CXII.—*The Polarity of the Halogens in Solutions of Pyridinium and Allied Dichloroiodides.*

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The reactions of pyridinium dichloroiodide, phenyltrimethylammonium dichloroiodide, and tetramethylammonium dichloroiodide have been investigated. The substances show very close similarity with rubidium dichloroiodide, which was studied by Sullivan (*Z. physikal. Chem.*, 1899, **28**, 539), for the dissolution of each in water was accompanied by separation of the chlorine and iodine atoms, the former as chloride ion and the latter as hypoiodous acid—chlorine gas and iodide ion being absent. A satisfactory reaction formula must express these facts. Since hypoiodous acid can give iodine, or iodide, only by reduction, *e.g.*, at a cathode, whereas iodide gives iodine only by oxidation, *e.g.*, at an anode, it is convenient to assign a positive charge to iodine in the former condition. The electrical conductivity of liquid iodine chloride and iodine bromide and of solutions of iodine in several solvents is another indication of the existence of positively charged iodine atoms. In the presence of water, doubtless, these discharge themselves by combination with negatively charged hydroxyl ions, forming hypoiodous acid. The following equation satisfactorily expresses the results obtained in this investigation :

$$\overset{+}{\mathrm{B}}\overset{-}{\mathrm{Cl}}\overset{+}{\mathrm{I}}\overset{-}{\mathrm{Cl}} + \mathrm{H_2O} \longrightarrow \overset{+}{\mathrm{B}} + \overset{-}{\mathrm{Cl}} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}} + \mathrm{IOH}.$$

The formula is intended to denote that the oppositely charged halogen atoms and the radical B are held together by electrostatic forces, like the sodium and chlorine atoms in sodium chloride, but it does not define the degree of electrolytic dissociation which the compound undergoes when dissolved. In water, this is certainly large; in dilute hydrochloric acid, less; and for a 0·001*M*-pyridinium dichloroiodide solution in *N*-hydrochloric acid, the dissociation is still appreciable. The effect of changes in hydrion and chlorine-ion concentration on the degree of dissociation of dichloroiodides has been measured.

EXPERIMENTAL.

Organic dichloroiodides give brown solutions in water, light brown solutions in *N*-sodium chloride, and bright yellow solutions in hydrochloric acid. These will be considered separately.

Procedure.—In a darkened laboratory, 0·001*M*-solutions of the dichloroiodides were made up below 50° with water free from carbon dioxide in steamed flasks of Jena glass. Measured portions at 15° were mixed with a solution of Lintner's soluble starch and the appropriate reagent in steamed test-tubes which were then corked, and kept under observation.

1. *Effect of Water.*—The deep brown 0·001*M*-solutions, which had an odour like that of iodine, remained brown in the presence of starch for more than 5 hours and then became blue. More dilute solutions (0·001—0·00005*M*) became blue more rapidly.

TABLE I.

Time of appearance of blue colour throughout the solution.*

Conc. (molar).	Pyridinium dichloroiodide.	Phenyltrimethylammonium dichloroiodide.
0·001	*after* 5¼ hours	*after* 5¼ hours
0·0006	2¾ ,,	*after* 5¼ ,,
0·0004	76 minutes	3 ,,
0·0003	3 ,,	40 minutes
0·00025	less than 2 ,,	5 ,,
0·00020 0·00015 .... 0·00010	,, ,, 1 minute	less than 1 minute
0·00005	colourless	colourless (discarded after 3 hours)

* When the starch solution was floated on to the dichloroiodide solution, the first appearance of blue colour was as a ring at the surface of contact of glass, starch solution, and dichloroiodide solution; this disappeared on shaking. The times given in Table I refer to the appearance of blue colour throughout the whole of the solutions, which had been mixed by shaking at the beginning of the time period.

2. *Electrolysis.*—When the 0·001*M*-aqueous solution was submitted to electrolysis between platinum wire electrodes in the presence of starch, a blue colour appeared around the cathode in 5 minutes (*E.M.F.*, 2 volts; 35 ⟶ 20 micro-amps.). The anode solution remained light brown. The experiment was repeated many times with the same result. The blue colour did not appear until the circuit was completed. Reversing the direction of the current with the electrodes *in situ* caused the blue colour to appear around the new cathode and dissipation of that around the old cathode. Hydrogen escaped from the cathode. In one experiment lasting 18 hours, a few tiny yellow crystals, which were probably the tetrachloroiodide, were deposited on the anode.

The production of the blue colour at the reducing pole is a fact of theoretical significance, since a substance acquires an electron when it is reduced. Even more significant, however, is the absence of the blue colour at the oxidising pole, showing that iodide ions are absent.

3. *Acidity of the Aqueous Solutions.*—The 0·001*M*-aqueous solutions were decidedly acid to litmus; they dissolved magnesium wire with evolution of hydrogen, and production of a blue colour if

starch was present. Although this result might be attributed to dissociation of the pyridinium complex, a similar reason cannot be put forward to explain the acidity of tetramethylammonium or phenyltrimethylammonium dichloroiodide. The natural inference is that dichloroiodides as they enter into solution withdraw hydroxyl ions from water, leaving the solution acid.

4. *Action of Carbon Disulphide.*—Almost the whole of the iodine was removed from a 0·001*M*-dichloroiodide solution in water by repeated shaking with carbon disulphide, the aqueous layer eventually becoming colourless. It remained colourless also after the addition of starch, but became blue on addition of potassium iodide and starch, possibly owing to the presence of iodate.

5. *Action of Sodium Hydroxide.*—The addition of sodium hydroxide (free from iodide) to the 0·001*M*-dichloroiodide solution in presence of starch caused the appearance of a blue colour at the times stated in Table II, from which it is seen that, whereas high concentrations of alkali prevent formation of the blue colour, intermediate concentrations cause its instantaneous formation, namely, when the molecular ratio of dichloroiodide to sodium hydroxide is 1 : 1 or 1 : 2.

TABLE II.

Action of sodium hydroxide on phenyltrimethylammonium dichloroiodide in presence of starch solution.

Total vol., 10 c.c. Vol. of 0·001*M*-$C_6H_5\cdot NMe_3ICl_2$, 5 c.c.

Vol. of NaOH.	Appearance of blue.	Vol. of NaOH.	Appearance of blue.
0	*not* within 2¼ hours	1·2 c.c. of 0·01*N*	at once
1 c.c. of 0·001*N*	2¼ hours	1·4 ,, ,, ,,	10 mins.
2 ,, ,, ,,	½ hour	1·6 ,, ,, ,,	
3 ,, ,, ,,	2 mins.	1·8 ,, ,, ,, and larger amounts	permanently colourless
5 ,, ,, ,,	at once		

Pyridinium dichloroiodide behaved similarly.

The non-production of the blue colour by an excess of sodium hydroxide is attributed to conversion of iodine into iodide, hypoiodite, and iodate. The accelerated production of the blue colour at the lower concentrations is attributed to upset of the balance of reversible reactions due to removal of hydrogen ions. These are possibly the following :

$$BClICl + H_2O \rightleftharpoons B^{\cdot} + H^{\cdot} + 2Cl' + IOH \rightleftharpoons B^{\cdot} + H^{\cdot} + 2Cl' + \tfrac{1}{5}HIO_3 + \tfrac{2}{5}I_2 + \tfrac{2}{5}H_2O.$$

$$I_2 + 2NaOH \longrightarrow NaI + NaOI + H_2O.$$

$$NaI + I_2 + \text{ starch} \longrightarrow \text{blue substance.}$$

6. *Action of Sodium Chloride.*—High concentrations of sodium chloride (free from iodide) accelerate the production of the blue colour with starch and a dichloroiodide, as shown below.

TABLE III.

Action of sodium chloride on dichloroiodide in presence of starch. (Total vol., 10 c.c.)

Pyridinium dichloroiodide (6 c.c. of 0·001*M*).		Phenyltrimethylammonium dichloroiodide (5 c.c. of 0·001*M*).	
NaCl.	Blue appears in	NaCl.	Blue appears in
0	177 mins.	1 c.c. of 0·1*N*	135 mins.
1 c.c. of 0·01*N*	142 ,,	5 ,, ,, 0·1*N*	5 ,,
1·5 ,, ,, 0·1*N*	20 ,,	1 ,, ,, *N*	immediately
4 ,, ,, *N*	immediately		

7. *Action of Hydrochloric Acid.*—A transient blue colour was obtained by dropping 4*N*-hydrochloric acid into 0·001*M*-dichloroiodide solution containing starch. The blue colour changed to pink in a few seconds and soon became almost colourless, faintly yellow. No blue colour was obtained if the dichloroiodide solution was more dilute than 0·001*M*.

Sulphuric acid produced no visible change in dichloroiodide solutions containing starch; sulphuric acid and sodium chloride together behaved like hydrochloric acid.

8. *Action of Iodides.*—An intense blue colour was obtained by adding potassium iodide to aqueous dichloroiodide solutions containing starch, iodine sometimes separating as a solid.

9. *Reducing Agents.*—In the absence of iodide, the gradual addition of 0·01*M*-sodium thiosulphate to 10 c.c. of 0·001*M*-dichloroiodide solution in water in presence of starch gave a deep blue colour, which was discharged by heating or by excess of thiosulphate. Sulphurous acid, sodium sulphite, stannous chloride, and more slowly, ferrous sulphate, zinc dust, and magnesium gave the same characteristic reaction.

The amount of thiosulphate needed to produce the blue colour and just to discharge it (in the absence of iodide) varied according to the speed of titration from 0·86 to 0·49 of the amount needed when potassium iodide and acid were present in excess.

10. *Oxidising Agents.*—Iodic acid, ferric chloride, cupric sulphate, and ammonium persulphate gave no visible sign of reaction with dichloroiodides and starch, but perhydrol and nitrous acid, which are occasionally used as reducing agents, gave the blue colour immediately.

The interpretation placed on these experiments may be thus summarised : Aqueous solutions of dichloroiodides undergo a change of composition with time. At first, they are strongly acid, are rich in chlorine ions, yield iodine to carbon disulphide with formation of some iodate, fail to give a blue colour with starch for several hours but do so at once if neutralised or made slightly alkaline, or if iodide is added, or in the presence of a large excess of sodium chloride, give the blue colour during electrolysis at the cathode only, and give it on treatment with inorganic reducing agents but not with oxidising agents (except perhydrol and nitrous acid). These solutions, therefore, contain iodine but no iodide; they contain some oxidising agent capable of removing iodide ions faster than they are produced by the action of iodine on the glass (during the first few hours); the oxidising agent is easily destroyed by reduction and it undergoes slow spontaneous decomposition: it is probably hypoiodous acid, which is known to change into iodine, iodic acid and water; or perhaps the compound I_3OH.

11. Cofman (J., 1919, **115**, 1044) has shown that hypoiodous acid interacts rapidly with phenols with production of iodophenols and water, and can be estimated in this way. If, therefore, the conclusions drawn from experiments 1 to 10 are correct, the addition of various phenolic substances to an aqueous solution of a dichloroiodide containing starch should produce a blue colour owing to the formation of iodide by the action of molecular iodine, I_2, on the glass. The following substances produced this effect: phenol, salicylic acid, α- and β-naphthol, cuminol, eugenol, euthymol, *o*- and *p*-cresol, *p*-hydroxybenzoic acid, *m*-hydroxytoluic acid, gallic acid, tannic acid, salicylaldehyde, and guaiacol; whereas a blue colour was not developed with benzoic acid, picric acid, anthraquinone, chloranil, phenanthraquinone, α- or β-naphthaquinone, thymoquinone, anisole, anisic acid, or phenetole. The presence of hypoiodous acid in aqueous dichloroiodide solutions was thus confirmed, and the reason why these solutions did not at first give a blue colour with starch, even though they contained iodine, either free or very loosely combined, became clear.

12. *Action of Amines.*—Since aromatic amines and phenols have many chemical properties in common, trial was made to ascertain if the former also would remove the hypoiodous acid, and allow the solution to develop the blue colour with starch. This took place immediately when dichloroiodides in aqueous solution were treated with aniline, *o*- or *p*-toluidine, *o*-4-xylidine, *o*-anisidine, α- or β-naphthylamine, sulphanilic acid, diethylaniline, phenylhydrazine, or morphine sulphate, and more slowly with acetanilide, *o*-, *m*-, or *p*-nitroaniline, 2-nitro-*p*-toluidine, phenyl-α-naphthylamine, or phenyl-β-naphthylamine.

13. *Action of Unsaturated Compounds.*—The following unsaturated compounds gave the blue colour under conditions similar to those recorded in section 12: cinnamic acid, cinnamaldehyde, terebene, amylene, and alcoholic stilbene. Ethyl or benzyl alcohol, acet-

aldehyde, benzaldehyde, dibenzoylstyrene, urea, alcoholic ethylamine, benzil, benzoin, and hydrobenzoin were without action.

14. *Pyridinium and* p-*Bromophenyltrimethylammonium Dichloroiodides in Hydrochloric Acid.*—These yellow solids are recrystallisable from concentrated hydrochloric acid. They are sparingly soluble in N-hydrochloric acid, giving about $0{\cdot}001M$-solutions the colour of which is like that of the crystals. The solutions do not give a blue colour with starch alone, but give successively red, purple, and blue colorations and then become colourless on gradual addition of sodium thiosulphate, sulphurous acid, nitrous acid, or ferrous sulphate, but not on addition of ferric chloride, potassium iodate, ethyl alcohol, or acetaldehyde.

15. *Electrolysis.*—Electrolysis of the dichloroiodides in $2N$-hydrochloric acid between platinum electrodes in presence of starch gave at the cathode a similar set of colour changes from red through purple to blue in the course of 6 hours, 25 microamps. being used; the anode solution remained yellow and deposited yellow crystals of the tetrachloroiodide on the anode.

16. *Perhydrol.*—This decolorised dichloroiodides in N-hydrochloric acid with evolution of oxygen. In presence of starch, a blue colour appeared only after 5 hours, and disappeared after 18 hours. The greater the amount of hydrochloric acid, the slower the production of the blue colour. The colourless solution finally obtained gave (*a*) with thiosulphate a blue colour, discharged by dilute hydrochloric acid or by an excess of thiosulphate, (*b*) a large precipitate of iodine after addition of potassium iodide, and (*c*) a colourless solution when treated with iodic acid, and hence contained iodate but not iodide.

17. *Halides.*—With potassium iodide, hydrochloric acid solutions of dichloroiodides gave an instant deep blue colour in presence of starch. With potassium bromide, a deeper yellow colour but no blue was obtained; addition of sodium thiosulphate to this solution gave successively a deep red, a blue, and a colourless solution.

18. *Immiscible Solvents.*—Carbon disulphide or benzene became pink, and ether became yellow, when shaken with dichloroiodides in hydrochloric acid. After separation and washing with water, the organic liquid failed to give a blue colour with starch solution unless thiosulphate or iodide was added.

19. *Action of Phenols.*—No blue colour was obtained in presence of starch on addition of phenols to the dichloroiodides in N-hydrochloric acid. Interaction between the phenol and the solution nevertheless took place, and was studied quantitatively (see section 25).

The hydrochloric acid solutions exhibit greater similarity of reaction with aqueous solutions than was expected from their different appearances; but they react more slowly, and they contain less hypoiodous acid and very little (if any) free iodine.

20. 0·001M-*Dichloroiodide Solutions in Aqueous Sodium Chloride.*—The colour of the dichloroiodides in aqueous sodium chloride varied from a light brownish-yellow with 0·1*M*- to a deep brown with 0·001*M*-sodium chloride, the solutions having the odour of iodine. Unlike the behaviour in water or in hydrochloric acid, solutions in aqueous sodium chloride of 0·001, 0·004, and 0·020*M*-concentration gave a blue colour with starch in 5 minutes. The solution in 0·1*M*-sodium chloride remained light brown, but became blue on dilution, a 1 in 2½ solution taking 72 hours, and a 1 in 5 solution, 2½ hours; more dilute solutions failed to turn blue.

21. *Action of Sodium Hydroxide on Dichloroiodides in Aqueous Sodium Chloride.*—Sodium hydroxide had a greater effect than water in accelerating the production of the blue colour with starch, the greatest effect being obtained when the ratio sodium hydroxide : dichloroiodide was about 2 : 1; the blue colour then appeared within 2 minutes. No blue colour appeared when the ratio was 4 : 1. The blue colour faded after a few days when the solutions were exposed to the action of light (in June) through a window facing west. The inner surface of the corks of the test-tubes became slightly yellow. At the end of the experiment shown in Table IV, iodide and hypoiodite were absent, and iodate was present in amount roughly proportional to the original dichloroiodide.

TABLE IV.

Action of sodium hydroxide (1 c.c. of 0·001*N*-solution) on 0·001*M*-pyridinium dichloroiodide in 0·1*M*-sodium chloride solution.

		Blue colour with starch.				Blue colour with starch.	
Solution (c.c.).	Water (c.c.).	First appearance.	Last appearance.	Solution (c.c.).	Water (c.c.).	First appearance.	Last appearance.
1	9	5 mins.	4 days	6	4	24 hours	21 days
2	8	17 hours	7 ,,	7	3	2 days	14 ,,
3	7		9 ,,	8	2	4 ,,	14 ,,
4	6	22 ,,	12 ,,	9	1	5 ,,	12 ,,
5	5	24 ,,	28 ,,	10	0	9 ,,	12 ,,

It is seen from the last column that the blue colour disappeared most slowly when the molecular ratio of sodium hydroxide : dichloroiodide was 1 : 5, which is clearly insufficient to neutralise the total acidity demanded by the equation $BClICl + H_2O \longrightarrow BCl + HCl + IOH$ but would suffice to remove the iodic acid formed in accordance with the further equation $5IOH \longrightarrow HIO_3 + 2H_2O + 2I_2$. No reason for this behaviour is yet known, but the large concentration of sodium chloride is a factor to be considered.

22. *Electrolysis of Dichloroiodides in Sodium Chloride Solution.*—The electrolysis of 0·001*M*-pyridinium dichloroiodide in 0·1*M*-sodium chloride solution containing starch in a U-tube with platinum wires as electrodes (2-volt battery) gave a blue colour around the cathode in 2 minutes; the anode solution remained light brown. Reversal of the current with the electrodes *in situ* produced a blue colour around the new cathode within 2 minutes.

23. *Acid.*—The blue colour with starch given by dichloroiodides in *dilute* sodium chloride solution was discharged by dilute sulphuric acid (but was *not* due to hydrolysis of the starch). This loss of colour was more marked the greater the concentration of either the acid or the sodium chloride. From colorimetric trials, small changes in the acidity had the same effect as large changes in the sodium chloride concentration. In Table V the intensity of the blue colour decreases from left to right.

TABLE V.

Intensity of the blue colour produced with starch, pyridinium dichloroiodide, sodium chloride, and dilute sulphuric acid.

(Total vol., 11 c.c.)

	Proportions in g.-mols.												
Pyridinium dichloroiodide × 10^{-6}	1	1	1	1	1	1	1	1	1	1	1	1	1
Sodium chloride × 10^{-6}	1	1	4	1	1	4	4	20	4	20	20	20	4
Sulphuric acid × 0·5 × 10^{-4}	6	7	6	8	9	7	8	6	9	7	8	9	10
Colour	Blue			Light-blue				Less blue			Colourless		

The colours were compared 20 minutes and 20 hours after the beginning of the experiment, and the same order was recorded in each case, though there was a general slight loss of blueness observed at the longer time.

24. Although convincing reasons for certain idiosyncrasies recorded in this section cannot yet be given, in their general characteristics the sodium chloride solutions of dichloroiodides lie between aqueous solutions and hydrochloric acid solutions. It seems likely that hydrochloric acid solutions and concentrated sodium chloride solutions give no blue colour with starch because formation of free iodine is prevented by the high chlorine-ion concentration. However, with less sodium chloride, free iodine due to the change $5IOH \longrightarrow HIO_3 + 2H_2O + 2I_2$ is probably present; and since Skrabal (*Monatsh.*, 1911, **32**, 167) has shown that electrolytes accelerate this change, these solutions are probably sufficiently rich in iodate and iodine to allow the latter to form sufficient iodide to give the blue colour with starch (by attacking the glass); for it is probable that in nearly neutral solution iodic acid decomposes iodides more slowly than does hypoiodous acid.

Freshly prepared aqueous solutions of dichloroiodides probably contain more hypoiodous acid than free iodine, and so they destroy iodide formed from the glass quickly enough to prevent the blue starch–iodide–iodine complex from being formed.

25. *The Influence of Hydrogen Ions and Chlorine Ions on the Composition of Solutions of Dichloroiodides.*—The rate at which phenol interacts with dichloroiodides was measured in mixtures of aqueous sodium chloride, sulphuric acid, and hydrochloric acid, in various proportions, so as to compare the relative retarding effects of the hydrogen and chlorine ions on the dissociation of the dichloroiodide, as computed from the content of hypoiodous acid. For the latter can be estimated by the difference in thiosulphate titre of aliquot portions containing potassium iodide, before and after the addition of phenol, which in acid solution removes hypoiodous acid quantitatively but does not act directly on iodine chloride (Cofman, *loc. cit.*).

Procedure. 0·001*M*-Solutions of pyridinium or phenyltrimethylammonium dichloroiodide were made up below 30° in the acid–sodium chloride solutions of the requisite composition and were then cooled rapidly to 2°, the volume being 848 c.c. 48·7 C.c. were withdrawn for computation of the concentration at time 0, by addition to potassium iodide and titration of the liberated iodine by 0·002*M*-sodium thiosulphate (x). Into the remainder, at time 0, 48·7 c.c. of 5% phenol solution at 2° were blown, and mixed by shaking for 40 seconds. Measured portions were then withdrawn rapidly by pipettes, discharged at recorded times into potassium iodide solution, and titrated with 0·002*M*-thiosulphate solution with starch as indicator. The phenol being in large excess, nearly constant values were obtained for the velocity coefficient by use of the formula $k = 2{\cdot}3\,(\log_{10} C_1 - \log_{10} C_2)/(t_2 - t_1)$, t being recorded in seconds and C in c.c. of 0·002*M*-thiosulphate. These results are summarised in Table VI, in which $\bar{k}$ is the arithmetic mean of the individual values of k when the difference $C_1 - C_2$ exceeded 1·5 c.c. of thiosulphate for 25 c.c. of dichloroiodide solution—other values being excluded. Column 5 shows the statistically calculated probable error of $\bar{k}$, and is of the order of 1 to 2% owing to end-point difficulties with the very dilute thiosulphate in acid solution. Column 6 shows roughly the order of the initial concentration of hypoiodous acid expressed as a percentage of the total titratable halogen, as computed from the mean $\bar{k}$ and less accurate C_1 and x.

From Table VI, it is evident that chlorine ions have decidedly the greater retarding effect, and hence it is probable that there is a stage intermediate between the undissociated dichloroiodide and its final ionised and hydrolysed products, such that the first and second

TABLE VI.

$0{\cdot}001M$-Pyridinium dichloroiodide.

Added electrolytes.					
M-NaCl.	N-HCl.	N-H_2SO_4.	$\bar{k}$.	Probable error of $\bar{k}$ ($\pm$).	Initial IOH%.
—	1·0	—	0·0603	0·0007	1·8
0·5	0·5	—	0·1032	0·0013	2·6
0·75	0·25	—	0·1567	0·0019	3·4
0·90	0·10	—	0·3705	0·0018	3·8
0·99	0·01	—	2·417	unknown	22
—	0·5	0·5	0·2808	0·0046	7
—	0·4	0·6	0·432	0·0055	(2)
—	0·3	0·7	0·662	0·0092	10

$0{\cdot}001M$-Phenyltrimethylammonium dichloroiodide.

—	1·0	—	0·0672	0·0017	2
0·5	0·5	—	0·0965	0·0019	1
0·75	0·25	—	0·202	0·0024	3·7
0·9	0·1	—	0·389	0·0049	4·5
—	0·5	0·5	0·308	0·0037	5
—	0·4	0·6	0·456	0·0055	6·5
—	0·3	0·7	0·849	0·0090	13

changes are retarded by hydrogen and chlorine ions to different extents: Undissociated BClICl + water $\rightleftharpoons$ Intermediate state $\rightleftharpoons$ $B^{\cdot} + Cl' + IOH + H^{\cdot} + Cl'$. The most likely alternatives for this intermediate state seem to be (*a*) $B^{\cdot} + Cl' + ICl +$ (water), (*b*) $B^{\cdot} + Cl' + I^{\cdot} + Cl'$, (*c*) $BClIOH + H^{\cdot} + Cl'$, (*d*) $B^{\cdot} + [ClIOH]' + H^{\cdot} + Cl'$. Of these, the substance BClIOH and its ion [ClIOH]′ are hypothetical and have never been isolated, nor their existence inferred from other properties; nevertheless they might exist temporarily. If, however, the supposition of their existence is considered unlikely, the choice of a suitable intermediate state lies between (*a*) and its ionised form (*b*). It is difficult to believe that iodine monochloride in (*a*) could be wholly un-ionised, for it is well known to be an electrolyte when prepared in more usual ways. The most probable intermediate state seems therefore to be (*b*) or a mixture of (*b*) and (*a*), either of which involves recognition of a positively electrified iodine atom having a separate existence, though momentary in the presence of water, owing to its affinity for the hydroxyl ion with which it forms hypoiodous acid, or "iodine hydroxide" as others have named it.

Thus in the reactions

$$BClICl \underset{\text{change 1}}{\rightleftharpoons} B^{\cdot} + Cl' + I^{\cdot} + Cl' \underset{\text{change 2}}{\overset{+\text{ water}}{\rightleftharpoons}} B^{\cdot} + Cl' + IOH + H^{\cdot} + Cl'$$

chlorine ions govern the extent of change 1 without influencing change 2, whereas hydrogen ions affect change 2 but not change 1, the tendency for the transformation from left to right being retarded by the presence of substances with these common ions. If this interpretation of these experiments is valid, the first change is the very simple one of the electrolytic dissociation of a double salt,* as opposed to the hydrolysis of a complex salt, and has constitutional significance. The device of writing + and — signs above the atoms in dichloroiodides, as was previously suggested for quaternary ammonium trihalides in general (J., 1926, 2528) to account for regularities in halogen replacement experiments, derives support from the experiments now recorded, and seems to be more than a mere mnemonic. The existence of charged atoms, however, does not prevent the substance from being in solution but undissociated, when the concentrations of chlorine ions and hydrogen ions are high owing to deliberate addition of substances containing these ions.

Summary.

Pyridinium and phenyltrimethylammonium dichloroiodides are highly dissociated in water, the solutions being rich in hydrogen ions, chlorine ions, hypoiodous acid and its decomposition products; molecular chlorine and iodide ions are absent. The retarding effect of electrolytes containing chlorine ions and hydrogen ions on the dissociation of the dichloroiodides has been measured. The probability that dichloroiodides are double salts containing a highly reactive, positively charged iodine atom is discussed. Hypoiodous acid behaves similarly towards phenolic substances and aromatic amines.

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