242. *Liquid Hydrogen Chloride as an Ionizing Solvent. Part III.*[1] *Solubilities and Reactions of Some Derivatives of Groups IV, V, and VI.*

By M. E. PEACH and T. C. WADDINGTON.

The conductivities of various derivatives, mainly organic, of elements of Groups IV, V, and VI in anhydrous liquid hydrogen chloride have been measured. All these compounds would act as solvobases, and conductivity titrations have been performed by using boron trichloride as an acid.

THIS paper concerns first compounds of the type Ph_3MX (M is an element of Group IV and $X = Cl$ or OH), and attempts to prepare the ions Ph_3M^+. The Ph_3C^+ ion is well characterised [2,3] and has been found in protonic solvents such as sulphuric acid [2] and in non-protonic solvents such as sulphur dioxide.[4] No cases of the ion Ph_3Si^+ have yet been reported,[5,6] although the recently prepared $Ph_3Si{\cdot}ClO_4$ may contain this ion.[7] No other

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[1] Parts I and II, Waddington and Klanberg, *J.*, 1960, 2329, 2332.

[2] Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 40.

[3] Sharp and Sheppard, *J.*, 1957, 674.

[4] Anderson, *J. Amer. Chem. Soc.*, 1935, **57**, 1674.

[5] Sharp, " Advances in Fluorine Chemistry," Butterworth Scientific Publ., London, 1960, Vol. I, p. 96.

[6] Gillespie and Robinson, " Advances in Inorganic and Radiochemistry," Academic Press Inc., New York, 1959, Vol. I, p. 385.

[7] Wannagat, Braudmair, Leihr, and Neiderprüm, *Z. anorg. Chem.*, 1959, **302**, 185.

ions of type Ph_3M^+ have been prepared but the somewhat similar ion Me_3Sn^+ has been detected in sulphuric acid[6] and in the compound $Me_3Sn^+[BF_3{\cdot}CF_3]^-$.[8]

Next, it concerns derivatives of elements of Group V, of the type Ph_3M, it being hoped to protonate the element to give Ph_3MH^+ and isolate this as the tetrachloroborate. The ions Ph_3NH^+ and Ph_3PH^+ have been found in sulphuric acid,[6] but there is no evidence for Ph_3AsH^+. After the success of the experiments in liquid hydrogen chloride with phosphine[1] attempts were made to prepare the arsonium ion, AsH_4^+.

Finally, it concerns elements of Group VI, but here only oxygen and sulphur were studied. The compounds were of the type ROR′, where R and R′ were H, Me, or Ph. The object was to make protonated derivatives; in sulphuric acid this is complicated by sulphonation.[2] The effect of the substituents on the electron-availability and hence proton-acceptability can be assessed very roughly by the magnitude of the equivalent conductivities.

EXPERIMENTAL

The apparatus and techniques used have been described.[1]

Boron trichloride or trifluoride was introduced from the gas phase, in known amounts, by freezing on top of the frozen solution of other reactants. Measured volumes of liquid materials were obtained by use of an Agla micrometer syringe.

The reactions in the liquid hydrogen chloride were followed conductometrically, or by weighing a cell before and after reaction. The conductivity cells were made of Pyrex glass, vacuum-tight metal-to-glass seals being obtained by using tungsten wire on to which a platinum electrode had been silver-soldered. In solvolyses where one material was precipitated, a Y-shaped apparatus was used, attached to a ball-and-socket joint; the reaction was performed in one limb and the supernatant liquid was then decanted into the other; the hydrogen chloride was then evaporated and the product analysed.

Vapour-pressure measurements were performed by means of liquid in a small bulb attached to a spiral gauge. The dead-space was reduced to a minimum (*ca.* 10—15 ml.), and pressures were read by using the spiral gauge as a null-point instrument.

Chloride was determined by the Volhard method, and boron acidimetrically as the mannitol-borate complex; carbon, hydrogen, and nitrogen were determined by microcombustion. Results for chloride and boron may be slightly low as the materials usually reacted violently with water.

Arsine was made by reduction of arsenic trichloride with lithium aluminium hydride in anhydrous ether. Diphosphine was made by a slight modification of Evers and Street's method.[9] Other reagents were available commercially or were prepared by our colleagues in other researches.

Infrared measurements were taken on a Perkin-Elmer 21 double-beam continuously recording spectrophotometer with rock-salt or potassium bromide optics: some of the less important spectra were taken on a Perkin-Elmer Infracord instrument.

Conductivities.—These results are shown in Table 1.

Group IV, *Compounds* Ph_3MX.—Triphenylmethyl chloride dissolved in the liquid hydrogen chloride to a yellow, highly conducting solution. The colour is characteristic of the Ph_3C^+ ion and the ions present are formed by the reaction $Ph_3CCl + HCl \longrightarrow Ph_3C^+ + HCl_2^-$. The solution was titrated against boron trichloride and a break in the curve was found at a 1 : 1 molar ratio. The yellow solid isolated was $Ph_3C^+BCl_4^-$ (Found: C, 60·5; B, 2·7; Cl, 34·7. Calc. for $C_{19}H_{10}BCl_4$: C, 59·0; B, 2·7; Cl, 35·8%).

Triphenylsilyl chloride was very sparingly soluble and it was not possible to form an adduct from it with boron trichloride; the product, after treatment of the triphenylsilyl chloride with a stoicheiometric excess of boron trichloride, contained less than 0·1% of boron.

Triphenylgermanyl chloride was sparingly soluble in liquid hydrogen chloride. No adduct was produced with boron trichloride and the compound appears to have disproportionated.

Analyses for carbon were unsatisfactory as the compound readily decomposes in moist air: because there was only a small amount of material available it was not possible to repeat the experiment in a weighed vessel.

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[8] Chambers, Clark, and Willis, *Proc. Chem. Soc.*, 1960, 114.

[9] Evers and Street, *J. Amer. Chem. Soc.*, 1956, **78**, 5727.

Triphenylstannyl chloride was almost insoluble and its conductivity changed with time. It disproportionated quantitatively in 2 hr. to dichlorodiphenylstannane (Found: C, 41·2; H, 3·0; Cl, 19·6, 19·7; loss of wt., 10·8%. Calc. for $C_{12}H_{10}Cl_2Sn$: C, 41·9; H, 2·9; Cl, 20·6; loss of wt., 10·9%).

TABLE 1. *Specific and molar conductances of compounds in liquid hydrogen chloride at —95°.*

Compound	Concn. (mole/l.)	Spec. conductance (ohm^{-1} cm.$^{-1}$)	Molar conductance (cm.^{2} ohm^{-1}) mole^{-1})
Ph_3CCl	0·15	0·518 × 10^{-4}	34·2
	0·25	1·064 × 10^{-4}	42·9
Ph_3SnCl	Satd.	1·53 × 10^{-6}	—
Ph_3GeCl	,,	1·11 × 10^{-6}	—
Ph_3SnCl *	,,	0·35 × 10^{-6}	—
Ph_3PbCl	,,	2·2 × 10^{-6}	—
Ph_3N	0·22	1·50 × 10^{-3}	6·85
Ph_3N	0·49	4·67 × 10^{-3}	9·54
Ph_3N	0·75	7·14 × 10^{-3}	9·48
Ph_3P	0·31	6·51 × 10^{-3}	21·1
Ph_3As	0·17	5·07 × 10^{-3}	30·7
Ph_3As	0·20	7·70 × 10^{-3}	39·3
Ph_3As	0·30	11·88 × 10^{-3}	39·5
Ph_3Sb *	Satd.	8·9 × 10^{-6}	—
Ph_3Bi *	,,	0·31 × 10^{-6}	—
P_2H_4	,,	2·17 × 10^{-5}	—
P_2H_4	,,	2·13 × 10^{-5}	—
AsH_3 †	,,	2·63 × 10^{-5}	—
AsH_3 †	,,	1·11 × 10^{-4}	—
NH_4Cl	,,	1·3 × 10^{-6}	—
$N_2H_4,2HCl$	,,	1·0 × 10^{-6}	—
$Ph_2N{\cdot}NH_2$	0·37	0·852 × 10^{-3}	2·30
H_2O	Satd.	4·3 × 10^{-6}	—
H_2S	,,	2·8 × 10^{-6}	—
MeOH	0·51	68·7 × 10^{-6}	0·13
MeSH	0·27	14·7 × 10^{-6}	0·054
PhOH	0·25	4·75 × 10^{-6}	0·019
PhSH	0·39	11·7 × 10^{-6}	0·030
PhOMe	0·32	6·8 × 10^{-6}	0·021
PhOPh	0·38	0·66 × 10^{-6}	0·0017
PhOPh	0·48	0·54 × 10^{-6}	0·0012
PhSPh	0·25	38·7 × 10^{-6}	0·15
MeOMe	0·26	114·4 × 10^{-6}	0·43
MeSMe	0·44	5·16 × 10^{-3}	11·8
MeSMe	0·35	3·95 × 10^{-3}	11·3
MeSMe	0·29	2·90 × 10^{-3}	10·1
$BiCl_3$	Satd.	0·46 × 10^{-6}	—

* Initial values as decomposition occurs. † Values at —111·6°.

Triphenylplumbyl chloride gave a yellow solution and a copious orange precipitate. It disproportionated but it is uncertain what the products are. The reaction may be impeded by the surface precipitation of lead tetrachloride.[1] After this chloride had been in liquid hydrogen chloride for 2 hr. a white solid was obtained on removal of the solvent (Found: C, 42·9; H, 3·1; loss of wt., 4·5. Calc. for $C_{18}H_{15}ClPb$: C, 45·6; H, 3·2. Calc. for $C_{12}H_{10}Cl_2Pb$: C, 33·4; H, 2·3; loss of wt., 8·8%).

Triphenylmethanol gave a red solution and a white precipitate. The soluble product of a solvolysis reaction was triphenylmethyl chloride (Found: Cl, 12·7. Calc. for $C_{19}H_{15}Cl$: Cl, 12·7%).

Triphenylsilanol was sparingly soluble. A solvolysis experiment showed that a little of the chloride had been formed (Found: Cl 0·8. Calc. for $C_{18}H_{15}ClSi$: Cl, 12·0%).

Group V.—(*a*) Triphenylamine was readily soluble, giving a pale brown or a deep blue solution. Pale brown solutions (0·29—0·51M) were obtained with freshly purchased material: a sample freshly sublimed *in vacuo* and then kept for 6 months gave a blue solution. The colour is not a function of concentration as 0·28—1·0M-solutions were all blue. The material acted as a strong base and was titrated against boron trichloride: the titration curve (Fig. 1) shows a sharp break at 1 : 1 molar ratio. The product was white, but this soon became blue in a dry box: it was *triphenylammonium tetrachloroborate* (Found: B, 2·5; Cl, 35·2; N, 3·8. $C_{18}H_{16}BCl_4N$ requires B, 2·7; Cl, 35·5; N, 3·5%).

Triphenylphosphine was readily soluble, giving a pale yellow solution. A conductivity titration against boron trichloride showed a sharp break at a 1 : 1 molar ratio. The infrared absorption included a weak PH^+ frequency [10] at 2300—2400 cm.$^{-1}$; its composition as *triphenylphosphonium tetrachloroborate* was confirmed by analysis (Found: B, 2·4; C, 35·8. $C_{18}H_{16}BCl_4P$ requires B, 2·6; Cl, 34·1%).

Triphenylarsine was readily soluble, giving a slightly brown solution: the solubility limit

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[10] Shelden and Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 2117.

was about 1M. It was a strong base and the conductivity titration against boron trichloride, shown in Fig. 2, gave a sharp break at the 1 : 1 molar ratio. The product at room temperature was the triphenylarsine–boron trichloride *adduct*, Ph_3As,BCl_3 (Found: B, 2·3; Cl, 25·4, 25·7; increase in wt., 38·5. $C_{18}H_{15}AsBCl_3$ requires B, 2·6; Cl, 25·1; increase in wt., 38·3%). The white solid residue obtained at −95° gave off slightly more than a mol. of hydrogen chloride at about −25°, but accurate quantitative investigation at this temperature was impossible. From the similarity of the conductivity curve to those of triphenylamine and boron trichloride the following reactions have been inferred:

$$Ph_3As + 2HCl \longrightarrow Ph_3AsH^+ + HCl_2^-$$
$$Ph_3AsH^+ + BCl_3 + HCl_2^- \longrightarrow Ph_3AsH^+BCl_4^- + HCl$$

One mol. of triphenylarsine and methanesulphonic acid were mixed in the solvent: the infrared spectrum of the solid product obtained on removal of the solvent showed the frequencies of the methanesulphonate ion, loss of O–H frequencies, and a very weak band in the 2400 cm.$^{-1}$ region which may be due to the AsH^+ stretching vibration.

FIG. 1. *Conductimetric titration*: 0·75M-Ph_3N-BCl_3.

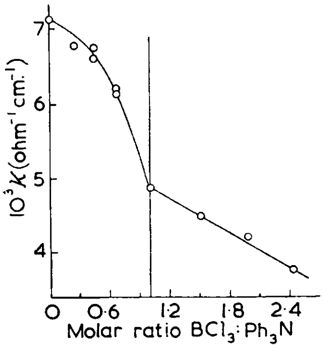
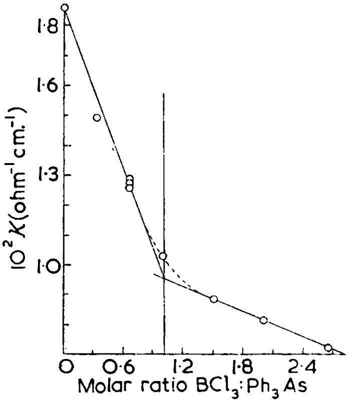


FIG. 2. *Conductimetric titration*: 0·30M-Ph_3As-BCl_3.



Triphenylstibine was incompletely soluble, giving a colourless solution. It slowly disproportionated and after 4 hr. had lost 19·5% of its weight ($Ph_3Sb \longrightarrow SbCl_3$; loss of wt., 35·4%). It was not possible to identify the product (Found: Cl, 13·4. Calc. for Cl_3Sb: Cl, 46·6%). The slowness of the reaction may be due to the formation of insoluble antimony trichloride [1] on the surface of the triphenylstibine.

Triphenylbismuthine was almost completely insoluble and slowly disproportionated (Found, in the product: C, 6·5; H, 1·6; Cl, 26·7; loss of wt., 22·1. Calc. for $BiCl_3$: Cl, 33·7; loss of wt., 28·3%).

(*b*) Ammonium chloride was sparingly soluble and attempts to prepare the tetrachloroborate failed (Found: B, 0; Cl, 65·6. Calc. for NH_4Cl: Cl, 66·2%).

Hydrazinium dichloride was sparingly soluble, and because of this no attempt was made to cause it to react with boron trichloride.

Hydrazobenzene gave a deep red solution and a yellow precipitate: the conductivity was time-variable. The infrared spectrum of the product showed that the hydrazobenzene had been converted into benzidine: $(NHPh\cdot)_2 + 4HCl \longrightarrow (\cdot C_6H_4\cdot NH_3^+)_2 2(HCl_2^-)$.

NN-Diphenylhydrazine gave a yellow solution. The conductivity titration against boron trichloride, shown in Fig. 3, gave a sharp break at the 1 : 1 molar ratio: the big drop in conductivity on addition of boron trichloride is due to precipitation. The light blue product was *NN-diphenylhydrazinium tetrachloroborate* (Found: C, 43·7; H, 3·9; B, 3·1; Cl, 4·20; N, 8·9. $C_{12}H_{13}BCl_4N_2$ requires C, 42·7; H, 3·9; B, 3·2; Cl, 42·0; N, 8·3). The infrared spectrum in the potassium bromide region showed tetrachloroborate frequencies at 693 and 670 cm.$^{-1}$.[11] In the rock-salt region NH bands were observed at 2680, 2460, and 1568

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[11] Kynaston, Larcombe, and Turner, *J.*, 1960, 1772.

cm.$^{-1}$. Although these data are insufficient to assign the proton to a specific nitrogen atom the compound probably has the structure $Ph_2N{\cdot}NH_3^+BCl_4^-$.

Diphosphine was not very soluble in liquid hydrogen chloride. Conductivity titrations with boron trifluoride and boron trichloride showed no breaks: addition of 0·1 mol. of boron trichloride gave a polymer. As diphosphine decomposes in the gas phase to phosphine and a yellow material no further experiments were performed.

Arsine was not very soluble and gave a brown precipitate, possibly arsenic. A vapour-pressure diagram of arsine and hydrogen chloride at $-95°$ showed a slight break at the 1 : 1 molar ratio. The infrared spectrum of gas in equilibrium with a liquid mixture of arsine (1 mol.) and hydrogen chloride (4 mols.) at $-95°$ showed an appreciable concentration of arsine, which was considerably reduced when just over a mol. of boron trichloride had been added. This indicates that AsH_3,BCl_3 or $AsH_4^+BCl_4^-$ is less dissociated than AsH_3,HCl. Conductivity titrations with boron trifluoride and boron trichloride are unsatisfactory but both show turning points at the 1 : 1 molar ratio. No solid product was obtained at room temperature; the gas given off on warming was a mixture of hydrogen chloride, arsine, and boron trihalide.

FIG. 3. *Conductimetric titration*: 0·37M-$Ph_2N{\cdot}NH_2$–BCl_3.

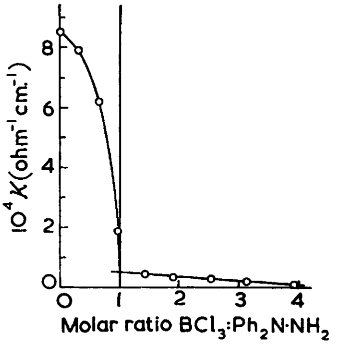
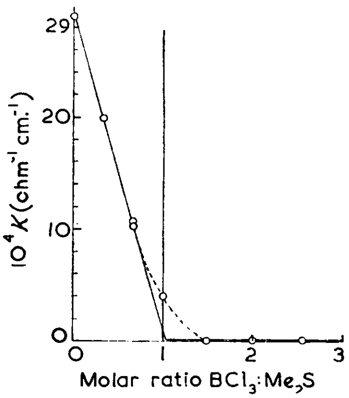


FIG. 4. *Conductimetric titration*: 0·29M-Me_2S–BCl_3.



Group VI: *Oxygen and Sulphur Compounds*.—Hydrogen sulphide was sparingly soluble, giving a white precipitate and a colourless solution. On addition of boron trichloride it became more soluble, and a conductivity titration showed a sharp initial rise, followed by a slow fall. A trace of insoluble residue was left at room temperature: this was not sulphur or hydrogen polysulphide as the infrared spectrum showed peaks at 3200 and 1190 cm.$^{-1}$.

Methanol gave a colourless solution. Conductivity titration with boron trichloride yielded a smooth curve. A liquid residue was obtained on evaporation at $-95°$; this was probably dimethoxyboron chloride, m. p. $-87{\cdot}5°$ [12] (Found: *M*, 108·6. Calc. for $C_2H_6BClO_2$: *M*, 108·4).

Methanethiol was readily soluble. With boron trichloride, it gave an adduct, which melted at about $-20°$ (decomp.) (Found: B, 5·5; Cl, 58·1%; Cl/B, 10·5; increase in wt., 246%. Calc. for CH_4BCl_3S: B, 6·5; Cl, 64·4%; Cl/B, 9·84; increase in wt., 244%). When kept in the dry box it remained liquid and it was not possible to obtain $(MeS{\cdot}BCl_2)_2$, m. p. 72·7°, which had previously been found.[13]

Dimethyl ether gave a highly conducting solution. Titration with boron trichloride showed a break at 1 : 1 molar ratio; from the low equivalent conductivity at this point (0·012 mho cm.^{2} mole^{-1}) it is assumed that an adduct has been formed in solution. This was confirmed as on warming to room temperature little gas (0·03 mole) was given off by the product (Found: B, 6·0; Cl, 65·1. Calc. for $C_2H_6BCl_3O$: B, 6·6; Cl, 65·1%).

Dimethyl sulphide was the most highly conducting oxygen or sulphur compound investigated Titration with boron trichloride showed a sharp break at the 1 : 1 molar ratio (Λ 0·033 mho cm.^{2}

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[12] Wiberg and Sätterlen, *Z. anorg. Chem.*, 1931, **202**, 1.

[13] Goubeau and Wittmeier, *Z. anorg. Chem.*, 1952, **270**, 16.

mole^{-1}) (Fig. 4). The product had a dissociation pressure of about 8 mm. at room temperature; analysis suggests that it was the methyl sulphide–boron trichloride adduct (Found: C, 5·6; Cl, 57·8%; Cl/B, 10·5. Calc. for $C_2H_6BCl_3S$: B, 6·0; C, 59·4%; Cl/B, 9·8). As only a small amount of gas was given off on warming to room temperature it can be assumed that the adduct was formed in the solution.

Phenol was soluble, up to about 1M-solutions. With boron trichloride, products of the type $(PhO)_xBCl_{3-x}$ were produced. The product gave off 0·15 mol. of gas on warming and its infrared spectrum showed loss of OH frequencies and appearance of frequencies at 1350 (B–O stretching?), 710, and 739 cm.$^{-1}$ (B–Cl). Analysis of the liquid product indicated it to be a mixture of PhO·BCl_2 and $(PhO)_2BCl$.

Thiophenol gave a poorly conducting solution: titration with boron trichloride produced a curve similar to that for hydrogen sulphide. The greenish, slimy product gave off 0·86 mole of a mixture of hydrogen chloride and boron trichloride at room temperature. It appears to decompose into PhS·BCl_2 and $(PhS)_2BCl$ (cf. the phenol product).

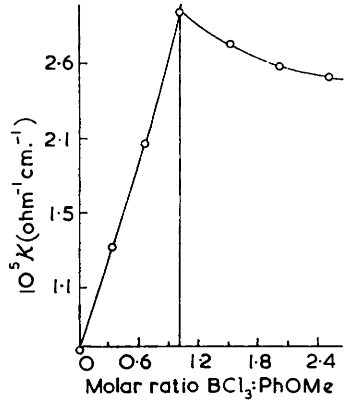

FIG. 5. *Conductimetric titration*: 0·32M-PhOMe–BCl_3.

Anisole gave a pale pink solution. Titration with boron trichloride is shown in Fig. 5: there is a break at the 1 : 1 molar ratio (Λ 0·093). The slightly purplish solid product had a vapour pressure of 15—20 mm. at room temperature, the vapour being boron trichloride. It melted to a purple liquid. Immediate weight analysis showed it to be the anisole–boron trichloride adduct (Found: increase in wt., 102. Calc. for $C_6H_5BCl_2O$: increase in wt., 118%). No methyl chloride was given off at room temperature.

Diphenyl ether gave a very poorly conducting solution. Titration with boron trichloride gave a smooth curve. On warming to room temperature the solution gave 0·56 mol. of a mixture of hydrogen chloride and boron trichloride, the product being diphenyl ether (Found: B, 0·9; Cl, 0·4%): this was confirmed by the infrared spectrum (cf. refs. 14 and 15).

Diphenyl sulphide gave a purple solution. Titration with boron trichloride gave a smooth curve: the greyish product gave off 0·18 mol. of boron trichloride at room temperature. The product fumed in the dry box and is probably the adduct which readily dissociates (Found: B, 2·5; Cl, 22·8; Cl/B, 9·0. Calc. for $C_{12}H_{10}BCl_3S$: B, 3·6; Cl, 35·1%; Cl/B, 9·7).

DISCUSSION

Use of Conductivity Titrations.—The equivalent conductivities at the beginning and equivalence point are shown for seven materials in Table 2 (in all cases boron trichloride is being used as an acid). From these figures it is seen that when an adduct is the main product the conductivity is usually low at the equivalence point and had changed very considerably. It can therefore be deduced that, from triphenylarsine, the salt $Ph_3AsH^+BCl_4^-$ is obtained at the equivalence point, whereas from methyl sulphide the

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[14] Colclough, Gerrard, and Lappert, *J.*, 1955, 907.

[15] Healy and Palka, *J. Chem. Phys.* ,1958, **28**, 211.

adduct Me_2S,BCl_3 is formed. It is also seen from Figs. 1, 2, and 4 that when an adduct is formed the curve is smooth in the 1/1 region whereas a sharp break occurs when tetrachloroborates are produced.

Colours of Solutions.—The only coloured solutions were from some phenyl derivatives, *e.g.*, anisole, triphenylphosphine. This may be due to slight protonation of the aromatic nucleus as various compounds of aromatic hydrocarbons are highly coloured, *e.g.*, $ArH_2^+AlCl_4^-$,[16] $ArH_2^+AlBr_4^-$,[17] $ArH_2^+BF_4^-$.[18] For triphenylamine a blue or brown colour was observed: it has previously been reported as blue.[19] This blue colour may be due to ions of the type Ar_3N^+, as $(p\text{-}C_6H_4Me)_3N^+ClO_4^-$ is blue.[20]

TABLE 2. *Conductivities at* 1 : 1 *molar ratio for boron trichloride titrations*

Base	Λ of base (mho cm.² mole⁻¹)	Λ at 1/1 ratio (mho cm.² mole⁻¹)	Ratio, Λ pure base/Λ 1/1	Product in solution
Ph_3N	12·6	7·8	1·62	$Ph_3NH^+BCl_4^-$
Ph_3As	39·5	20·4	1·94	$Ph_3AsH^+BCl_4^-$
Me_2O	0·43	0·012	25·8	Me_2O,BCl_3
Me_2S	10·05	0·033	304·6	Me_2S,BCl_3
Ph_3CCl	42·9	20·0	2·15	$Ph_3C^+BCl_4^-$
Ph_3P	21·1	15·6	1·35	$Ph_3Ph^+BCl_4^-$
Ph_3As *	39·5	37·9	1·04	$Ph_3AsH^+Me{\cdot}SO_3^-$

* On use of methanesulphonic acid.

Group IV *Compounds.*—The formation of a salt $Ph_3C^+BCl_4^-$ and the solvolysis of triphenylmethanol is probably due to the stability of the carbonium ion. The driving force in the latter reaction may be the insolubility of hydroxonium chloride: $Ph_3C{\cdot}OH + 4HCl \longrightarrow Ph_3C^+ + HCl_2^- + H_3O^+Cl^-$. The absence of solvolysis of the silanol must mean that it does not occur by an ionic mechanism: this should be contrasted with the method of formation of the triphenylsilyl chloride by bubbling gaseous hydrogen chloride through an ethereal solution of the silanol.[21] In all the other cases disproportionation occurs to varying extents; this is not really surprising since triphenyl-lead chloride reacts quantitatively, to give diphenyl-lead dichloride, when hydrogen chloride is passed into its benzene solution.[22] The following disproportionations have also been observed with somewhat similar tin compounds:

$$(p\text{-}MeO{\cdot}C_6H_4)_2SnPh_2 \xrightarrow[\text{HCl}]{\text{Conc. aq.}} Ph_2SnCl_2 \quad . \; . \; . \; . \; . \; . \quad (\text{ref. } 23)$$

$$Ph_3Sn{\cdot}OH \xrightarrow{\text{Dry HCl}} Ph_2SnCl{\cdot}OH \quad . \; . \; . \; . \quad (\text{ref. } 24)$$

However, not all reactions proceed similarly in liquid and in aqueous hydrogen chloride; *e.g.*, stannic and plumbic chloride are both insoluble [1] in liquid hydrogen chloride but form complex ions MCl_6^{2-} in the concentrated aqueous acid.

Group V *Compounds.*—With the triphenyl derivatives of the elements of higher atomic weight disproportionation occurs as with Ph_3MCl. In the series nitrogen, phosphorus, and arsenic, it is noteworthy that the conductivity and hence, presumably, basic strength, increases in that order, perhaps owing to the increasing size of the central atom. The

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[16] Brown and Frith, *Proc. Indiana Acad. Sci.*, 1953, **63**, 740.

[17] Brown and Wallace, *J. Amer. Chem. Soc.*, 1953, **75**, 6268.

[18] Olah and Kuhn, *Nature*, 1956, **178**, 1344.

[19] Kemmitt, Nuttall, and Sharp, *J.*, 1960, 40.

[20] Weitz and Schwechten, *Ber.*, 1926, **59**, 2307; 1927, **60**, 545.

[21] Kaus and Rosen, *J. Amer. Chem. Soc.*, 1925, **47**, 2746.

[22] Gilman and Robinson, *J. Amer. Chem. Soc.*, 1929, **51**, 3112.

[23] Bobashinkaya and Kochesharka, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **8**, 1850; *Chem. Zentr.*, 1940, I, 359.

[24] Chambers and Scherer, *J. Amer. Chem. Soc.*, 1926, **48**, 1055.

product $Ph_3PH^+BCl_4^-$ is similar to the known salt [25] $Et_3PH^+BCl_4^-$. With arsine the species in the solution is undoubtedly Ph_3AsH^+ and the material at the end-point of the titration is $Ph_3AsH^+BCl_4^-$, but this loses hydrogen chloride on warming to room temperature. Previous attempts to make the similar salt $Me_3AsH^+BCl_4^-$ by condensing hydrogen chloride on to Me_3AsBCl_3 failed [25] as hydrogen chloride was recovered when the mixture warmed to room temperature: this case may be similar to that of triphenylarsine and a salt $Me_3AsH^+BCl_4^-$ may be present at low temperatures.

After the success of the triphenylarsine and phosphine experiments,[1] arsine itself was studied. Failure to produce the arsonium ion is, however, not surprising as the dissociation pressure of phosphonium chloride is ~1 atm. at —40°, and 10 mm. at —80°, and of ammonium chloride is ~250 mm. at 300°. The results probably indicate slight formation of $AsH_4^+Cl^-$ in liquid hydrogen chloride, and greater stability of the arsonium ion in solution when boron trichloride is also present.

The failure to make ammonium tetrachloroborate must be due to the extreme insolubility of ammonium chloride, as the salt has been prepared in 91% yield by grinding the reactants in chloroform.[11]

With hydrazine no attempt was made to prepare the tetrachloroborate after the failure with ammonium chloride. It was possible to make a substituted hydrazinium tetrachloroborate, $Ph_2N{\cdot}NH_2,HBCl_4$. It is not possible to assign a complete structure from the infrared spectrum but the product certainly contains the tetrachloroborate ion.

Group VI *Compounds*.—In this series, remarkably, no stable protonated derivative was formed with boron trichloride; the adducts and their decomposition products were produced. All the compounds that contained an active hydrogen readily lost hydrogen chloride, in accord with previous observations, for, *e.g.*, methanol–boron trichloride and phenol–boron trichloride.[26]

Various protonated derivatives with hydrogen chloride have previously been reported, *e.g.*, $(MeOH)_3(HCl)_2$,[27] m. p. —64°, MeOH,HCl,[28] m. p. —62°, $Me_2O,5HCl$,[28] and Me_2O,HCl in the gas phase; [29,30] so it seems surprising the onium salts are not formed. Absence of protonation of diphenyl ether has also been observed in sulphuric acid and is attributed to forms such as $Ph{\cdot}O^+{:}C_6H_4^-$, and it is also not possible to form boron trichloride adducts.[14,15]

The present work differs from earlier work in that phenol and anisole were previously reported to be insoluble in hydrogen chloride.[31] It was not possible to promote fission of anisole, to give $PhO{\cdot}BCl_2$ and methyl chloride—the latter was not evolved even when the compound melted: from a previous report [32] it is not quite clear when fission is supposed to occur. Phenoxyboron chlorides from phenol and boron trichloride dissociate readily, phenoxyboron dichloride at —15°, the ultimate products being triphenyl borate and boron trichloride.[14]

A general study of the equivalent conductivities shows them to increase in the order diphenyl ether, phenol, anisole; this must be due to the relative electron-releasing powers, $Ph < H < Me$. This conclusion is, in general, confirmed for the series diphenyl ether, water, and dimethyl ether, and diphenyl sulphide, hydrogen sulphide, and dimethyl sulphide.

One of us (M. E. P.) acknowledges his indebtness to the D.S.I.R. for a maintenance grant.

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[30] Maas and Morrison, *J. Amer. Chem. Soc.*, 1923, **45**, 1675.
[31] Maas and McIntosh, *J. Amer. Chem. Soc.*, 1911, **33**, 70.
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