207. *Complex Iron Compounds.   Part I.   The Formation and Solvation of Ferrous Chloride in Non-aqueous Liquids.*

By D. R. CHESTERMAN.

THERE is at present no satisfactory theory to explain why solutions of hydrogen chloride in some liquids will dissolve metals whilst those in other liquids fail to do so.   Considerable work has been carried out on the subject, and in some cases co-ordination compounds of the metallic chloride with the liquid have been isolated (cf. Patten, *J. Physical Chem.*, 1903, 7153; Koppell, *Z. anorg. Chem.*, 1901, **28**, 461; Hamilton and Butler, J., 1932, 2283; Chesterman, J., 1933, 796).

The action on iron of hydrogen chloride dissolved in a number of organic liquids of widely different structure has now been investigated, and it has been found possible to divide these liquids into three classes, *viz.*,

Group I.	Group II.	Group III.
(Water)	Methyl acetate	Carbon tetrachloride
Methyl alcohol	Ethyl acetate	Carbon disulphide
Ethyl alcohol	Ethyl ether	Light petroleum
*iso*Propyl alcohol	Chloroform	Benzene
Acetone		

Group I.—Solutions of hydrogen chloride in these liquids attack iron very rapidly with evolution of heat, the ferrous chloride and the liquid forming a co-ordination compound which is very soluble in the latter.

Group II.—Solutions in these liquids attack iron more slowly with no appreciable evolution of heat.   The period of induction is also much longer.   A co-ordination compound is again formed, but it is either slightly soluble (ester compounds) or insoluble.

Group III.—Solutions in these liquids do not attack iron.

It is significant that in no reaction was anhydrous ferrous chloride formed.   Apparently iron is attacked by hydrogen chloride only in the presence of a liquid with which it can co-ordinate.   The reactions took place in solutions which were eventually saturated with hydrogen chloride.   The factors controlling the reaction should therefore be (*a*) suitability of the liquid for co-ordination, *e.g.*, whether polar or non-polar; (*b*) solubility of hydrogen chloride in the liquid; (*c*) the extent of ionisation of the hydrogen chloride in the liquid, shown by measurement of the conductivity of the saturated solution; (*d*) the solubility of anhydrous ferrous chloride in the liquid.

The solubilities (*s*, in g. of HCl per g. of solution) and conductivities (κ) of the solutions were measured and are shown in Tables I and II.   Values are accurate to the significant figures given.   The cols. headed " I.C.T." give those values which are available in International Critical Tables.   The value for methyl alcohol at 25° in Table I was obtained

TABLE I.

Solubility of hydrogen chloride at 25° at atmospheric pressure.

Liquid.	S.	Press., mm.	I.C.T. (760 mm.).	Liquid.	S.	Press., mm.
Methyl alcohol	0·44	750	0·449	Benzene	0·02	767
Ethyl alcohol	0·39	752	0·398	Chloroform	0·004	730
isoPropyl alcohol	0·17	771	—	Carbon disulphide	0·004	766
Ethyl ether	0·22	760	0·222	Petroleum	0·003	757
Methyl acetate	0·46	760	—	Carbon tetrachloride	0·001	765
Ethyl acetate	0·21	765	—	Acetone	(decomposed)	

TABLE II.

Conductivities (mhos) of saturated HCl solutions at 25°.

Liquid.	κ for pure liquid. Obs.	κ for pure liquid. I.C.T.	κ for satd. HCl soltn.	Liquid.	κ for pure liquid. Obs.	κ for pure liquid. I.C.T.	κ for satd. HCl soltn.
MeOH	$8·3 \times 10^{-6}$	2×10^{-7}	$9·8 \times 10^{-3}$	$CHCl_3$	$<1 \times 10^{-9}$	$<2 \times 10^{-8}$	$<1 \times 10^{-9}$
EtOH	$5·7 \times 10^{-7}$	135×10^{-11}	$4·0 \times 10^{-2}$	CCl_4	$<1 \times 10^{-9}$	$4 \times 10^{-18*}$	$<1 \times 10^{-9}$
$Pr^{\beta}OH$	24×10^{-7}	35×10^{-7}	$1·2 \times 10^{-2}$	CS_2	$<1 \times 10^{-9}$	$78 \times 10^{-19*}$	$<1 \times 10^{-9}$
$Me·CO_2Me$	$2·9 \times 10^{-7}$	34×10^{-7}	$1·1 \times 10^{-5}$	Petroleum	$<1 \times 10^{-9}$	1×10^{-18}	$<1 \times 10^{-9}$
$Me·CO_2Et$	$<1 \times 10^{-9}$	$<1 \times 10^{-9}$	$1·6 \times 10^{-5}$	C_6H_6	$<1 \times 10^{-9}$	$<1 \times 10^{-18}$	$<1 \times 10^{-9}$
Et_2O	$<1 \times 10^{-9}$	$<4 \times 10^{-13}$	$5·5 \times 10^{-5}$	$COMe_2$			(Decomp.)

* At 18°.

graphically from values given for other temperatures. The conductivity values of the pure liquids are compared with the I.C.T. values solely as criteria of purity. The methyl acetate was probably purer than that described in the I.C.T. The values are all the mean of those given in two or more concordant experiments.

The conductivity of a saturated solution of hydrogen chloride in methyl alcohol may be influenced by the slight reaction between these two substances, forming water (cf. Carter and Butler, J., 1924, **125**, 963; Carter and Megson, *J. Soc. Chem. Ind.*, 1927, **46**, 31T).

The results may now be correlated with the classification. The liquids in Group I are all strongly basic (water is actually amphiprotic), and the hydrogen chloride is shown by Table II to be strongly ionised. The reaction is presumably $XOH + H^+ \rightleftharpoons X,H_2O^+$ ($X = H, CH_3, C_2H_5$, etc.). The high ionisation is increased by the high solubility of the gas. The iron is thus attacked by an ionic reaction, with simultaneous co-ordination of the liquid, probably due to attachment of the X,H_2O^+ ion, with a subsequent readjustment of charges which liberates hydrogen.

Since solutions of hydrogen chloride in the liquids of Group II were un-ionised or almost so, the mechanism of the reaction must be different : it is probably similar to the decomposition of water by sodium (Horiuti and Szabo, *Nature*, 1934, **133**, 327), so that hydrogen chloride *molecules* actually attach themselves through their chlorine atoms to the metallic surface, with simultaneous solvation. The hydrogen again would thus be subsequently eliminated.

The reaction with dry chloroform (in which hydrogen chloride is only slightly soluble) occurred only in the presence of a trace of water. It is possible that this acted as a catalyst solely by increasing the solubility of the hydrogen chloride. Conductivities measured while the reaction was proceeding showed no detectable difference in the conductivity of (*a*) pure chloroform, (*b*) pure chloroform saturated with hydrogen chloride, (*c*) the reacting mixture of iron, hydrogen chloride, and chloroform (first exposed to the atmosphere for a few seconds to acquire moisture, as the chloroform had been dried for some months with phosphoric oxide), which was evolving hydrogen. Hence, the quantity of water required for catalysis is very small and insufficient to cause measurable ionisation of the hydrogen chloride.

The reaction in ether was somewhat similar but proceeded even when the liquid was perfectly dry. Hydrogen was evolved from the iron, and a white co-ordination *compound* was formed from ferrous chloride and ether, whilst the liquid remained a perfect insulator.

The conductivity increased if dry air was admitted, owing to formation of an ionised ferric compound. The ferrous co-ordination compound was always formed in a pile of flat layers, each made up of many minute crystals. The phenomenon was probably caused by the insolubility of the compound, the layers being forced up as hydrogen was evolved beneath them. Ether is decomposed by the continued action of hydrogen chloride. After standing for some hours, the saturated solution showed a conductivity which increased to the limiting value given in Table II; at the same time a small quantity of an oily liquid was formed, as shown on evaporation of the ether.

The liquids in Group III were all aprotic. The slight solubility of hydrogen chloride was probably mechanical, comparable with that of air in water. It showed no ionisation, and there was no tendency for the liquid to co-ordinate.

The last factor (*i.e.*, solubility of anhydrous ferrous chloride in the liquid) does not appreciably influence the reaction, for although anhydrous ferrous chloride is quite insoluble in dry ether, yet an ethereal solution of hydrogen chloride reacts very vigorously with iron. This again suggests that attack of the iron does not take place before co-ordination. If the anhydrous salt were formed first, it would presumably cover the metallic surface and prevent further action, as in the reaction between lead and hydrochloric acid.

The reaction between acetone, iron, and hydrogen chloride could not be investigated fully, as the acetone was decomposed by hydrogen chloride, forming polymerised oily compounds.

The results obtained are not fully in agreement with those of Patten (*loc. cit.*), who found no action with chloroform, but obtained *ferric* chloride when using carbon tetrachloride. His iron was not pure.

It is proposed to discuss the ionisation of the co-ordination compounds in a subsequent paper; the present analyses show that large molecules are less able to co-ordinate with ferrous chloride than smaller molecules; *e.g.*, under comparable conditions, the two salts $FeCl_2,4MeOH$ and $FeCl_2,Pr^\beta OH$ were formed. In this respect ferrous chloride is analogous to chromic chloride (cf. Chesterman, *loc. cit.*).

<center>EXPERIMENTAL.</center>

In the preliminary experiments iron wire was used, but as this invariably contained traces of carbon, in all the remaining work pure reduced iron was used. The details of the purification of liquids are given in Table III.

Ferrous Chloride Methyl Alcoholates.—The *dimethylalcoholate*, $FeCl_2,2MeOH$, was prepared by passing dry hydrogen chloride into iron suspended in 25 c.c. of methyl alcohol. The apparatus was similar to that used in the preparation of the corresponding chromium compounds (*loc. cit.*). The iron rapidly dissolved, and the solution (filtered if iron wire had been used) was left over-night in a vacuum desiccator over sulphuric acid. Well-defined colourless needles separated, and after the residual liquid had been decanted these were washed with dry ether, and the ether removed on a porous plate. They oxidised rapidly in moist air, becoming yellow, but since the yellow compound was soluble and the undecomposed ferrous salt was insoluble in ether, the crystals could be prepared fairly pure (Found: Fe, 29·33; Cl, 36·61. $C_2H_8O_2Cl_2Fe$ requires Fe, 29·27; Cl, 37·16%).

The tetramethylalcoholate, $FeCl_2,4MeOH$, was prepared by passing a very rapid current of hydrogen chloride into iron suspended in a very small quantity (5—10 c.c.) of the methyl alcohol. It was a metastable form, but under these conditions the solution crystallised very rapidly to give well-defined, white, monoclinic crystals. It was difficult to analyse this compound, since it tended to lose 2MeOH, and also was oxidised in moist air very rapidly. The crystals were analysed after rapid drying on a porous plate to remove mother-liquor and transference at once to a well-stoppered weighing-bottle (Found: Fe, 22·48; Cl, 28·47; Fe : Cl : MeOH = 1 : 1·994 : 3·722. Calc.: Fe, 21·91; Cl, 27·83%). They disintegrated in ether, apparently forming the dialcoholate. Benrath (*J. pr. Chem.*, 1905, **72**, 220) prepared this compound by the action of sunlight on ferric chloride dissolved in methyl alcohol. The present method is more rapid and gives a purer product.

Ferrous Chloride Ethylalcoholate, $FeCl_2,EtOH$.—The reaction was very similar to that in which methyl alcohol was used, but the co-ordination *compound* did not crystallise so readily; it usually crystallised as white needles when the hot mother-liquor, filtered from the excess

of iron, was left in a vacuum desiccator. It was extremely soluble, and if the solution was not saturated with hydrogen chloride, crystals did not form. They were purified by washing with dry ether. In the air they rapidly turned yellow (Found : Fe, 32·45; Cl, 41·31. $C_2H_6OCl_2Fe$ requires Fe, 32·31; Cl, 41·04%).

Ferrous Chloride iso*Propylalcoholate*, $FeCl_2,Pr^\beta OH$.—This *salt* was very similar to the preceding one, but it was still less readily crystallisable, and oxidised very much more readily (Found : Fe, 31·09; Cl, 40·28. $C_3H_8OCl_2Fe$ requires Fe, 29·73; Cl, 7·76%).

Ferrous Chloride Monomethylacetate, $FeCl_2,CH_3 \cdot CO_2CH_3$.—This *salt* was prepared in the pure state by dissolving iron in an excess of pure methyl acetate saturated with hydrogen chloride. A white mass of minute needles was formed, and the excess of hydrogen chloride and ester was blown off by a vigorous stream of dry hydrogen. It was hoped to use this method as a check on the analyses by converting a weighed quantity of iron completely into the co-ordination compound, and weighing this in an atmosphere of hydrogen, but removal of the last traces of liquid required an excessive amount of hydrogen. The salt was stable in an inert atmosphere, but decomposed rapidly in the air, becoming hydrated and oxidised (Found : Fe, 27·39. $C_3H_6O_2Cl_2Fe$ requires Fe, 27·81%).

A similar salt was formed with ethyl acetate. This was even more readily decomposed, and the difficulties of removing the excess of ester were also accentuated. The dry salt gave off ethyl acetate on heating, but could not be prepared sufficiently pure for analysis.

The compounds with ether and with chloroform decomposed rapidly in the dry state, and could not be prepared pure. Both consisted of minute white needles (seen under the microscope) which on isolation from mother-liquor gave up the co-ordinated liquid; in moist air they were converted into the tetrahydrate. Although readily decomposed, these compounds were not oxidised in the air as rapidly as the alcoholic compounds. Both were insoluble in the mother-liquor.

Ferrous Chloride–Ether Compound.—This was washed free from hydrogen chloride with dry ether, and the excess of ether removed on a porous plate. The dry *compound*, which smelt of ether, was analysed (Found : Fe, 34·12, 34·23; Cl, 46·45. $C_4H_{10}OCl_2Fe$ requires Fe, 27·79; Cl, 35·30%).

Measurement of Conductivity.—These were carried out in a cell of special design (see fig.). The whole cell was of Pyrex glass, including the delivery tube C, which was bent round (see inset) to avoid the electrodes D. These were coated with platinum-black. Beyond the ground-glass joints A and B, the apparatus was of soda glass. The experiments were all carried out in an electrically controlled thermostat with two glass sides. Hydrogen chloride, made from concentrated sulphuric acid and pure sodium chloride which had been previously heated, was washed through sulphuric acid, and in the preliminary experiments was dried finally by passage through a phosphoric oxide U-tube. Owing to the possibility of the formation of phosphorus trichloride (cf. Partington and Fairbrother, *Trans. Faraday Soc.*, 1934, **30**, 872, 873), in the final measurements the phosphoric oxide tube was replaced by two tubes of anhydrous aluminium chloride. Hydrogen chloride was bubbled slowly through the liquid, and measurements of conductivity were taken at intervals until saturation was complete. Resistances were measured on a calibrated sliding bridge wire, an accurate resistance box being used. The high-frequency current was supplied by a Cambridge reed hummer (new type) working on 2 or 4 volts at about 1000 cycles. At the end of a run the cell was treated with dilute sulphuric acid (if iron had been used), then with cleaning acid, and finally steamed out, and dried with a stream of warm air.

Measurement of Solubility.—These were carried out in the conductivity apparatus. About 4 c.c. of the saturated solution at atmospheric pressure and 25° were mechanically pipetted into a weighed, well-stoppered weighing bottle. After being re-weighed, the bottle was opened under an excess of standard alkali, and the acid estimated by back-titration.

The liquids were all the purest obtainable. They were carefully dried before use and distilled straight into the cell, out of contact with atmospheric moisture (see Table III). All the glass apparatus was dried, either in an electric oven or by hot air, immediately before each run. The cell constant (0·3917) was checked at intervals against standard A.R. potassium
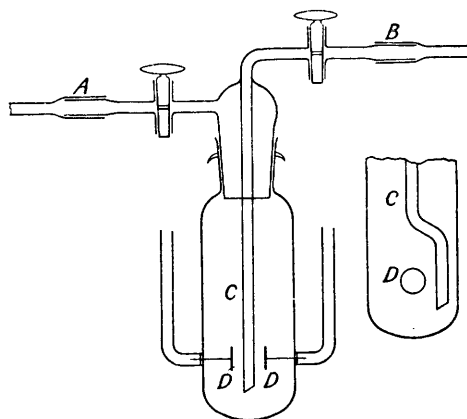
chloride solution in conductivity water. In all the conductivity experiments, reduced iron only was used, from one large bottle kept in a desiccator. All temperatures were read on previously calibrated thermometers.

TABLE III.

Purity of liquids used.

Liquid.	B. p.	Drying agent and purification.
Methyl alcohol	66·0°/759 mm.	Synthetic alcohol freed from acetone by conversion of the latter into iodoform, and dried with sodium.
Ethyl alcohol	77·7/752 mm.	Absolute alcohol dried with CaO, refluxed with CaO, and fractionated through glass-wool.
*iso*Propyl alcohol ...	80·5/745 mm.	Purified by Boot's; dried over Ca.
Ethyl ether	35·5/765 mm.	Freed from alcohol and acetone; dried with Na.
Methyl acetate	57·3—57·8/760 mm.	Dried P_2O_5.
Ethyl acetate	76·8—77·2/765 mm.	Dried P_2O_5.
Chloroform	59·5—59·8/729 mm.	A.R.; freed from acetone and alcohol; dried P_2O_5.
Carbon tetrachloride	77—77·5/760 mm.	A.R.; dried P_2O_5.
Carbon disulphide ...	46—47/759 mm.	Undried.
Light petroleum	60—80/750 mm.	Sodium-dried.
Benzene	79·5—80/767 mm.	A.R.; sodium-dried and redistilled.
Acetone	—	Pure redistilled.