465. *Liquid Hydrogen Chloride as an Ionizing Solvent. Part I. Conductivities of Materials.*

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The conductivities of substances in anhydrous liquid hydrogen chloride, particularly of halides of Groups III—V elements, have been investigated. The compounds are classified according to the effect they have on the conductivity of liquid hydrogen chloride into strong, moderately strong, and weak electrolytes.

APART from some earlier work,[1,2] the study of the properties of anhydrous, liquid hydrogen chloride as an ionizing solvent has been virtually neglected. This may seem surprising considering the vast increase in the number of chlorides and oxy-chlorides [3] investigated for their ionizing properties in recent years, and the many interesting features exhibited by anhydrous, liquid hydrogen fluoride.[4,5] This lack of information is due to two factors. First, there are considerable experimental difficulties not encountered in more conventional ionizing solvents. The liquid range of hydrogen chloride is narrow and exists at an inconveniently low temperature; over this range it has a high vapour pressure, which gives rise to considerable manipulative difficulties in a closed system. Secondly, the physical properties of hydrogen chloride, low dielectric constant and low boiling point, would not suggest it as a good ionizing solvent. A resumé of the physical properties of hydrogen chloride and fluoride is given by Mellor.[6]

EXPERIMENTAL

Apparatus and Procedure.—All experiments were carried out in a vacuum system, to which a number of storage bulbs holding about 40 l. of gaseous hydrogen chloride were attached. 10 l. of gas correspond to about 6 ml. of liquid, the amount required for each individual experiment. Taps in contact with the main line were greased with Kel-F grease. Hydrogen chloride was generated from ammonium chloride and concentrated sulphuric acid in a Kipp apparatus and dried by distillation through two freezing traps, immersed in toluene-slush baths. The vapour pressure of hydrogen chloride at this temperature (−96°) is sufficiently high to allow the gas to pass through the baths which retain all traces of water. The exclusion of air during the generation of the gas is not always possible. Air is removed by freezing the hydrogen chloride with liquid nitrogen and pumping off the remaining permanent gases. The vapour pressure of solid hydrogen chloride at −196° is practically negligible. A conductivity cell was attached to the main line in the vicinity of the bulbs. This cell was designed to permit introduction both of hydrogen chloride and, when necessary, other volatile compounds through a second inlet. The procedure for measurements of the solubility and the conductivity of particular compounds is as follows.

(a) *Involatile solid.* The solid, usually 1—3 mmoles, was weighed in a closed bottle and transferred to the cell in a dry-box. The cell was connected to the system, evacuated, and then immersed in a bath of liquid nitrogen. The main line was disconnected from the pump, and hydrogen chloride admitted from the storage bulbs. After measurement of pressure, each quantity of hydrogen chloride could be condensed in the cell as required. The cell was then closed again and the liquid nitrogen replaced by either baths of toluene- or carbon disulphide-slush, in which the solid hydrogen chloride gradually liquefied. The volume of liquid in the cell was calculated, by use of the gas laws, from the pressure difference in the bulb (or bulbs) before and after condensation of hydrogen chloride in the cell, the volume of the bulb, the temperature, and the density of the liquid. From these the molar concentration of the solution

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[1] McIntosh and Archibald, *Z. phys. Chem.*, 1906, **55**, 150.

[2] Beckmann and Waentig, *Z. anorg. Chem.*, 1910, **67**, 17.

[3] Gutmann and Baaz, *Angew. Chem.*, 1959, **71**, 57.

[4] Fredenhagen, *Z. anorg. Chem.*, 1939, **242**, 23.

[5] Clifford, Beachell, and Jack, *J. Inorg. Nuclear Chem.*, 1958, **5**, 57, 71.

[6] Mellor, " Comprehensive Treatment on Inorganic and Theoretical Chemistry," Supplement II, Part I, 1956, pp. 85 *et seq.*, 413 *et seq.*

under investigation follows. Pressures were measured by using a spiral gauge as a null-point instrument. The spiral side of the gauge was connected to the main line, and the opposite side to a conventional mercury manometer.

(b) *Volatile liquid.* The empty cell was attached to the system and evacuated. The volatile liquid was distilled into the cell from a specially designed vessel through the second inlet. The quantity of material condensed in the cell was measured by difference weighings of the detachable vessel. The small amount of air which entered the connecting space between the vessel and the cell, after each detachment, had to be pumped off before another distillation could proceed. There was a minimum weight of liquid that could be distilled with accuracy into the cell depending upon the geometry of the system and the tare weight of the distillation vessel; with the arrangement described this were about 30 mg. The condensation of hydrogen chloride and the calculation of the concentration was then as in (a).

(c) *Gas.* As representatives of this class we have investigated boron trifluoride and nitrosyl chloride. Boron trifluoride was taken from a commercial cylinder, and stored in a small bulb attached to the system. It was dried in the same way as hydrogen chloride and then used without further purification. Nitrosyl chloride was treated similarly. The material employed in our experiments showed the reported melting point of $-61°$.[7]

The electrodes of the cell were of platinum, and in order to avoid polarization, they were replatinized from time to time. A difficulty not normally encountered in conductivity work arose from the numerous freezing operations involved in the experiments: the electrodes were liable to bend, producing deviations from the initially measured cell constant. It was therefore necessary to check the cell constant very frequently, and no figure of overall validity can be given here. Values of the conductivity were measured with a Mullard bridge, Type E 7566.

Materials.—Tetramethyl- and tetraethyl-ammonium chloride were made from the corresponding hydroxides by Lewis and Wilkins's procedure.[8] When treated with hydrogen chloride in aqueous solution tetraethylammonium chloride retains hydrogen chloride additional to its stoicheiometric formula which is only given off with remarkable reluctance, at 60° and on evaporation of the solvent *in vacuo*. Obviously this behaviour is due to the formation of the very stable tetraethylammonium hydrogen dichloride, Et_4NHCl_2. All the other materials, unless stated otherwise, were of reagent grade quality. Liquids were usually distilled repeatedly before introduction into the cell.

Analytical Methods.—Chlorine was determined volumetrically by a modified Volhard method.[9] This gave excellent and reliable results during a very large number of determinations. When, as in a few of the compounds reported already,[10] the chlorine value found was more than 1% lower than expected, the deviation was entirely due to the extreme difficulties involved in the performance of an accurate hydrolysis. Phosphonium salts such as the tetrachloroborate and chlorotrifluoroborate are, in this respect, particularly unpleasant to handle. Not only had the hydrolysis, as usual, to be accomplished in a closed vessel, but also great care had to be taken to exclude oxygen, to avoid phosphine explosions. Fluorine was precipitated as lead chloride fluoride, which compound was, after being dried, either weighed or its chlorine content titrated. Phosphorus was determined volumetrically by the phosphomolybdate method. Phosphorus not present in the quinquevalent state was oxidized with potassium chlorate, after hydrolysis. Tin was determined as stannic oxide and sulphur as barium sulphate, according to standard procedures.

Boron compounds were, whenever possible, directly hydrolyzed, and the boron titrated immediately as the boric acid–mannitol complex, a reliable technique demonstrated earlier for nitrosyl tetrachloroborate by Partington and Whynes[11] being adopted. This cannot, however, be properly employed in the presence of phosphoric acid. Compounds containing both phosphorus and boron were, therefore, hydrolyzed in a mixture of much methanol and a little water; concentrated sulphuric acid was added, and the methyl borate distilled into dilute sodium hydroxide solution. After acidification, the boric acid–mannitol complex was titrated with sodium hydroxide. This method was also found to be the most useful one in the case of boron trifluoride compounds. With some experience, it is quite practicable to accomplish

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[7] Houtgraaf and DeRoos, *Rec. Trav. chim.*, 1953, **72**, 963.

[8] Lewis and Wilkins, *J.*, 1955, 56.

[9] Swift, Arcand, Lutwack, and Meier, *Analyt. Chem.*, 1950, **22**, 306.

[10] Waddington and Klanberg, *Naturwiss.*, 1959, **20**, 578.

[11] Partington and Whynes, *J.*, 1949, 3135.

a boron determination of this kind in one hour. Carbon and hydrogen were determined by the usual micro-combustion techniques, and nitrogen by a micro-Kjeldahl method.

DISCUSSION

Table 1 gives a list of the compounds which have been studied in liquid hydrogen chloride. All the solubilities given refer to toluene-slush bath temperatures.

In Table 1 the terms "large," "moderate," and "small" refer to the molar conductivity and denote the following: large, 5—50; moderate, 0·5—0·005; and small or very small <0·005 cm.^{2} ohm^{-1} mole^{-1}.

TABLE 1. *Solubilities of compounds in liquid hydrogen chloride.*

(*a*) Readily soluble with large increase of conductance: Me_4NCl, PCl_5, $(C_6H_5)_3CCl$, pyridine.
(*b*) Readily soluble with moderate increase of conductance: Et_4NCl, $POCl_3$, $CH_3{\cdot}COCl$, SbF_5, HSO_3Cl.
(*c*) Readily soluble with small or very small increase of conductance: NOCl, $SOCl_2$, PCl_3, $SiCl_4$,* $AlCl_3$, BCl_3, BF_3, $B(C_2H_5)_3$.
(*d*) Sparingly soluble, small increase of conductance: $SbCl_5$, PH_4Cl, PH_4I. ICl_3, H_2O.
(*e*) Insoluble, no increase of conductance: $GeCl_4$, $SnCl_4$, $PbCl_4$, $AsCl_3$, $SbCl_3$.

* $SiCl_4$ does not measurably increase the conductance.

Table 2 gives the specific and molar conductivities of the compounds we have investigated.

TABLE 2. *Specific and molar conductivities of compounds in liquid hydrogen chloride*

Compound	Concn. (mole/l.)	Specific conductance (ohm^{-1} cm.$^{-1}$)	Molar conductance (cm.^{2} ohm^{-1} mole^{-1})
PCl_5	0·20	50·0 × 10^{-4}	25·0
PCl_5	0·36	93·5 × 10^{-4}	25·9
Me_4NCl	0·14	44·0 × 10^{-4}	31·1
Me_4NCl	0·32	67·9 × 10^{-4}	21·5
Pyridine	1·03	62·2 × 10^{-4}	6·0
Ph_3CCl	0·11	48·6 × 10^{-4}	44·0
Et_4NCl	0·13	31·0 × 10^{-6}	0·23
$POCl_3$	0·48	93·5 × 10^{-6}	0·20
$CH_3{\cdot}COCl$	1·13	115·0 × 10^{-6}	0·46
SbF_5	0·28	14·1 × 10^{-6}	0·05
HSO_3Cl	0·38	2·67 × 10^{-6}	0·007
NOCl	0·93	0·70 × 10^{-6}	7·5 × 10^{-4}
$SOCl_2$	0·39	0·27 × 10^{-6}	7·0 × 10^{-4}
BCl_3	0·32	0·13 × 10^{-6}	4·0 × 10^{-4}
BF_3	1·43	0·09 × 10^{-6}	0·6 × 10^{-4}

Compound	Concn. (mole/l.)	Specific conductance (ohm^{-1} cm.$^{-1}$)
$SbCl_5$	satd.	1·16 × 10^{-6}
PH_4Cl	,,	1·06 × 10^{-4}
PH_4I	,,	1·36 × 10^{-6}
ICl_3	,,	3·19 × 10^{-6}
H_2O	,,	4·30 × 10^{-6}
$AsCl_3$	,,	0·37 × 10^{-6}
$SiCl_4$, $GeCl_4$ ... $SnCl_4$, $PbCl_4$ ...	,,	<5 × 10^{-8}

The predominantly ionic alkali and alkaline-earth halides are insoluble in liquid hydrogen chloride, as also are the more common salts of nickel, iron, mercury, lead, tin, manganese, and chromium.[1] We have not repeated each of the older experiments, but, as far as our investigations overlap with the earlier work they are generally in accord with it. The only noted exception is stannic chloride, which McIntosh and Archibald[1] report to be soluble but which we found not to be. Table 2 shows that it is impossible to relate the solubility of materials in liquid hydrogen chloride to the nature of their bonding. Both compounds with essentially covalent bonding and with a salt-like structure are equally soluble. This is only one fact which demonstrated clearly the close similarities in the general solvent properties of hydrogen chloride and hydrogen fluoride. For, although the number of materials soluble in liquid hydrogen chloride is more limited than in liquid hydrogen fluoride, it still covers a wide range of structurally dissimilar compounds.

Water has an unexpectedly small influence on the conductivity of anhydrous hydrogen chloride, as it is largely insoluble. When small amounts of water are distilled into pure hydrogen chloride, the conductivity attains a value of $4{\cdot}3 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$, an increase by a power of two of the self-conductance of hydrogen chloride. On further addition of much water, for instance 20 mmoles of water to 8 ml. of liquid hydrogen chloride, the conductivity remains almost constant. A white precipitate forms which presumably is $H_3O^+Cl^-$.

The compounds listed in groups (*a*)—(*c*) of Table 1 form water-clear solutions, with the exception of nitrosyl chloride and triphenylmethyl chloride. Solutions of nitrosyl chloride, in liquid hydrogen chloride are blood-red, those of triphenylmethyl chloride are deep yellow. This is almost certainly due in the case of triphenylmethyl chloride to the coloured triphenylmethyl cation.

Contrary to the behaviour of alkylammonium chlorides and pyridine, the treatment of triphenylmethyl chloride with hydrogen chloride does not yield a stable hydrogen dichloride. The yellow product that is formed at —85° [12] decomposes at —45°,[13] and recently Sharp [14] has pointed out that only those triarylmethyl chlorides that contain a large number of electron-releasing groups attached to the ring system form hydrogen dichlorides stable at room temperature. It is perhaps significant that chlorides such as stannic chloride, lead tetrachloride, and, to a great extent, antimony pentachloride are insoluble in liquid hydrogen chloride in spite of the fact that the corresponding hexachloro-acids are well-known. Lead tetrachloride, for instance, dissolves in concentrated hydrochloric acid to give dihydrogen hexachloroplumbate. The differences in this behaviour will be considered in the following paper.[12]

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[12] Waddington and Klanberg, following paper.
[13] Meyer, *Ber.*, 1908, **41**, 2576.
[14] Sharp, *J.*, 1958, 2558.