466. *Liquid Hydrogen Chloride as an Ionizing Solvent. Part II.*[1]
Neutralization Reactions in the Solvent and Applications in Preparative Work.

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Neutralization reactions in liquid hydrogen chloride were performed; the following new co-ordination compounds have been obtained:

Me_4NSO_3Cl, PCl_4SO_3Cl, PCl_4BF_3Cl, PH_4BF_3Cl, PH_4BCl_4, $POCl_3 \cdot BF_3$.

Materials soluble in the solvent are classified in the groups: strong solvo-bases, PCl_5, Me_4NCl, $(C_6H_5)_3CCl$, pyridine; medium-strong solvo-bases, Et_4NCl, CH_3COCl, $POCl_3$, PH_3; weak solvo-acids, SbF_5, HSO_3Cl.

In Part I[1] we showed that anhydrous, liquid hydrogen chloride acts quite readily as a solvent for a number of polar and non-polar materials. Some of the solutions thus obtained have so high a conductance that they closely resemble aqueous solutions of electrolytes. Hence, it is necessary to discuss the nature of the ions responsible for the conductivity.

The self-conductance of liquid hydrogen chloride is approximately the same as that of conductivity water. To account for this, self-ionization is assumed, basically of one molecule of hydrogen chloride:

$$HCl \rightleftharpoons H^+ + Cl^- \quad \dots \dots \dots \dots \dots \quad (1)$$

This equilibrium corresponds to the simplest expression for the self-ionization of water. But, as in water, association effects have to be considered and the ionization equilibrium is better represented by:

$$3HCl \rightleftharpoons H_2Cl^+ + HCl_2^- \quad \dots \dots \dots \dots \quad (2)$$

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[1] Part I, preceding paper.

The existence of the hydrogen dichloride ion, HCl_2^-, as a kinetic entity in solution in nitrobenzene has already been postulated.[2] Besides, from the work of West,[3] Waddington,[4] Sharp,[5] and from our present investigations, it is obvious that the HCl_2^- ion must be present, both in the solid, and in some organic and inorganic solvents, including water.

The postulated cation H_2Cl^+ is known to exist in the gas,[6,7] but there is no evidence in the literature of its existence in solution. If the self-ionization of liquid hydrogen chloride according to equilibrium (2) is accepted, two definitions each of acids and bases are applicable based upon a difference of emphasis, rather than of principle. This arises from the fact that either chloride ion- or proton-transfer can be regarded as the primary step in equilibrium (2). Consequently, bases may be defined as chloride-ion donors. In liquid hydrogen chloride, these ions are immediately transformed into hydrogen dichloride ions, and hence the concentration of the solvent anions is increased. Correspondingly, acids are chloride-ion acceptors which indirectly diminish the HCl_2^- ion concentration.

In the second pair of definitions, acids are defined as proton donors. The protons combine with an un-ionized solvent molecule to give the solvent's own cation, H_2Cl^+. Materials which indirectly decrease the concentration of these cations are, therefore, bases.

Our results show that the first pair of definitions is unquestionably the more useful. Anhydrous, liquid hydrogen chloride, in spite of its similarity to anhydrous liquid, hydrogen fluoride, is a " chloridotropic "[8] solvent (in which chloride-ion transfers are of fundamental importance) rather than a proton-active solvent.

EXPERIMENTAL

The apparatus and procedures were described in Part I.[1] The distillation of a material possessing a melting point above the temperature of a toluene slush-bath into the conductivity cell is somewhat troublesome, since the material is liable to condense above the level of the solvent. It is impossible to achieve complete dissolution except by evaporating the solvent into a closed, evacuated system and recondensing it when the compound involved (*e.g.* stannic chloride) has melted. This procedure is workable but time-consuming. Phosphine was generated from pure phosphonium iodide with sodium hydroxide and subjected to a freeze-drying procedure, described in Part I. Analyses were carried out as outlined in Part I.

RESULTS

Tetramethylammonium chloride with hydrogen chloride gives the corresponding hydrogen dichloride:[4]

$$Me_4NCl + HCl \longrightarrow Me_4N^+ + HCl_2^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$
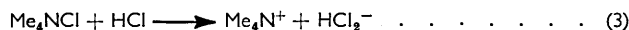
The high conductivity of this compound's solutions in liquid hydrogen chloride indicates that ionization is complete, at least in dilute solutions, so that tetramethylammonium chloride is also a strong base. The result of a conductometric titration of this strong donor with a prospective chloride ion-acceptor, such as boron trichloride, is shown in Fig. 1. The conductance of the tetramethylammonium chloride solution varied uniformly with the molar ratio until a ratio of 1 : 1 was reached. The resulting *tetramethylammonium tetrachloroborate* is soluble in liquid hydrogen chloride, but can be isolated as a solid when the solvent is evaporated. Its chemical analysis confirms its composition Me_4NBCl_4 (Found: B, 4·9; Cl, 62·6. $C_4H_{12}BCl_4N$ requires B, 5·1; Cl, 62·5%).

The plot of a conductometric titration of boron trifluoride against a solution of tetramethylammonium chloride in liquid hydrogen chloride was essentially similar to the above (Fig. 1). Again, there is a break in the conductance at a molar ratio of 1 : 1, indicating the formation of the compound tetramethylammonium chlorotrifluoroborate, which can also be isolated as a

[2] Herbrandson, Dickerson, and Weinstein, *J. Amer. Chem. Soc.*, 1954, **76**, 4046.
[3] West, *J. Amer. Chem. Soc.*, 1957, **79**, 4568.
[4] Waddington, *J.*, 1958, 1708.
[5] Sharp, *J.*, 1958, 2558.
[6] Schisler and Stevenson, *J. Chem. Phys.*, 1956, **24**, 926.
[7] Field and Lampe, *J. Amer. Chem. Soc.*, 1958, **80**, 5583.
[8] Gutmann and Lindquist, *Z. phys. Chem.*, 1954, **203**, 250.

solid (Found: C, 25·5; H, 6·9; B, 6·1; Cl, 17·5; N, 7·6. Calc. for $C_4H_{12}BClF_3N$: C, 27·1; H, 7·1; B, 6·1; Cl, 20·2; N, 7·9%).

Although stannic chloride is insoluble in liquid hydrogen chloride, it can be titrated against a solution of a soluble base. The result of a run with tetramethylammonium chloride and stannic chloride is shown in Fig. 2. During the titration a white salt was precipitated, corresponding with the break in the conductance–molar ratio plot which occurred at a ratio of 2 : 1. When the hydrogen chloride is evaporated and the excess of stannic chloride pumped off, the well-known bistetramethylammonium hexachlorostannate is obtained. Germanium tetrachloride when treated in the same way shows rather different behaviour. A conductometric titration of tetramethylammonium chloride in liquid hydrogen chloride with germanium tetrachloride is plotted in Fig. 2.

The result is reproducible but difficult to understand. The conductivity of germanium tetrachloride alone in liquid hydrogen chloride is negligible and one would not expect it to raise the conductance of an already highly conducting solution. Germanium tetrachloride does not function as a chloride-ion acceptor in liquid hydrogen chloride, and no hexachlorogermanates

FIG. 1.

$10^4 K (ohm^{-1} cm.^{-1})$

Molar ratio A:B
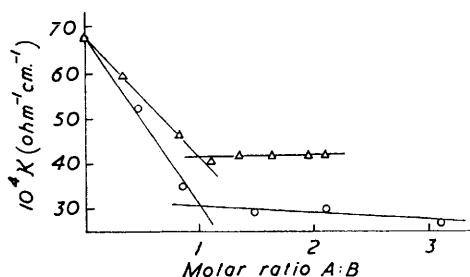
Conductometric titration plots: △, 0·32M-Me$_4$NCl + BCl$_3$; ○, 0·31M-Me$_4$NCl + BF$_3$.

FIG. 2.

$10^4 K (ohm^{-1} cm.^{-1})$

Molar ratio A:B
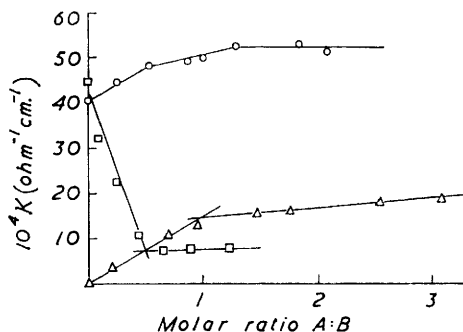
Conductometric titration plots: ○, 0·18M-Me$_4$NCl + GeCl$_4$; □, 0·22M-Me$_4$NCl + SnCl$_4$; △, 0·13M-Et$_4$NCl + BCl$_3$.

are obtainable. There is also no evidence that it undergoes ionization in the reverse sense to give $GeCl_3^+$ or even $GeCl_2^{2+}$.

Germanium tetrachloride has never been investigated in other chlorine-containing non-aqueous solvents and hence no comparisons with its behaviour in hydrogen chloride can be made.

Tetraethylammonium chloride is less soluble in liquid hydrogen chloride than the tetramethylammonium salt and gives less readily conducting solutions. Its solubility limit is attained in solutions just above 0·1M. When such a solution is titrated with boron trichloride, the conductivity rises appreciably until the equivalent point of a 1 : 1 compound is reached. Thereafter the increase is only slight. Tetraethylammonium tetrachloroborate is soluble in liquid hydrogen chloride and remains as a solid when the solvent is removed (Found: B, 3·8; Cl, 49·7. Calc. for $C_8H_{20}NCl_4B$: B, 3·8; Cl, 50·1%). Tin tetrachloride titrated against tetraethylammonium chloride gives the expected bistetraethylammonium hexachlorostannate.

Pyridine, 1M-solutions of which in liquid hydrogen chloride are easily prepared, adds two moles of hydrogen chloride to give pyridinium hydrogen dichloride. The conductivity data demonstrate that, in liquid hydrogen chloride, this compound is largely ionized into pyH$^+$ and HCl$_2^-$. When boron trichloride is distilled into this solution a fine white precipitate appears and the conductivity drops to about one-third of its initial value. The solid is pyridinium tetrachloroborate, originally prepared by Lappert [9,10] by another method (Found: B, 4·6; Cl, 60·1. Calc. for $C_5H_6NCl_4B$: B, 4·7; Cl, 60·8%).

Payne's [11] transport-number experiments support the existence [12] of PCl$_4^+$ and PCl$_6^-$ ions in solutions of solvents with high dielectric constants. A minimum in the conductometric

[9] Lappert, *Proc. Chem. Soc.*, 1957, 121.
[10] Gerrard and Lappert, *Chem. Rev.*, 1958, **58**, 1081.
[11] Payne, *J.*, 1953, 1052.
[12] Cf. Clark, Powell, and Wells, *J.*, 1942, 642.

titration of tetramethylammonium chloride against phosphorus pentachloride in acetonitrile has been detected by Fialkov and his co-workers [13] which has been ascribed to the formation of tetramethylammonium hexachlorophosphate. Extensive attempts [14] to prepare hexachlorophosphates have been unsuccessful, but recently,[15] Gutmann and Mairinger claim to have obtained a precipitate which stoicheiometrically corresponded to Et_4NPCl_6 when solutions of tetraethylammonium chloride and phosphorus pentachloride in phosphorus oxychloride were combined. Conversely, Groeneveld has repeatedly [16] demonstrated the strong donor properties of phosphorus pentachloride.

FIG. 3.

Conductometric titration plots: □△, 0·36M-PCl₅ + BCl₃; ○, 0·20M-PCl₅ + BF₃.
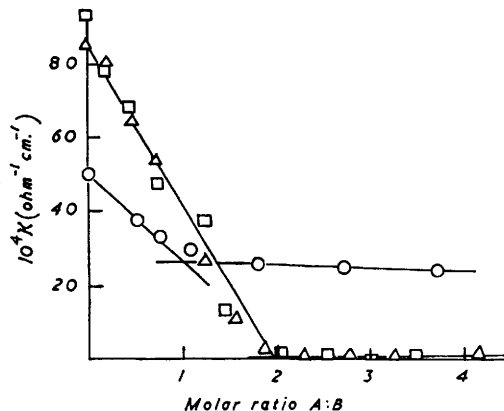
There is no doubt that in liquid hydrogen chloride phosphorus pentachloride is merely a chloride-ion donor. The dissolution of solid phosphorus pentachloride in the solvent can be represented as:

$$PCl_4PCl_6 + 2HCl \longrightarrow 2PCl_4^+ + 2HCl_2^- \quad \quad \quad \quad \quad (4)$$
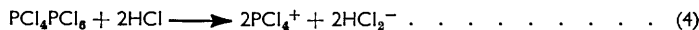
Mixtures with tetramethylammonium chloride in liquid hydrogen chloride form clear solutions which behave like one strong base with two cations. After evaporation of the solvent the solid remaining consists of a mixture of tetramethylammonium hydrogen dichloride and unmodified phosphorus pentachloride. This is clearly shown by infrared and X-ray examinations of the solid. No tetramethylammonium hexachlorophosphate was formed.

A conductometric titration of a solution of phosphorus pentachloride in liquid hydrogen chloride with boron trifluoride as an acceptor is plotted in Fig. 3. The slope is of the usual kind for this type of acid–base reaction in liquid hydrogen chloride, with a break at a ratio corresponding to the formation of the compound *tetrachlorophosphonium chlorotrifluoroborate*. This compound is isolated as a solid on evaporation of the solvent. Its infrared spectrum [17] suggests an ionic structure $PCl_4^+BF_3Cl^-$ (Found: B, 3·8; Cl, 64·7; F, 19·1; P, 11·3. BCl_5F_3P requires B, 3·9; Cl, 64·2; F, 20·7; P, 11·2%). Unexpectedly, a different result is obtained when boron trichloride is titrated against phosphorus pentachloride (Fig. 3). The conductivity of the pentachloride solution drops, on the addition of boron trichloride, much further than in the BF_3 titration and the plotted results show a break only at or slightly below a molar ratio of two. The initial- and end-values of the conductance differ by the unusually large factor of almost 200. The reaction product of phosphorus pentachloride and boron trichloride is soluble in liquid hydrogen chloride until a molar proportion of $BCl_3 : PCl_5 = 0·8$—$0·9$ is reached. Above this ratio a white precipitate separates which continues to form as more boron trichloride is added. The shape of the plot of the conductometric titration leads to the conclusion that in liquid hydrogen chloride a *compound* corresponding to the formula $PCl_5,2BCl_3$ is formed. The analysis of the precipitate is in accord with this conclusion (Found: B, 4·9, 5·1. $B_2Cl_{11}P$ requires B, 4·9%).

[13] Fialkov, Kuzmenko, and Kostromina, *Ukrain. khim. Zhur.*, 1955, **21**, 556.
[14] Gutmann, *Monatsh.*, 1952, **83**, 583.
[15] Gutmann and Mairinger, *Z. anorg. Chem.*, 1957, **289**, 279.
[16] Groeneveld, *Rec. Trav. chim.*, 1952, **71**, 1152; 1956, **75**, 594; Groeneveld and Zuur, *ibid.*, 1953, **72**, 617.
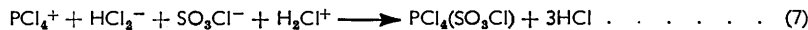[17] Waddington and Klanberg, *J.*, in the press.

At room temperature, the precipitate cannot be stored in sealed tubes without losing half of its boron trichloride. The structure of the 1 : 2 addition compound is not yet known, but its instability suggests that the second molecule of boron trichloride may be only loosely associated with the stable compound tetrachlorophosphonium tetrachloroborate (Found: B, 3·2; Cl, 87·1; P, 9·4. Calc. for BCl_8P: B, 3·3; Cl, 87·2; P, 9·5%). It is noteworthy that the existence of an analogous addition compound corresponding to the formula $PCl_5,2BBr_3$ has been reported.[18]

Typical neutralization reactions in liquid hydrogen chloride may also be studied by purely preparative methods when chlorosulphuric acid is made one partner. The acid is soluble in liquid hydrogen chloride and partly ionizes according to the process:

$$HSO_3Cl + HCl \rightleftharpoons H_2Cl^+ + SO_3Cl^- \quad \dots \dots \dots \dots \quad (5)$$

With solvo-bases such as tetramethylammonium chloride or phosphorus pentachloride, acid–base reactions can then proceed according to the schemes:

$$Me_4N^+ + HCl_2^- + SO_3Cl^- + H_2Cl^+ \longrightarrow Me_4N(SO_3Cl) + 3HCl \quad \dots \dots \quad (6)$$

$$PCl_4^+ + HCl_2^- + SO_3Cl^- + H_2Cl^+ \longrightarrow PCl_4(SO_3Cl) + 3HCl \quad \dots \dots \quad (7)$$

The resulting salts, *tetramethylammonium chlorosulphate* and *tetrachlorophosphonium chlorosulphate* are readily soluble in liquid hydrogen chloride but can be obtained as white solids when the solvent is evaporated (Found: Cl, 18·3; S, 17·1. $C_4H_{12}ClNO_3S$ requires Cl, 18·7; S, 16·9%. Found: Cl, 61·2; P, 10·9; S, 11·3. Cl_5O_3PS requires Cl, 61·5; P, 10·7; S, 11·1%).

A mole of hydrogen chloride is formed for each mole of salt produced in the reaction. This increase of the volume of hydrogen chloride can easily be measured and assigned to the quantitative reaction.

The tetrachlorophosphonium chlorosulphate, PCl_4SO_3Cl, which is easily, and possibly even exclusively, obtainable in liquid hydrogen chloride can also be regarded as an adduct of phosphorus pentachloride and sulphur trioxide. In this sense, the compound exhibits a close correlation to the well-known addition compounds of selenium and tellurium tetrachlorides, and sulphur trioxide, the structures of which have recently been interpreted in terms of salts of chlorosulphuric acid: $SeCl_3^+SO_3Cl^-$ and $TeCl_3^+SO_3Cl^-$.[19]

Tetrachlorophosphonium chlorosulphate cannot be made, however, from sulphur trioxide or chlorosulphuric acid and phosphorus pentachloride either directly or by using organic solvents. Under these conditions, the products of a vigorously exothermic reaction invariably consist of a mixture of phosphorus oxychloride, sulphonyl chloride, and other secondary products. The white salt tetrachlorophosphonium chlorosulphate is unstable at room temperature, and starts decomposing after some time into a liquid mixture.

Recent developments have shown that the view, introduced by Gutmann,[20] that complex formation with phosphorus oxychloride is achieved by chloride-ion donation, has to be modified as oxygen co-ordination appears to play a vital part in the structure of some solid phosphorus oxychloride adducts.[21] On the other hand, Baaz and Gutmann[22] have argued supporting the existence of an equilibrium $POCl_3 \rightleftharpoons POCl_2^+ + Cl^-$ in solution. Results by Spandau and Beyer,[23] who carried out an electrolysis of phosphorus oxychloride, also apparently favour the existence of an individual $POCl_2^+$ ion.

We believe that our results on the behaviour of phosphorus oxychloride in liquid hydrogen chloride suggest that, in these solutions, phosphorus oxychloride undergoes ionization according to the scheme:

$$POCl_3 + HCl \rightleftharpoons POCl_2^+ + HCl_2^- \quad \dots \dots \dots \dots \quad (8)$$

Fig. 4 shows the conductometric titration of a solution of phosphorus oxychloride in liquid hydrogen chloride with boron trichloride. The initial conductance drops sharply and reproducibly when a small addition of boron trichloride is made. Then the conductivity increases steadily until a molar ratio of 1 : 1 is reached. The addition compound corresponding

[18] Tarible, *Compt. rend.*, 1901, **132**, 83.
[19] Gerding, *Rec. Trav. chim.*, 1956, **75**, 589.
[20] Gutmann, *Z. anorg. Chem.*, 1952, **270**, 179; *Monatsh.*, 1952, **83**, 164.
[21] Lindquist, *Acta Chem. Scand.*, 1958, **12**, 135.
[22] Baaz and Gutmann, *Monatsh.*, 1959, **90**, 426.
[23] Spandau and Beyer, *Naturwiss.*, 1959, **46**, 400.

to the formula $POCl_3,BCl_3$ is obtained as a white solid after evaporation of the solvent. It can, if necessary, be purified further by sublimation *in vacuo* (Found: B, 4·1; Cl, 78·7. Calc. for BCl_6OP: B, 4·0; Cl, 78·6%). We are unable to explain the curious initial behaviour of the conductivity during the titration of boron trichloride against phosphorus oxychloride.

Previous attempts to prepare a co-ordination compound of boron trifluoride and phosphorus oxychloride have been unsuccessful,[24] even when the components were mixed in light petroleum at temperatures as low as −80°. In liquid hydrogen chloride, however, the preparation presents no difficulties. The *adduct* had m. p. −3° (decomp.) (Found: B, 5·0; Cl, 46·2; F, 25·2; P, 14·1. BCl_3F_3OP requires B, 4·9; Cl, 48·1; F, 25·8; P, 14·1%).

We then re-investigated the reaction between thionyl chloride and boron trichloride; however, we have obtained results only confirming those of Burg and Ross.[24] Neither the conductometric titration nor preparative work gives any evidence of a co-ordination compound. In liquid hydrogen chloride the donor strength of thionyl chloride is very feeble and the compound is inappreciably ionized.

Fig. 4.

Conductometric titration plots: △, 0·86M-PH₄Cl + BF₃; ○, 0·34M-POCl₃ + BCl₃.
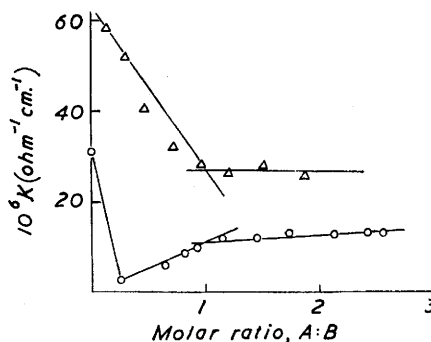
The passing of phosphine into liquid hydrogen chloride yields phosphonium chloride which is to some extent soluble in the solvent and gives a moderately conducting solution. This solution can be titrated with boron trichloride or trifluoride; the curve for the latter is recorded in Fig. 4. The limited solubility probably gives rise to some deviations from linearity, but there is a clear break when the ratio of the reactants is 1 : 1. *Phosphonium chlorotrifluoroborate* is a slightly yellowish solid; its stability is greater than that of phosphonium bromide but lower than that of phosphonium iodide. Under its own dissociation pressure it can be kept in sealed tubes, which have to be cooled before being opened (Found: B, 7·7; Cl, 22·1. $BClF_3H_4P$ requires B, 7·8; Cl, 25·6%).

In exactly the same way, *phosphonium tetrachloroborate*, PH_4BCl_4, has been prepared. In the absence of air this compound is as stable as phosphonium iodide (Found: B, 5·8; Cl, 73·9. BCl_4H_4P requires B, 5·8; Cl, 75·9%).

Since Clusius and Haimerl[25] had found rapid exchange to occur between PCl_3 and $H^{35}Cl$ and had attempted to explain this by postulating $HPCl_4$ as an intermediate, we have performed some experiments with phosphorus trichloride in liquid hydrogen chloride. Although phosphorus trichloride is very soluble in this solvent, the solutions are non-conducting, provided no traces of phosphorus oxychloride are present. With a strong base, such as tetramethylammonium chloride, no reaction takes place. A conductometric titration of phosphorus trichloride in liquid hydrogen chloride with an acceptor, such as boron trichloride, disproves any reaction in which ionic species are involved. However, after the removal of the solvent and excess of boron trichloride by evaporation a colourless liquid is obtained which corresponds to the formula PCl_3,BCl_3 (Found: B, 4·1; Cl, 83·7. Calc. for BCl_6P: B, 4·3; Cl, 83·6%).

Liquid phosphorus trichloride and boron trichloride are also miscible in every proportion without precipitation. A 1 : 1-molar mixture solidifies at −63° to −64°. Stieber[26] first mentioned the existence of the compound phosphorus trichloride–boron trichloride but it is doubtful whether he ever obtained it. His statement that it is a white solid at room temperature which can be sublimed without decomposition has to be revised. It is significant that

[24] Burg and Ross, *J. Amer. Chem. Soc.*, 1943, **65**, 1637.
[25] Clusius and Haimerl, *Z. phys. Chem.*, 1942, *B*, **51**, 347.
[26] Stieber, *Compt. rend.*, 1932, **195**, 610.

these wrongly ascribed properties actually coincide with those of the adduct of phosphorus oxy-chloride and boron trichloride.

<center>DISCUSSION</center>

Addition compounds of phosphorus trichloride are generally established by dative bonding between the π-electron pair of phosphorus and vacant d- or p-orbitals of an acceptor. Ionic structures such as PCl_4^- or PCl_2^+ are so highly unfavoured that their contributions can be virtually excluded. There is every reason to suppose that the covalent boron–phosphorus bond in the 1 : 1 phosphorus trichloride–boron trichloride adduct is relatively weak and that the forces between the two molecules are only van der Waals forces, so that the low melting point of the compound, $-64°$, becomes quite explicable.

On the basis of the results presented in this paper and in Part I,[1] it is possible to classify the investigated materials as regards their donor- or acceptor-function for chloride ions in liquid hydrogen chloride. Qualitatively, the following compounds are donors or acceptors:

Donors: Me_4NCl, Et_4NCl, PCl_5, $POCl_3$, $CH_3 \cdot COCl$, PH_3, $NOCl$, $(C_6H_5)_3CCl$, Pyridine
Acceptors: HSO_3Cl, SbF_5, BF_3, BCl_3, $AlCl_3$.

A more elaborate distinction between these materials can be made if their relative strengths as donors or acceptors, *i.e.*, their relative abilities to furnish H_2Cl^+ or HCl_2^- ions in liquid hydrogen chloride, are taken into account. These criteria allow four classes of materials to be distinguished, namely strong bases, medium strong bases, weak acids, and practically non-ionized substances.

<center>*Acid–base behaviour in liquid hydrogen chloride.*</center>

Very strong bases	PCl_5, Me_4NCl, $(C_6H_5)_3CCl$, Pyridine
Medium strong bases	Et_4NCl, $CH_3 \cdot COCl$, $POCl_3$, PH_3
Weak acids	SbF_5, HSO_3Cl
Feebly ionized compounds and non-electrolytes	$NOCl$, $SOCl_2$, PCl_3, $SiCl_4$, BCl_3, BF_3, $AlCl_3$, $B(C_2H_5)_3$

One general deduction that can be drawn from the Table is the striking preponderance of base-like compounds over acid-like materials. Bases tend to be strong or very strong while acids are few and also weak. It is interesting that relatively the strongest acid we have found is a fluoride. We have not yet examined arsenic and phosphorus pentafluorides which possibly might behave similarly. An example of the unpredictability of the donor- or acceptor-strength of compounds in liquid hydrogen chloride is the case of boron trifluoride. This is one of the most powerful acceptor molecules so that a strongly acidic solution might be expected in liquid hydrogen chloride. In fact, 0·1—2 molar solutions are very poorly conducting. The same holds for boron trichloride. This is highly soluble in the solvent but the conductance of its solution indicates very feeble ionization. More-over, as Martin[27] has pointed out, the existence of the free acid $HBCl_4$ seems doubtful.

Both conductometric measurements[28] and exchange reactions[29] have shown that the equilibrium concentration of $AlCl_4^-$ in liquid hydrogen chloride is also extremely low. These results entirely fit in with the picture of the behaviour of the boron halides.

The general infrequency of occurrence of acids in liquid hydrogen chloride is one of the features in which this material resembles liquid hydrogen fluoride most closely. In both cases, the relative ease with which the corresponding anions HF_2^- and HCl_2^- are formed is contrasted by a great reluctance to form cations H_2F^+ and H_2Cl^+ corresponding to them.

[27] Martin, *J. Phys. Chem.*, 1947, **51**, 1400.
[28] Richardson and Benson, *J. Amer. Chem. Soc.*, 1951, **73**, 5096.
[29] Blau, Carnall, and Willard, *J. Amer. Chem. Soc.*, 1952, **74**, 5762.