alcohols are similar.

The characteristics of the solvolysis of tri*iso*propylsilyl chloride in propan-2-ol and propan-2-ol–water are clearly different from those of the corresponding tin compound. In hydrolysis, in the range of water concentration studied, a second-order reaction is observed which is not catalysed by pyridine: this is further evidence for a synchronous displacement process at silicon. The solvolysis by propan-2-ol–water has a low energy of activation and a very low steric factor which again is consistent with synchronous displacement.

Catalysis by pyridine in solvolysis rather than in hydrolysis in propan-2-ol may be explained as follows. The transition state is probably of the form [3] (*A*) in which S is a proton acceptor. In hydrolysis (R′ = H) it is probably as easy sterically for a propan-2-ol molecule to accept a proton as for a pyridine molecule: in solvolysis by propan-2-ol (R′ = Pr^i) catalysis would be expected if it is easier for a pyridine rather than a propan-2-ol molecule to approach the proton. Even if the steric requirements of the proton-transfer to pyridine and propan-2-ol are similar in the transition state, pyridine would be more effective in proton removal by virtue of its greater basic strength.

(*A*)



Kinetic data on silicon [3] and germanium [16] halides also indicate that R_3M^+ ions do not

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[16] Johnson and Schmall, *J. Amer. Chem. Soc.*, 1958, **80**, 2931.

occur as intermediates in the solvolyses of these halides: the S_N1 mechanism is energetically unfavourable in the reactions of the halides R_3MCl of silicon, germanium, and tin.

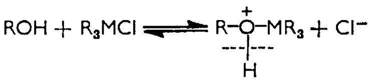
Conductivity Data.—A necessary condition for dissociation of an organotin halide is the presence of a donor, S, the process being written $S\!: + R_3SnCl \rightleftharpoons {}^+S\!:\!SnR_3$ (I) + Cl^-, where the species, I, may or may not undergo subsequent reaction, *e.g.*, proton transfer when S is hydroxylic. The extent of this subsequent reaction depends upon the nature of R and S. The extent of the dissociation depends upon S, and its dependence upon the medium is shown strikingly by the effect of water on the conductivity of tri*iso*propyltin chloride in dioxan: a 2×10^{-3}M-solution of the chloride does not conduct significantly until the water concentration reaches 2M. Not only must a donor molecule be present but the properties of the medium must be such as to promote dissociation: this medium effect could arise electrostatically or it could be a specific solvent effect.

In water–dioxan of constant composition (26% w/w of water; dielectric constant 15 [17]) some interesting features are shown when R is varied in R_3SnCl. The values of Λ_∞ (R = Et, 35; R = Pr^i, 110; R = Ph, 300) can be interpreted in terms of the properties of the corresponding hydroxy-compounds: Et_3SnOH is basic,[18] Pr^i_3SnOH only faintly so; [18] and Ph_3SnOH is acidic.[19] The dissociation constant of the acidic cation $R_3SnOH_2^+$ should therefore increase from ethyl to phenyl and this is reflected in the values of Λ_∞. That of the ethyl compound is typical for a 1 : 1 electrolyte with a large cation in a medium of this dielectric constant. Thus, interpolation of Kraus and Fuoss's data [20] on tetra*iso*pentylammonium nitrate gives Λ_∞ 35·2, in satisfactory agreement with the value for triethyltin chloride in this medium. This confirms Dennison's finding [6] that in water triethyltin bromide behaved as a typical 1 : 1 electrolyte having Λ_∞ 112 ohm^{-1} cm.^{2}. If acid dissociation of the complex is substantial the high mobility of the proton should give a much larger value of Λ_∞. The Λ_∞ value for tri*iso*propyltin chloride shows that the acidic mode of dissociation makes a contribution, and in the triphenyl compound this appears to be considerable: this is consistent with the known basic propertes of the corresponding organotin hydroxides.

In propan-2-ol the relative values of the equivalent conductivity under the same conditions of temperature and concentration are:

Pr^i_3SiCl	$\gg$	Et_3SnCl	$>$	Pr^i_3SnCl	$>$	Bu^t_3SnCl
100		3		1		<0·9

The value for Bu^t_3SnCl is maximal because the halide contained the dihalide as impurity. This emphasises a basic difference between the solvolysis of organosilyl chlorides and organotin chlorides ascribable to the differing extents of fission of the O–H bond in the scheme:



$$ROH + R_3MCl \rightleftharpoons R\!-\!\underset{\underset{H}{|}}{\overset{+}{O}}\!-\!MR_3 + Cl^-$$

Whereas when M is silicon, fission is essentially complete, when M is tin, fission is very limited.

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[17] Kraus and Fuoss, *J. Amer. Chem. Soc.*, 1933, **55**, 21.
[18] Luijten, personal communication.
[19] Swain, personal communication.
[20] Kraus and Fuoss, *J. Amer. Chem. Soc.*, 1957, **79**, 3301.