284. *A Study of the Polyhalides. Part III. Behaviour in Solution.*

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THE polyhalides may be divided into three classes according to their behaviour in solution : (1) Those containing more than one iodine atom, which yield free iodine by dissociation and do not suffer appreciable hydrolysis : these have been carefully investigated by earlier workers and have therefore not been examined in detail again. (2) Those containing one iodine atom, including the salts of the series $RIBr_2$, RIBrCl, $RICl_2$, and $RICl_4$. In the solid state these yield iodine halides (IBr, ICl, or ICl_3) by dissociation. The iodine halides are decomposed by water, and the polyhalides are hydrolysed similarly with formation of iodate, the aqueous solutions containing little or no iodine halide. The authors have investigated the nature of the equilibria established and the reactions of the solutions in some detail, there being comparatively little published data on the subject. (3) Those containing no iodine; these yield bromine, chlorine, or bromine chloride by dissociation, and suffer hydrolysis, as is shown by their acid reaction. The solutions contain considerable quantities of free halogen.

The experiments now described are concerned mainly with solutions of the second class. They appear to indicate that the main equilibrium established in solution is $5IBr_2' + 3H_2O \rightleftharpoons 2I_2 + IO_3' + 10Br' + 6H^{\cdot}$ for a dibromoiodide, and similarly for a dichloroiodide, $5IBrCl' + 3H_2O \rightleftharpoons 2I_2 + IO_3' + 5Br' + 5Cl' + 6H^{\cdot}$ for a chlorobromoiodide, and $5ICl_4 + 9H_2O \rightleftharpoons I_2 + 3IO_3' + 20Cl' + 6H^{\cdot}$ for a tetrachloroiodide. The establishment of such an equilibrium may be explained as follows, potassium dibromoiodide being taken as an example. The compound may be assumed to ionise primarily to $K^{\cdot} + IBr_2'$; the anion then dissociates in the same way as in the dry state, *viz.*, $IBr_2' \rightleftharpoons Br' + IBr$, and the iodine bromide suffers hydrolysis, $IBr + HOH \rightleftharpoons IOH + H^{\cdot} + Br'$, the hypoiodous acid finally decomposing in the usual way : $5IOH \rightleftharpoons 2I_2 + H^{\cdot} + IO_3' + 2H_2O$. On keeping a solution, a state of equilibrium between the products is established. In this particular case the degree of hydrolysis is small and insufficient to cause precipitation of iodine, but with some polyhalides such precipitation does occur on standing, as in the case of the dichloroiodides observed by Reade (J., 1929, 853). Whilst these equations represent the main equilibria, it is probable that traces of other substances may be present (*e.g.*, $HIBr_2$, BrI_2', etc.). Solutions of chlorobromoiodides may contain the ions IBr_2' and ICl_2' as well as $IBrCl'$; this might be expected on theoretical grounds, and would account for the tendency of cæsium dibromoiodide to separate on recrystallisation of the chlorobromoiodide. Such complications render it inadvisable to attempt to determine any equilibrium constants, but the relative degrees of hydrolysis may be estimated as described on p. 2040.

EXPERIMENTAL.

Reactions in Solution.

When a reagent is added to a solution of a polyhalide, if it is capable of reacting with one of the mols. or ions present, thereby removing it from the solution, the equilibrium will be displaced. Hence, towards such a reagent a polyhalide may react as if it were not hydrolysed, whereas, towards a substance which reacts with one of the products of hydrolysis, it may react as if it were completely hydrolysed. Thus the behaviour with different reagents may be used in order to establish the presence or absence of the various ions in a polyhalide solution. In this way, evidence has been obtained for the presence in $KIBr_2$ aq. of $K^{\cdot}$, IBr_2', I_2, Br', HIO, IO_3', and $H^{\cdot}$, and for the almost complete absence of $K^{\cdot\cdot\cdot}$, Br_2, IBr, I', HBrO, BrO_3', and complex kations such as $KIBr^{\cdot}$ and $KBr_2^{\cdot}$. All the reactions investigated confirm the view that the hydrolysis follows the course described above.

(1) *Evidence for the Existence of the Ordinary Metallic Kations in Solution.*—In solutions of a polyhalide the metal gives its normal reactions; thus, K_2SiF_6 and $KClO_4$ are pptd. as readily from KI_3 aq. or $KIBr_2$ aq. as from KI or KBr aq. Similarly, simple salts of the bivalent metals may be pptd. from solutions of their polyhalides. None of the reactions affords any evidence for the existence of metallic kations of abnormal valency or of complexes such as $KIBr^{\cdot}$. That the alkali metals are present in solutions of their polyhalides entirely as univalent kations is further supported by their absorption spectra and by the quantitative data given later (p. 2040).

(2) *Evidence for the Existence of Polyhalide Anions.*—Sparingly sol. polyhalides are pptd. whenever a solution of a polyhalide of the same series is added to one of a salt of the metal or base forming the insol. derivative : *e.g.*, $KIBr_2 + NMe_4NO_3 = KNO_3 + NMe_4IBr_2$(ppt.). Solutions of the compositions $HIBr_2$, $HICl_2$, and $HICl_4$ act as precipitants of IBr_2', ICl_2', and ICl_4' respectively. These double decomp. reactions make it probable that the polyhalide solutions and the corresponding free acids contain the above anions, a conclusion which is confirmed by the absorption spectra and other quant. investigations. Details of these, including evidence for $IBrCl'$, are given later (p. 2040).

(3) *Evidence for the Existence of Free Halogens in Polyhalide Solutions.*—It is well known that solutions of polybromides contain much free Br_2, while those of polyiodides contain a small proportion of their I_2 in the free state. This is shown by the high bromine v. p. of the polybromide solutions, and by the fact that halogens may be extracted from the solutions by, *e.g.*, CCl_4. When this is shaken with an *M*/20-solution of $KIBr_2$, KClBrI, $KICl_2$, or $KICl_4$, I_2, but no appreciable quantity (less than 1%) of Br_2 or Cl_2 and no acid passes into the CCl_4. Of the substances produced during the hydrolysis of these polyhalides, I_2 is evidently the only one appreciably sol. in CCl_4 which is present in more than traces. Since Br_2, Cl_2, IBr, ICl, and ICl_3 are all readily sol. in CCl_4, the polyhalide solutions can contain very little of these substances. This is true even of the solutions obtained by shaking IBr and ICl with H_2O. Table I gives the compositions of the different phases at equilibrium, when 1 g.-mol. of IBr is shaken with 2 l. of CCl_4 and 20 l. of H_2O at 25°. Table II gives the corresponding figures for ICl.

TABLE I.

	I_2.	Br_2.
Concn. in H_2O ...	0·025*N*	0·050*N*
Concn. in CCl_4 ...	0·227*N*	0·000*N*
Solid phase	100%	0%

TABLE II.

	I_2.	Cl_2.
Concn. in H_2O ...	0·011*N*	0·050*N*
Concn. in CCl_4 ...	0·227*N*	0·000*N*
Solid phase	100%	0%

By shaking conc. solutions of the polyhalides with a much larger proportion of CCl_4, it may be shown that traces of the other halogens are extracted. Nevertheless, for the purpose of the quant. work described on p. 2040, this small trace may be ignored.

(4) *Evidence for the Existence of Monohalide Ions.*—In ordinary analytical work, the monohalide anions are usually tested for by adding a solution of a

salt of a metal which forms insol. halides. When such tests are performed on solutions of polyhalides, they give the reactions of monohalides; but the halogens are not present entirely as monohalide ions and solutions of IBr_2', $ClBrI'$, ICl_2', and ICl_4' contain no I' ions. This is in accordance with the above theory, and is supported by the following observations : (*a*) $HgCl_2$ gives no ppt. with solutions of these polyhalides. (*b*) No ppt. is obtained on mixing sat. solutions of $KIBr_2$ and $Pb(NO_3)_2$, although $PbBr_2$ is pptd. from more dil. solutions. (*c*) When *N*/10-$AgNO_3$ is run slowly into a large excess of *N*/10-$KIBr_2$, the Ag is first pptd. quantitatively as pure AgBr (Found : 0·1857 g. Calc. : 0·1867 g.). Soon, however, free I_2 begins to be pptd. simultaneously, attaining a max. when about 2 mols. of $AgNO_3$ per mol. of $KIBr_2$ have been added. The I_2 is destroyed by an excess of $AgNO_3$, the reaction being complete when 3 mols. of $AgNO_3$ have been added. The resultant solution contains 1 mol. of KNO_3 and 2 mols. of HNO_3 and the ppt. is a mixture of AgBr, AgI, and $AgIO_3$. These facts are in agreement with the equation

$$3KIBr_2 + 9AgNO_3 + 3H_2O = 6AgBr + 2AgI + AgIO_3 + 3KNO_3 + 6HNO_3.$$

The course of the reaction may be explained as follows : in a solution of a dibromoiodide there is an equilibrium

$$5IBr_2' + 3H_2O \rightleftharpoons 2I_2 + IO_3' + 10Br' + 6H^{\bullet}$$

Addition of $AgNO_3$ ppts. AgBr; if $AgIBr_2$ exists at all, it must be considerably more sol. than AgBr, otherwise it would be pptd.; AgI is not pptd., since there is no I' present, and $AgIO_3$ is not pptd. because it is 60 times as sol. as AgBr and the concn. of IO_3' ion in the solution is only 0·1 of that of the Br' ion. The removal of Br' from the solution causes the equilibrium to move to the right. Eventually a point is reached when the concn. of I_2 attains the sat. value, and thereafter it is pptd. along with the AgBr. 2 Mols. of $AgNO_3$ are required to ppt. all the Br'; then $AgIO_3$ is pptd., 0·2 mol. of $AgNO_3$ being required per mol. of original $KIBr_2$, whilst the I_2 is destroyed by the $AgNO_3$, $3I_2 + 6Ag^{\bullet} + 3H_2O = 5AgI + 6H^{\bullet} + AgIO_3$, 0·8 mol. of $AgNO_3$ being required per mol. of $KIBr_2$. Summation of these equations shows that the completed reaction is represented by the equation already given.

$AgNO_3$ reacts similarly with KClBrI and $KICl_2$. In the former case, the ppt. produced in the first stages of the reaction consists of pure AgBr in quant. yield (Found : 0·0833, 0·0837 g. Calc. : 0·0831 g.); AgCl is not pptd. at first, since it is nearly 15 times as sol. as AgBr.

With $KICl_4$ the reaction follows a similar course : $3KICl_4 + 15AgNO_3 + 6H_2O = 12AgCl + AgI + 2AgIO_3 + 3KNO_3 + 12HNO_3$. The different stages of the reaction were established quantitatively and follow exactly the same lines as in the case of $KIBr_2$. The odour of the solutions suggests that some substance such as HIO or HIO_2 may be present in appreciable quantity in the intermediate stages of the reactions (see Taylor, J., 1913, **103**, 31). Its presence, however, would not be expected to affect the nature of the final products.

In the above reactions with $AgNO_3$, H_2O takes part, and the action is evidently one between the $Ag^{\bullet}$ ions and the hydrolysis products of the polyhalide, rather than with the polyhalide itself. It follows that in non-aqueous solution, the action, if it occurs at all, must follow a different course. In a solvent such as MeOH, no hydrolysis can occur, and there is no evidence for alcoholysis with formation of MeBr and IO_3'. Thus, solutions of $KIBr_2$ and

$AgNO_3$, both in MeOH, give a ppt. of AgBr and AgI, free from $AgIO_3$, and much I_2 remains in solution even after excess of $AgNO_3$ has been added. The authors have investigated in more detail the reaction between $M/20$-solutions of $AgNO_3$ and IBr in MeOH, a simpler reaction which follows a similar course. When 1 mol. of $AgNO_3$ is run in drop by drop with constant stirring, the Ag and Br are completely pptd. as AgBr (Found: 0·1645, 0·1657 g. Calc.: 0·1643 g.), so that the solution has the composition of $M/40$-iodine mononitrate: $IBr + AgNO_3 = AgBr + I(NO_3)$. The solution is pale orange, but on evaporation at room temp. under reduced pressure it leaves a white solid residue. The product is very deliquescent and is decomposed by H_2O with formation of free I_2, HNO_3, and HIO_3, probably according to the equation $5INO_3 + 3H_2O = 2I_2 + HIO_3 + 5HNO_3$. Addition of another 0·5 mol. of $AgNO_3$ to the MeOH solution ppts. the Ag quantitatively as AgI (Found: 0·1755, 0·1748, 0·1755 g. Calc.: 0·1755 g.), and the solution, which is colourless, has a composition corresponding to that of iodine trinitrate: $2INO_3 + AgNO_3 = AgI + I(NO_3)_3$. Excess of $AgNO_3$ produces no further change. Although the compositions of the solutes are those of $I(NO_3)$ and $I(NO_3)_3$, it cannot be stated with certainty that these two nitrates are actually present, although this seems the simplest explanation of the results. Kappeler (*Ber.*, 1911, **44**, 3496) states that a nitrate or basic nitrate of tervalent I is formed when HNO_3 acts on HIO_3 under suitable conditions, but he gives no analysis. The high velocity and smoothness of the reaction and the nature of the products suggest that the reaction is ionic, and hence that I is capable of forming uni- and ter-valent kations in a non-hydrolysing strongly ionising solvent such as MeOH: $IBr \rightleftharpoons I^{\cdot} + Br'$; $Ag^{\cdot} + Br' = AgBr$; $2I^{\cdot} \rightleftharpoons I' + I^{\cdot\cdot\cdot}$; $Ag + I' = AgI$ (see also p. 2039).

(*d*) $TlNO_3$ gives with $KIBr_2$ aq. a ppt. of TlBr, free I_2 being liberated, and the solution giving the reactions of a thallic salt. There is no evidence for the formation of either IO_3' or I', and the reaction is probably essentially a reduction of the IBr_2' to Br' and free I_2, $2IBr_2' + Tl^{\cdot} = Tl^{\cdot\cdot\cdot} + 4Br' + I_2$ (compare p. 2036).

(5) *Evidence for the Existence of Halogen Oxyacids or their Anions.*—There is no evidence for the existence of any oxy-acids of Cl or Br in solutions of polyhalides of the second class (p. 2031), although traces of ClO_3' or BrO'_3 may be formed when their solutions are made alkaline. Reade (J., 1929, 853) has obtained evidence for the presence of HIO in solutions of dichloroiodides. When a solution of any iodine polyhalide is made alkaline, it contains a high concn. of IO', since the presence of OH' ion shifts the equilibrium in this direction (see below). Some polyhalide solutions give a slight ppt. of $Ba(IO_3)_2$ with $BaCl_2$ aq. indicating the presence of IO_3' in the solution, and di- and tetra-chloroiodides sometimes give iodates on attempts to crystallise them from water. Iodate is also formed when the equilibrium is disturbed by the removal of halide or $H^{\cdot}$ ions (p. 2034 and below) or of free I_2 by means of an org. solvent (p. 2040).

(6) *Evidence for the Existence of Hydrogen Ions.*—Solutions of trihalides containing one I atom, but not those containing more than one, show a strong acid reaction to indicators; this is in accordance with the hydrolysis theory already advanced (p. 2032); *e.g.*, the acidity of solutions of IBr_2' is due to partial hydrolysis: $5IBr_2' + 3H_2O \rightleftharpoons 2I_2 + IO_3' + 10Br' + 6H^{\cdot}$. On adding an excess of $NaHCO_3$ to $KIBr_2$aq., the $H^{\cdot}$ ions are removed and the hydrolysis is carried to completion. The reaction is approx. $5KIBr_2 + 6NaHCO_3 =$

$3H_2O + 6CO_2 + 2I_2 + IO_3' + 10Br' + 5K^\cdot + 6Na^\cdot$: it was found that 1·18 mols. of $NaHCO_3$ were required to destroy 1 mol. of $KIBr_2$ (theory, 1·20) and that the solution contained considerable Br′, a smaller concn. of IO_3', and traces only of I_2, IO′, and BrO_3', free I_2 being pptd. and CO_2 evolved. A similar reaction occurs when NaOH aq. or KOH aq. is run into $KIBr_2$ aq., I_2 being pptd. and then redissolved by excess of alkali, the resultant solution containing Br′, I′, IO′, and IO_3'. On acidifying such a solution, the polyhalide is re-formed. Similar reactions occur with other dibromoiodides, and with chlorobromo-, dichloro-, and tetrachloro-iodides. With NH_3, impure NI_3 is pptd. (J., 1930, 2750).

(7) *Action of Reducing Agents on Polyhalide Solutions.*—When a solution of a polyhalide containing 1 I at. is acted upon by a reducing agent, it is first reduced to bromide or chloride, the I_2 being first precipitated in the free state (*e.g.*, $2KIBr_2 + 2H = 2KBr + 2HBr + I_2$), and then reduced by an excess of a sufficiently strong reducing agent to HI. The intermediate pptn. of I_2 is bound to occur, since monoiodides react with these polyhalides with liberation of I_2, *e.g.*, $KI + KIBr_2 = 2KBr + I_2$; excess of iodide brings about the formation of polyiodide; in the case of organic polyhalides the polyiodide is often sparingly sol. and remains undissolved. Polyhalide solutions (*e.g.*, $KIBr_2$ aq.) are reduced in the above way by nascent H_2 (quantitatively), Mg powder (even in the absence of acid), SO_2 (quantitatively in dilute sol.: $2KIBr_2 + 2H_2O + SO_2 = 2KBr + 2HBr + I_2 + H_2SO_4$; $I_2 + 2H_2O + SO_2 = 2HI + H_2SO_4$), H_2S, $Fe^{\cdot\cdot}$ salts, ferrocyanides (oxidised to ferricyanides), etc. Nitrites precipitate I_2, slowly if no acid is added but immediately in the presence of acid, presumably according to the equation $NaNO_2 + 2KIBr_2 + H_2O = NaNO_3 + 2KBr + I_2 + 2HBr$. The reduction does not proceed further in this case, since mono- and poly-iodides are oxidised by acid solutions of nitrites, *e.g.*, $2NaNO_2 + 2KI_3 + 4HX = 2NaX + 2KX + 2H_2O + 2NO + 3I_2$.

The reactions between polyhalides and $Na_2S_2O_3$ are of particular interest owing to the importance of the tri-iodide–thiosulphate reaction in volumetric analysis. In an ordinary ' iodine ' titration, the reaction may be represented by $I_3' + 2S_2O_3'' = 3I' + S_4O_6''$. When, on the other hand, free bromine or tribromide solutions are titrated directly with $Na_2S_2O_3$, this is oxidised almost entirely to sulphate. Solutions of dibromo- and tetrachloro-iodides give intermediate results, the relative proportions of S_4O_6'' and SO_4'' formed varying largely according to the rate of titration and other conditions.

The quant. oxidation of $Na_2S_2O_3$ to $Na_2S_4O_6$ by means of a dibromoiodide is represented by the equation (*a*) $IBr_2' + 2S_2O_3'' = I' + 2Br' + S_4O_6''$, strictly analogous to that for the I_3' reaction, and the quant. oxidation to SO_4'' would follow the equation (*b*) $4IBr_2' + S_2O_3'' + 5H_2O = 4I' + 8Br' + 2SO_4'' + 10H^\cdot$. When $KIBr_2$ aq. is run slowly into $Na_2S_2O_3$ aq., 99% of the $KIBr_2$ reacts according to equation (*a*), but when the order of addition is reversed, only about 50% so reacts. If, however, the $KIBr_2$ aq. is first saturated with KBr, in order to suppress its hydrolysis, 94—97% reacts according to (*a*). This suggests that the IBr_2' ion reacts in the same way as the I_3' ion, oxidising the $Na_2S_2O_3$ to $Na_2S_4O_6$, and that it is the HIO_3 or HIO formed by hydrolysis which causes the formation of SO_4''. Since the addition of acid also tends to suppress the hydrolysis of dibromoiodides, one would expect less SO_4'' to be formed in an acidified solution, an effect which has been confirmed experimentally. Thus, in a solution containing 8% of HCl, reaction (*a*) occurred to the extent of 52%, while in one containing 25% of HCl it occurred to the extent of 68%. When the $Na_2S_2O_3$ aq. is run drop by drop into the $KIBr_2$ aq. in the absence of added bromide or acid, with constant stirring, the reaction occurs in well-marked stages. In the first, I_2 is pptd. and SO_4'' and acid are formed, apparently according to the equation $8IBr_2' + S_2O_3'' + 5H_2O = 16Br' + 4I_2 + 2SO_4'' + 10H^{\cdot}$, the reaction probably occurring *via* the hydrolysis products of the $KIBr_2$. The quantity of IBr_2' destroyed and that of acid formed, per c.c. of $Na_2S_2O_3$ aq. run in, agree with those required by this equation during the early stages of the reaction. The subsequent reaction consists merely in the redissolution of the I_2 as polyiodide, which oxidises the S_2O_3'' to S_4O_6'' in the ordinary way, no more sulphate being formed. Although the reaction occurs in stages, the final result is the same as if the reactions (*a*) and (*b*) occurred simultaneously and to the same extent, $4IBr_2'$ reacting according to (*a*) and $4IBr_2'$ according to (*b*).

With ICl_4' solutions, the reaction producing S_4O_6'' occurred to the extent of about 40% (mean of several experiments), and with tribromide or free bromine solutions to about 7%. The exact proportion of SO_4'' and S_4O_6'' formed, however, varies with the method of titration.

In order to determine a polyhalide by $Na_2S_2O_3$ titration, an excess of KI aq. should first be added to convert all the polyhalide into polyiodide, which can then be titrated quantitatively.

(8) *Action of Oxidising Agents on Polyhalide Solutions.*—Powerful oxidising agents such as acid $KMnO_4$ oxidise solutions of dibromoiodides and dichloro- and tetrachloro-iodides to iodate, with liberation of Br_2 or Cl_2, but no I_2 : *e.g.*, $KIBr_2 + 3O = KIO_3 + Br_2$.

(9) *Action of Halogens on Polyhalide Solutions.*—Halogens may act on polyhalides in aq. solution, causing either addition, substitution, or oxidation of the type just mentioned. For instance, Cl_2 passed through an aq. solution of a dichloroiodide, first forms tetrachloroiodide, which is converted by excess into IO_3': *e.g.*, $KICl_2 + Cl_2 = KICl_4$; $KICl_4 + Cl_2 + 3H_2O = KIO_3 + 6HCl$ (Part I, J., 1931, 1864). Dibromoiodides react similarly after the Br_2 has been liberated (*e.g.*, $KIBr_2 + Cl_2 = KICl_2 + Br_2$). From polyiodides I_2 is liberated. The action of Br_2 is similar to that of Cl_2 in all these cases, but I_2 has little or no action. The reaction $KIBr_2 + 2Br_2 + 3H_2O = KIO_3 + 6HBr$ was found to be reversible. On mixing $KIBr_2$ aq. and Br_2 aq. in the proportion indicated by this equation, the colour fades considerably but not completely, and the solution gives the reactions of both IO_3' and IBr_2'. A similar solution is obtained on adding HBr aq. to KIO_3 aq. When a large excess of Br_2 is used, the product no longer gives the reactions of a dibromoiodide (*e.g.*, a ppt. of I_2 with $NaHCO_3$ and of NI_3 with NH_3), but it gives those of IO_3' (*e.g.*, a ppt. with $BaCl_2$ aq., not given by the $KIBr_2$ aq.) and of Br′. Also, as indicated in Table III, the obs. solubility of Br_2 in $KIBr_2$ solutions of different concn., at 25°, agrees with the assumption that oxidation to IO_3' is almost complete in solutions satd. with Br_2.

TABLE III.

Molarity of $KIBr_2$ solution	0·00	0·013	0·0415	0·063
Solubility of Br_2 (mols./l.), obs.	0·20	0·27	0·48	0·58
Solubility of Br_2 (mols./l.), calc.	0·20	0·27	0·46	0·58

In calculating the values, it is necessary to allow for the high sol. of Br_2 in the HBr formed during the reaction. The experimental data do not provide any evidence concerning the existence of tetrabromoiodides in aqueous solution; they are unknown in the solid state.

(10) *Action of Stabilisers on Polyhalide Solutions.*—Theoretically, if to a solution of a polyhalide we add one of the substances formed by its hydrolysis (*e.g.*, in the case of a dibromoiodide, free I_2, IO_3', $H^\cdot$, or Br'), the equilibrium, as given on p. 2032, will be shifted towards the left, *i.e.*, hydrolysis will be suppressed, and the reactions which are due to the presence of hydrolysis products should be inhibited. Owing to its sparing solubility, it is impossible to increase the concn. of I_2 appreciably. The stabilising action of IO_3' is not very pronounced in the case of a trihalide, since only one IO_3' ion is produced for every 5 polyhalide ions hydrolysed. The stabilising influence of acidification is far more pronounced, as would be expected from theory, and the influence of acid on the reaction between IBr_2' and S_2O_3'' is also in accordance with the belief that addition of $H^\cdot$ ions suppresses hydrolysis, just as their removal (addition of alkali) brings about hydrolysis. The stabilising action of acid may also be due, in part, to formation of stable un-ionised mols. of hydrogen polyhalide, *e.g.*, $HICl_2$ (see Table V). The addition of monohalide also has a considerable suppressing effect on the hydrolysis, as shown by the results of work on the CCl_4 equilibrium (p. 2041), the absorption spectrum (see below), thiosulphate reaction (p. 2036), etc. Dichloroiodide solutions which deposit I_2 on standing are generally stable in the presence of a sufficient excess of Cl′, while dibromoiodide solutions which have been saturated with KBr do not give a ppt. of I_2 even when made neutral or alkaline, an effect due partly to the suppression of hydrolysis by the Br′ ions and partly to the high solubility of I_2 in KBr aq. (presumably due to the formation of the ion I_2Br'). Addition of K salts, other than KIO_3 or halide, to a solution of a K polyhalide has no apparent effect on its absorption spectrum and chemical properties, showing that the K atom does not enter into the hydrolysis equilibrium.

Absorption Spectra.

During our work on these absorption spectra, papers on the subject were published by Gilbert, Goldstein, and Lowry (J., 1931, 1092) and by Gillam and Morton (*Proc. Roy. Soc.*, 1931, *A*, **132**, 152). Since we had independently arrived at almost the same conclusions as these investigators, it is not necessary to discuss the matter in detail, but we record our numerical data in Table IV.

TABLE IV.

λ in $\mu\mu$.	700	650	600	570	550	540	530	520	510
1. $KIBr_2$ in sat. aq. KBr	0·1	0·1	0·6	1·6	2·6	4·2	6·2	8·6	11·5
2. Dibromoiodides	1·0	1·1	1·4	3·2	6·2	10·0	12·1		
3. C_5H_5NIBr in MeOH	1·3	2·1	3·3	5·7	8·6	11·1			
4. IBr in MeOH	1·6	1·8	3	7	10				
5. $KIBr_2$ in aq. starch soln.	8	13	26	70	123	165			
6. IBr in CCl_4	10	18	28	68	126	168			

λ in $\mu\mu$.	530	520	510	500	490	480	470	460	450	440	430	425
7. $KIBr_2$ in H_2O		13	15	18	21	29	47	64	77			
8. IBr in MeOH	34	50	77	96	139	179	226	266	289	296		
9. IBr in CCl_4 ...	210	275	333	359	357	351	341	300	244	191	138	116

The figures give the value of k in the equation $kcd = \log_{10} I_0/I$. The results were obtained visually, in Expts. 6 and 7 by means of a revolving sector apparatus and in the remainder by using a Nutting photometer. In Expts. 1—4 the solutions were $M/20$; but in the others, more dil. In these dil. solutions the value of k is not altered greatly by variation of the concn. Within the limits of experimental error, the same values (Expt. 2) were obtained for the dibromoiodides of K, NH_4, and $C_5H_5N{\cdot}H$ in both MeOH and H_2O. The identity in absorption spectrum of the different dibromoiodides confirms the view already expressed that the metal or base does not form part of the complex ion, and that the degree of dissociation of the different polyhalides of the same series is independent of the kation. Gilbert, Goldstein, and Lowry observed a difference in intensity of ultra-violet absorption between solutions in H_2O and in EtOH, which they attributed to hydrolysis in the former solvent, although the present work does not bear out their ideas as to the nature of the hydrolysis. For instance, the action $H_2O + RI_3 \rightleftharpoons ROH + HI_3$ does not occur when ROH is a strong base, while the equilibrium $ICl_2' \rightleftharpoons I' + Cl_2$ is impossible owing to the action of Cl_2 on the I' ion (an irreversible reaction producing Cl' ions and free I_2) and is further untenable since the present work indicates definitely that the aq. solutions of dichloroiodides contain free I_2 but no free Cl_2. The fact that no difference is observable in the visible region between solutions of dibromoiodides in H_2O and those in MeOH may be attributed to similarity in absorption spectrum between the dibromoiodide ions and the products of hydrolysis, and to the small degree of hydrolysis of IBr_2'.

Solvation probably occurs in H_2O and in MeOH but not in CCl_4. The similarities and differences in spectrum are accounted for satisfactorily by assuming the following equilibria, which, from general considerations, would be expected to be established :

(1) $KIBr_2$ in sat. aq. KBr : all hydrolysis and dissociation suppressed by the bromide ion, the chief absorbent being IBr_2'.

(2*a*) Dibromoiodides in H_2O : see p. 2032.

(2*b*) Dibromoiodides in MeOH : $IBr_2' \rightleftharpoons Br' + IBr$, and the equilibria given in (4) below.

(3) C_5H_5NIBr in MeOH : $C_5H_5NIBr \rightleftharpoons C_5H_5N + IBr$; possibly also $C_5H_5NIBr \rightleftharpoons C_5H_5NI^{\cdot} + Br'$ (compare Cremer and Duncan, J., 1931, 1861, 2250; Williams, *ibid.*, p. 2783). When this solution is mixed with an equimol. quantity of $AgNO_3$ in MeOH, quantitative pptn. of AgBr occurs, which, however, would be expected according to both these modes of dissociation.

(4) IBr in MeOH : $IBr \rightleftharpoons I^{\cdot} + Br'$; $Br' + IBr \rightleftharpoons IBr_2'$; and, to a small extent, $2IBr \rightleftharpoons I_2 + Br_2$.

These equilibria must, presumably, also be established in all the above cases where IBr is formed in MeOH aq. by dissociation. The simple reaction with $AgNO_3$ (p. 2034) depends on the insolubility of AgBr, the equilibria being displaced by removal of Br' ions.

(5) $KIBr_2$ and starch : the intense coloration is probably analogous to the blue colour obtained with a tri-iodide and starch.

(6) IBr in CCl_4 : $2IBr \rightleftharpoons I_2 + Br_2$, the ionic reactions not occurring in this solvent.

The free acids $HIBr_2$, $HICl_2$, and $HICl_4$ give absorption spectra similar to those of their salts.

Solutions of IBr in different solvents show a variation in colour similar to that shown by I_2 solutions, due, no doubt, to variation in solvation and in the equilibrium constants of the above reactions. The solutions in general show one broad absorption band, and are quite different from the superimposed absorption spectra of I_2 and Br_2. There is a gradual change in the position of max. absorption, from the green for non-solvating solvents such as ligroin, C_6H_6, CCl_4 (500 $\mu\mu$), $C_6H_4Me_2$, and tetrahydronaphthalene, through the blue for solvents such as CCl_4, ethylene dichloride and dibromide, and $C_6H_5{\cdot}NO_2$, to the violet for solvating solvents such as glycerol, Et_2O, AcOH, $COMe_2$, EtOH, and MeOH (420 $\mu\mu$). For the dibromoiodides, where the IBr is definitely combined, the max. absorption is at 390 $\mu\mu$, while for the compound with C_5H_5N it is in the ultra-violet.

Equilibria between Aqueous Solutions of Polyhalides and Carbon Tetrachloride.

The effect of shaking CCl_4 with an aq. solution of a polyhalide has already been mentioned (p. 2033). The concn. of I_2 in the CCl_4 at equilibrium is a measure of the relative degrees of hydrolysis of the different polyhalides of the type under investigation, a high value indicating a relatively high concn. of free I_2 in the aq. layer and consequently considerable hydrolysis. For a polyhalide which undergoes considerable hydrolysis with pptn. of I_2, the addition of a small quantity of CCl_4 merely dissolves some of the pptd. I_2 and does not disturb the equilibrium. In the case of polyhalides which do not of themselves give a ppt. of I_2, CCl_4 causes an increase in the degree of hydrolysis, but if the temp., concn. of the aq. solution, and proportion of CCl_4 are fixed, the concns. of I_2 in the CCl_4 in equilibrium with different polyhalides will be in the same order as the degrees of hydrolysis. In the cases given in Table V, the CCl_4 was shaken with 10 times its volume of an *M*/20-aqueous solution of each polyhalide at 25° until equilibrium was reached, 3 days sufficing. Col. 1 gives the composition of the solute; the properties of the solution, including the equilibrium with CCl_4, are independent of the mode of prep. and depend only on the composition and temp., so it is possible to obtain data for solutions of compounds which cannot be isolated in the solid state (*e.g.*, NaIBrCl and the free acids). Col. 2 gives the % of the total I which remains in the aq. layer, col. 3 the % present in the CCl_4 and col. 4 the % pptd. as solid I_2 (calc. by diff.). Col. 5 gives the % hydrolysis, which is assumed to take place according to the simple equations on p. 2032, the intermediate products being neglected; there is, however, probably a considerable concn. of HIO in the solutions.

TABLE V.

1.	2.	3.	4.	5.
$HICl_4$	96	4	0	13
$KICl_4$	96	4	0	13
ICl_3	91	9	0	24
$KIBr_2$	78	22	0	29
$HIBr_2$	77	23	0	30
NH_4IBr_2	75	25	0	33
HIBrCl	64	36	0	47
KIBrCl	55	45	0	59
NaIBrCl	53	45	2	61
IBr	50	45	5	65
$HICl_2$	46	45	9	70
$KICl_2$	36	45	19	83
$NaICl_2$	34	45	21	86
NH_4ICl_2	33	45	22	87
ICl	23	45	32	100

Within the limits of experimental error the figures are the same for all polyhalides belonging to the same series, showing that the metal does not enter into the equilibrium in dil. solution (compare J., 1931, 2249; this vol., p. 2039). These results agree with qual. observations of the stabilities of the solutions; thus, *M*/20-solutions of the tetrachloro- and dibromo-iodides, ICl_3, and the free acids $HICl_4$, $HIBr_2$, and HIBrCl are stable, whereas those of chlorobromo- and dichloro-iodides deposit I_2 on standing, IBr and ICl also being decomposed with separation of I_2. The polyhalides are all hydrolysed to a smaller extent than the iodine halides from which they are derived; this may also be expressed by the statement that the hydrolysis of the iodine halides is suppressed by increasing the concn. of monohalide ions. This observation is in agreement with the assumption that stable complex ions are formed consisting of a compound of the iodine halide with monohalide ions. It is very difficult on any other assumption to account for this effect, and in particular to account for the fact that chlorides suppress the hydrolysis of IBr; although this effect is not very great with dilute solutions, it becomes very pronounced with conc. solutions of chlorides. Neutral salts, other than halides and iodates, have no effect on the hydrolysis of iodine halides, while acids suppress hydrolysis, the suppressing action of acid and iodate being less with the more stable compounds.

The difference between the two chlorides of iodine as regards behaviour towards water is very striking: ICl_3 dissolves to form a clear solution which may be kept indefinitely without separation of I_2, whereas ICl is almost completely hydrolysed. In the former case it is possible that hydrolysis may occur without liberation of I_2 (*e.g.*, $ICl_3 + H_2O \rightleftharpoons OICl + 2HCl$, or $ICl_3 + 2H_2O \rightleftharpoons HIO_2 + 3HCl$). In the above investigation, owing to the very small concn. of halogen found in the CCl_4 layer in the case of ICl_3 and the tetrachloroiodides, it is difficult to prove that only I_2 was extracted, as was done in the other cases, and it is possible that the solutions contain ICl_3, as such or in an ionised condition. There is some evidence for the presence of tervalent iodine kations: thus ICl_3 aq. gives with H_2SO_4 a ppt. which is said to be iodine sulphate (Mellor, "Comprehensive Treatise, etc.," 1922, Vol. II, p. 121). On the other hand, Faull and Baeckström (*J. Amer. Chem. Soc.*, 1932, **54**, 620) have shown by a simple transport method that a solution of ICl in HCl aq. contains no iodine kations, the I being present in the anion. Repetition of this experiment with ICl_3 might give interesting results. The difference between ICl_3 and the tetrachloroiodides, on the one hand, and ICl and the dichloroiodides, on the other, may be due to the existence in aq. solutions of the former of relatively stable tervalent iodine kations, whereas univalent iodine kations are not stable in aqueous solution. Most of the known salts of I contain this element in the tervalent state.

Summary.

The polyhalides may be divided into three classes according to their behaviour in aqueous solution, *viz.*, (1) compounds formed from free iodine and monohalides; their solutions contain polyhalide ions, monohalide ions, and free iodine, but no hydrolysis products (iodate, acid, etc.); (2) compounds of iodine halides with monohalides; their solutions contain polyhalide ions, monohalide ions, and the products resulting from the hydrolysis of the iodine halides, but no appreciable concentration of iodine halide itself; (3) compounds of bromine, chlorine, or bromine chloride with monohalides; their solutions contain polyhalide ions, monohalide ions, free halogens, and the hydrolytic products of the last (*e.g.*, bromic acid).

The nature of the equilibria existing in aqueous solutions of

polyhalides of the second class has been established; their reactions have been examined in detail and measurements made of absorption spectra and of the degree of hydrolysis as indicated by partition experiments with carbon tetrachloride.

Evidence is given for the existence, at least in methyl-alcoholic solution, of iodine mononitrate, INO_3, and iodine trinitrate, $I(NO_3)_3$, and of the ions $I^{\cdot}$ and $I^{\cdot\cdot\cdot}$. The possibility of the existence of these ions in aqueous solution is also considered.

The nature of the equilibria in solutions of iodine monobromide and its additive compounds ($KIBr_2$, C_5H_5NIBr, etc.) in various solvents is also discussed.

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