54. *A Study of the Polyhalides. Part IV. Reactions in the Absence of a Solvent.*

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THE tendency of the polyhalides to dissociate into monohalides and halogen or halogen halide has a considerable influence on their reactions in the absence of a solvent. Although some of these are apparently due to the reactivity of the solid polyhalide, yet in many cases the reacting substance is really one of the products of dissociation, usually the halogen or halogen halide. When the polyhalide reacts with another solid, one may be reasonably certain that reaction occurs through the vapour phase, *i.e.*, that the attacking substance is the halogen or halogen halide vapour given off by the polyhalide. When a gas acts on a solid polyhalide, however, both types of reaction are possible, reaction by way of the dissociation products being most frequent in the case of compounds of high dissociation pressure.

Several reactions are described in illustration of the above general statements. For instance, passage of air or carbon dioxide over a polyhalide removes the gaseous products of dissociation if their vapour pressure is sufficiently high, but otherwise has little effect. For a similar reason, the most stable monohalide may contaminate the product if the inert gas is replaced by one which has any chemical action on the polyhalide.

Ammonia forms addition compounds with dibromoiodides (*e.g.*, $RIBr_2,2NH_3$) if the dissociation pressure of the polyhalide is low ($< 0{\cdot}005$ mm.); otherwise it reacts with the products of dissociation to give nitrogen tri-iodide: $RIBr_2 \rightleftharpoons RBr + IBr$; $3IBr + NH_3 \longrightarrow 3HBr + NI_3$; $HBr + NH_3 \longrightarrow NH_4Br$ (cf. J., 1930, 2750). Dichloroiodides apparently react similarly (Dobbin and Masson, J., 1885, **47**, 60; 1886, **49**, 850). Organic amines also form additive compounds with dibromoiodides, but these have not yet been investigated in detail.

Ozone converts potassium dibromoiodide quantitatively into iodate (apart from about 1% of bromide formed as indicated above). The reaction is shown to be $KIBr_2 + O_3 \longrightarrow KIO_3 + Br_2$, and not $KIBr_2 + 3O_3 \longrightarrow KIO_3 + Br_2 + 3O_2$. If it be accepted that in the iodate crystal the iodine atom has a positive charge, the oxygen atoms being attached by semipolar bonds, this reaction indicates that the dibromoiodide has a similar structure, the bromine atoms being negatively charged and possibly attached to the iodine atom by singlet linkages.

The consensus of recent opinion (Reade, J., 1926, 2528; 1929, 853; Gilbert, Goldstein, and Lowry, J., 1931, 1092; Cremer and Duncan, J., 1931, 2250) is in favour of a structure in which the least electronegative halogen in the polyhalide becomes the positively charged centre of the anion, and this is supported by many experiments now recorded in which halogens or halogen halides act upon a polyhalide. In general, this central atom is not replaceable by a more electronegative atom, whereas other atoms attached to it can be so replaced; for instance, chlorine will readily replace the bromine in potassium dibromoiodide, but no trace of any iodine displacement can be detected: $KIBr_2 + Cl_2 \longrightarrow KICl_2 + Br_2$; similarly, although bromine will convert CsI_2Br or CsI_3 into $CsIBr_2$, it will not give $CsBr_3$, neither will it react with $CsIBr_2$. It seems probable that the central atom cannot be replaced directly, even by a more electropositive halogen. In one case in which this generalisation appears to fail, *viz.*, $RBr_3 + I_2 \longrightarrow RIBr_2 + IBr$, it seems probable that the reaction takes place *via* the bromine molecule formed by dissociation, iodine bromide thus formed reacting with the resulting bromide. Similarly, the conversion of potassium tetrachloroiodide into chloride by the prolonged action of chlorine is attributable to the removal of iodine trichloride vapour, just as if chlorine were an inert gas (see above), for air or carbon dioxide has the same effect.

It is remarkable that, although direct addition of halogens to a polyhalide often occurs (*e.g.*, $KICl_2 + Cl_2 \longrightarrow KICl_4$), no case is known in which a halogen halide can be added. This is probably due to the fact that such an addition would involve a change of sign of the more electropositive atom in the addendum. The formation of interesting mixed higher polyhalides $\left(e.g.,\ \mathrm{CsICl_2 + IBr \longrightarrow Cs^{\bullet}} \left[\begin{matrix} {}_{-}\overline{\mathrm{Cl}} \\ \mathrm{Cl\,I^{+}I^{-}} \\ \mathrm{Br^{-}} \end{matrix}\right]'\right)$ is thus precluded.

The formation of polyhalides by addition of halogens to monohalides has been investigated in greater detail than in Part I, with especial attention to thermodynamic considerations. The equilibrium product should depend only on the total composition of the system, and this is confirmed. For instance, the mixtures $KI + Cl_2$, $KCl + ICl$, and $KI + KICl_4$ all become converted into $KICl_2$ ultimately, the system then having minimum free energy. These reactions, of course, occur with varying degrees of facility, and these rates have been studied and the properties of the intermediate mixtures investigated. They fall into two classes according to whether the starting materials are, or are not, identical with the substances formed by spontaneous dissociation of the polyhalide; *e.g.*, $KBr + IBr \longrightarrow KIBr_2$ or $KI + Br_2 \longrightarrow KIBr_2$.

(1) In the former case, the polyhalide is readily formed if the pressure of the addendum exceeds the dissociation pressure, and its rate of formation is roughly proportional to the

quantity of unchanged (finely divided) monohalide. Disturbances are caused in the later stages by the formation of a crust of polyhalide and also, in some cases, by the formation of a liquid phase: in the latter case, absorption of gas proceeds at constant velocity until the solid is all dissolved, and then continues more slowly. Traces of water also affect the velocity. The effect of temperature is two-fold, since a stage is reached at which increased rate of reaction is counterbalanced by decreased stability of polyhalide. Reactions involving the vapours of iodine monobromide and trichloride showed that at room temperature they exist, at least in part, as such, and are not completely dissociated.

(2) The action of chlorine or bromine on alkali iodides has been studied in detail. Rae's results (J., 1915, **107**, 1286; 1918, **113**, 880) were confirmed in general, but potassium, ammonium, and rubidium dibromoiodides absorbed bromine to give a liquid phase, and some evidence was obtained for the formation of $NaIBr_2$. (These differences may be due to the fact that Rae worked in Ceylon, where the room temperature is some 15° higher than in London.) Of the two possible modes of reaction: (1) direct addition, $RI + Br_2 \longrightarrow RIBr_2$ and (2) substitution followed by combination of the products, $2RI + Br_2 \longrightarrow 2RBr + I_2$, $I_2 + Br_2 \longrightarrow 2IBr$, $RBr + IBr \longrightarrow RIBr_2$, it has been found that the first occurs with cæsium iodide, and the second with other alkali iodides. This difference is attributed to the high velocity of formation of $CsIBr_2$ and to its very low dissociation pressure.

We have always found that where any one polyhalide was prepared by alternative methods, which might be expected to give isomeric products, only one of the possible isomerides was formed. We therefore investigated three cases of reported isomerism in this group of compounds, but failed to obtain any evidence in favour of the phenomenon.

Finally, certain incidental observations are reported dealing with the effect of moisture, the formation of liquid phases, the solubility of polyhalides in liquid halogens or halogen halides, and the adsorption of small proportions of the latter by solid halides.

EXPERIMENTAL.

Many of the facts recorded above need no experimental description, and this section is confined to amplification of other statements.

Action of Ozone on Potassium Dibromoiodide.—Ozonised O, containing about 10% by wt. of O_3 and dried thoroughly by means of P_2O_5, was passed over dry $KIBr_2$ at room temp. The $KIBr_2$ was converted slowly but quantitatively into KIO_3, Br_2 being evolved. No intermediate products could be detected, qual. and quant. analysis of the partially converted material showing it to be a mixture of $KIBr_2$ and KIO_3. The final product was pure KIO_3, mixed with about 1% of KBr, no doubt produced by decomp. of the $KIBr_2$ as already described. After passing over the $KIBr_2$, the gas had a distinct colour of Br_2 vapour. It was passed through pure NaOH aq. (free from halides), which was finally found to contain Br but no I. In order to distinguish between the two possible processes (p. 182), the reaction was carried out in a flask closed by means of a H_2SO_4 manometer. In this way small changes in the vol. of gas during the reaction are easily observed. The flask was placed in a bath at a steady temp. and protected from the light. It was calc. that the quantity of Br_2 liberated would be about 0·02 of that required to saturate the space with Br_2 vapour. Hence, for the present purpose Br_2 may be regarded as a gas. According to the first equation there will be no vol. change during the reaction, whilst according to the second there will be an expansion. The quantities were so chosen that the theor. expansion would be 200 mm. in the manometer. Actually a slight contraction (2 mm.) was observed. It thus seems probable that the O_3 molecule as a whole attacks solid $KIBr_2$, the three O atoms replacing the two Br atoms directly (see first equation, p. 182). The crystal structure of the $KIBr_2$ is broken up, the KIO_3 being obtained as a very fine powder.

Action of Halogens and Halogen Halides on Polyhalides.—The reactions which may occur fall into various types, *viz.*:

(1) Replacement of a halogen in a polyhalide by a more electronegative one, *e.g.*, $KIBr_2 + Cl_2 = KICl_2 + Br_2$. Such reactions usually proceed smoothly and apparently without the formation of intermediate products; *e.g.*, in the example given, there is no evidence for the liberation of I_2, IBr, ICl, or ICl_3 during the reaction.

(2) Replacement of the positive halogen by a more strongly electropositive one, *e.g.*, $RBr_3 + I_2 = RIBr_2 + IBr$, appears to occur in some cases, although it is doubtful whether direct

replacement takes place; it is more probable that the reaction occurs through the dissociation products, $RBr_3 = RBr + Br_2$; $Br_2 + I_2 = 2IBr$; $RBr + IBr = RIBr_2$.

(3) Conversion of the polyhalide into monohalide, the stream of halogen vapour merely acting as an inert gas.

(4) Replacement of a halogen or halogen halide formed by dissociation of the polyhalide by another halogen or halogen halide, *e.g.*, $RClIBr + ICl = RClICl + IBr$. It is difficult to distinguish this type of reaction from type (1), although the two are really distinct. If the reaction were of the present type, it would occur in stages : $RClIBr = RCl + IBr$; $RCl + ICl = RClICl$. Theoretically, since the individual stages are reversible, reactions of this type are reversible. The above reaction might conceivably be forced to proceed in the reverse direction by prolonged passage of a stream of air satd. with IBr vapour over $CsICl_2$; the current of gas would first decompose the $CsICl_2$ [type (3), $CsClICl = CsCl + ICl$], sweeping away the ICl, and the IBr would then combine with the CsCl formed ($CsCl + IBr = CsClIBr$). In such a way it might even be possible to convert $CsIBr_2$ into $CsBr_3$ by the action of Br_2, but such an indirect action could hardly be considered to be a violation of the principles of replaceability already propounded. In practice, the relative stabilities are such that in no case can the reaction be made to proceed in opposition to these principles, although in the presence of a solvent in which the desired product is only sparingly sol. it may be possible to do so (cf. the anomalous results obtained by McCombie and Reade through using solvents; J., 1923, **123**, 141; 1924, **125**, 148; 1926, 2528).

(5) Direct addition of halogen may occur (*e.g.*, $KICl_2 + Cl_2 = KICl_4$), but, in spite of many attempts, we have been unable to effect direct addition of halogen halide to a metallic polyhalide. Specific cases where no addition takes place are given in Table I.

(6) Polyhalides are frequently sol. in liquid halogens or halogen halides, forming solutions from which the original polyhalide crystallises on evapn. of the solvent; *e.g.*, $KIBr_2$ is sol. in Br_2, and, if the solid $KIBr_2$ be left in contact with satd. Br_2 vapour, it will take up the latter, forming a solution, the phenomenon being analogous to the deliquescence of salts in a moist atm. Table I gives the results obtained in a number of cases with carefully dried materials at room temp. The results may be considerably modified by changes in conditions (temp., presence of traces of H_2O, etc.).

TABLE I.

Satd. vapour employed.	Polyhalides which form a liquid solution.	Polyhalides which are unaffected.
Br_2	$KIBr_2$, NH_4IBr_2, $RbIBr_2$, most of the org. dibromoiodides described in Part I (J., 1931, 1860)	$KICl_4$, $CsIBr_2$, $CsIBrCl$, $CsBr_2Cl$, $CsBr_3$, $CsICl_2$
IBr (the vapour in equil. with solid of the comp. IBr)	$NaIBr_2$,* $KIBr_2$, NH_4IBr_2	KIBrCl, NH_4IBrCl, CsIBrCl, CsIBrF, $CsIBr_2$, $CsICl_2$
ICl	$NaICl_2$,* $KICl_2$, NH_4ICl_2, $CsICl_2$. The compds. containing Br were converted into dichloroiodides, which then deliquesced.	—
ICl_3	—	$KICl_4$

* See J., 1931, 1859, 1863.

Although on one occasion a specimen of $CsBr_3$ absorbed Br_2 from its satd. vapour, frequent repetition of the expt. with pure materials failed to show absorption even after some weeks; hence it is assumed that the result first obtained was due to the presence of impurities. With pure $CsBr_3$ no absorption occurred even when it was left in a desiccator containing the two-phase mixture of Br_2 and H_2O. It is therefore very doubtful whether any polybromide of Cs exists at room temp., either anhydrous or hydrated, containing more than three atoms of Br (cf. Rae, J., 1931, 1578; Cremer and Duncan, *ibid.*, p. 1865). It might be expected that $CsBr_3$ would absorb H_2O under the above conditions, forming an aq. solution; that this does not occur may be due to the sparing solubility of $CsBr_3$; the satd. solution probably has a higher v. p. than the partial press. of H_2O over satd. Br_2 aq.

Since this work was completed, Harris (J., 1932, 2709) has investigated the system $CsBr$–Br_2–H_2O, and confirms our conclusion that $CsBr_3$ is the only polybromide formed at ordinary temp.

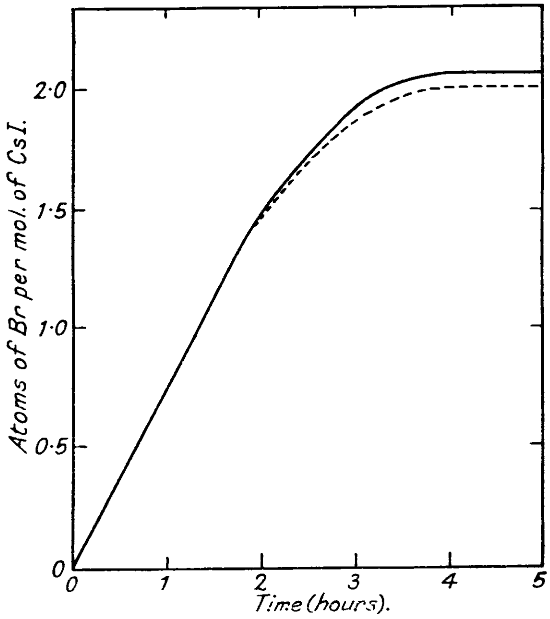
When a polyhalide is exposed to the vapour of a halogen halide, the liquid phase formed does not necessarily contain the halogens in the same proportions as the vapour. As will be seen from the table, the polyhalides of high dissociation press. show the greatest tendency to absorb halogen in this way. In none of the above cases is there any evidence of the formation of a higher polyhalide, though such may exist in the solutions.

(7) Even where such solution formation does not occur, polyhalides frequently take up a trace of halogen vapour, probably owing to adsorption. Thus, $CsBr_2Cl$ absorbs 0·1% of its mass of Br_2, and the dichloroiodide $CsICl_2$ absorbs 1%, when left in contact with satd. Br_2 vapour. The adsorption does not proceed further and the extra Br is lost immediately on evacuation.

Formation of a Polyhalide from its Dissociation Products.—The exptl. results indicate, as would be expected, that a polyhalide may always be prepared by the direct union of its dissociation products (solid monohalide and halogen or halogen halide), provided that the partial press. of the halogen be not less than the dissociation press. of the polyhalide. In order that the velocities might be studied under comparable conditions, the dry, finely powdered monohalides were left in contact with air satd. with the vapour of the halogen or halogen halide at room temp., and weighed at intervals (cf. Part I, J., **1931**, 1858). In this way curves were obtained giving the rate of absorption of halogen. When a liquid phase is produced, the quantity of polyhalide formed may be determined after evaporation of the liquid halogen in vac. The results obtained are summarised on p. 183. The observed forms of the curves are in accordance with theoretical expectations.

FIG. 1.

Rate of absorption of Br_2 *by* CsI (Br_2 *not specially dried*).



The following polyhalides were obtained in this way; they are formulated as additive compounds in order to indicate the compounds from which they were formed and into which they dissociate. They are arranged in order of decreasing velocity of formation, the number in brackets indicating the approx. number of days required for half the monohalide to be converted into polyhalide under similar exptl. conditions. $CsBr,Br_2$ (1); $CsCl,Br_2$ (2); CsCl,IBr (3); CsCl,ICl (4); CsBr,IBr (5); NH_4Cl,IBr (9); KCl,ICl (10); NH_4Br,IBr (10); RbCl,IBr (15); $CsCl,ICl_3$ (16); NH_4Cl,ICl (16); CsF,IBr (23); KCl,ICl_3 (25); KBr,IBr (35); NaCl,ICl (?) (40); NaBr,IBr (?) (60); KCl,IBr (70). In the case of the systems NaCl–IBr, KNO_3–IBr, KBr–I_2, KBr–Br_2, and KI–I_2, no absorption (apart from a trace of adsorption) occurred during several months, confirming evidence obtained in other ways that no compounds exist in these cases (cf. Grace, J., **1931**, 594; Harris, J., **1932**, 1696; Cremer and Duncan, J., **1931**, 1865, 2249). Attempts to add on halogens and halogen halides to NH_4F and KF gave indefinite results; although some reaction appeared to occur in several cases, no additive compounds could be isolated. We failed to isolate KF,ICl_3 and NH_4F,ICl_3, but compounds of this type have recently been isolated by Booth, Swinehart, and Morris (*J. Amer. Chem. Soc.*, 1932, **54**, 2560; *J. Physical Chem.*, 1932, **36**, 2779).

The above results indicate that the higher the concn. of halogen vapour and the lower the dissociation press. of the product, the more rapidly does the reaction occur. The velocity is increased by the presence of H_2O, but the effect of a trace of H_2O is not so pronounced as with the replacement reactions mentioned below.

Formation of a Polyhalide from Substances other than its Dissociation Products.—The action $RI + Br_2 = RIBr_2$ might be expected to follow one of two courses: (1) direct addition, $RI + Br_2 = RIBr_2$; or (2) substitution, followed by combination of the products, $2RI + Br_2 = 2RBr + I_2$, $I_2 + Br_2 = 2IBr$, $2RBr + 2IBr = 2RIBr_2$. The two possibilities may be distinguished by observing whether darkening (due to liberation of I_2) occurs during the reaction, by examination of the partially converted product (microscopically, by the action of solvents, etc.), and by measuring the velocity of the reaction. If a liquid phase is formed, the free Br_2 must be removed (by evaptn. at room temp. under reduced press., or by leaving in a desiccator over NaOH or KOH), in order to obtain a correct measure of the velocity of combination. In the curves (Figs. 1—3), the velocity determined in this way is shown by a broken line, the continuous line indicating the total quantity of Br absorbed, whether combined or not. When the reaction occurs in stages, the broken curve really represents the combined velocity of the first two stages. The last stage is unaccompanied by change in wt., but may be followed by observing the change in colour. It is a slower reaction than the other two. Exact interpretation of the velocity data is also complicated by the formation of solid solutions instead of a definite compound, IBr. When the reaction follows course (1) the curve shows no break, but when it follows course (2) there is usually a sharp break, the first stage of the reaction being far more rapid than the subsequent stages. The reaction $2RI + Br_2 = 2RBr + I_2$ is considerably accelerated by the presence of H_2O. When KI, dried by heating, was exposed to the action of Br_2 which had been dried over P_2O_5 for a week, only 4% was converted into KBr in 1½ hr., whereas in the presence of H_2O the reaction is instantaneous. Hence, when the drying has been intense, the break is not found. In general, the action of Br_2 on iodides follows course (2), but direct addition of Br_2 to CsI appears to occur without liberation of I_2 : $CsI + Br_2 = CsIBr_2$. The difference between the action with CsI, on the one hand, and that with, *e.g.*, KI, on the other (*viz.*, $2KI + Br_2 = 2KBr + I_2$; $I_2 + Br_2 = 2IBr$; $2KBr + 2IBr = 2KIBr_2$), may be attributed to the following causes : (*a*) $CsIBr_2$ has a very low dissociation press. and the reaction $CsI + CsIBr_2 = 2CsBr + I_2$ does not occur to any appreciable extent; $KIBr_2$ has a high dissociation press. and reacts with KI *via* the vapour phase : $KIBr_2 = KBr + IBr$; $IBr + KI = KBr + I_2$; (*b*) the high velocity of formation of $CsIBr_2$, which may be connected with its stability (compare the velocities of the reaction $RBr + IBr = RIBr_2$, when R = Cs and K, given on p. 185) or with similarity in crystal structure of CsI and $CsIBr_2$. The tetra-alkylammonium dibromoiodides are even more stable

FIG. 2.

Rate of absorption of Br_2 *by* NH_4I (Br_2 *not specially dried*).

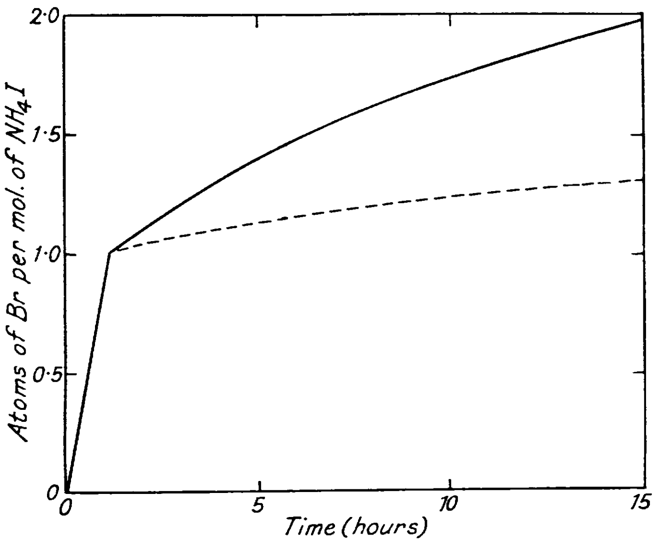
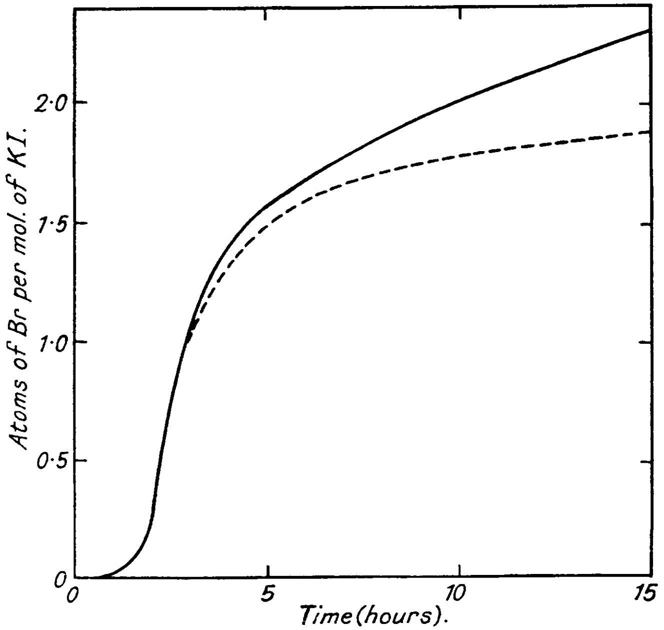


FIG. 3.

Rate of absorption of Br_2 *by* KI (Br_2 *dried for* 1 *week by* P_2O_5).



than the Cs salt, but the action of thoroughly dried Br_2 on these has not yet been investigated; in the presence of more than a trace of H_2O, I_2 is liberated even from the Cs salt, owing to the oxidisability of the I' ion in the presence of H_2O.

The following reactions have been investigated in this way. The first equation indicates the nature of the initial reactants and final products after an excess of the halogen or halogen halide vapour has been allowed to act on the monohalide at room temp. until no further change occurs. Conversion is then complete, and the products obtained are always those which would be expected according to the principles already expounded. The subsequent equations indicate the main course of the reaction, as observed experimentally. Side reactions occur in some cases, but always result in the same final products.

(1) $CsBr + Cl_2 = CsBrCl_2$. Apparently a direct addition, no displacement of Br occurring.

(2) $KI + 2Cl_2 = KICl_4$: in the stages $2KI + Cl_2 = 2KCl + I_2$; $I_2 + Cl_2 = 2ICl$; $2ICl + 2Cl_2 = 2ICl_3$; $2KCl + 2ICl_3 = 2KICl_4$. Very little $KICl_2$ is formed during the reaction, although, if the passage of Cl_2 be stopped when the comp. reaches $KICl_2$, and the mixture, which is mainly black, be kept for a few months, it is slowly but completely converted into the yellow compound $KICl_2$.

(3) $KI + 2ICl = KICl_2 + I_2$: in the stages $KI + ICl = KCl + I_2$; $KCl + ICl = KICl_2$. If the materials are kept in a finely ground state, the first stage is complete before the second begins, as $KICl_2$ reacts immediately with KI, thus: $KI + KICl_2 = 2KCl + I_2$ (cf. $KIBr_2$, above). During this stage no liquid phase is formed, but as soon as $KICl_2$ begins to accumulate in the product, rapid absorption of ICl sets in, with formation of a pasty mixture.

(4) $CsBr + 2ICl = CsICl_2 + IBr$: in the stages $CsBr + ICl = CsCl + IBr$; $CsCl + ICl = CsICl_2$. The course of the reaction is closely similar to that described in the last paragraph. Apparently some CsIBrCl is formed during the reaction: $CsBr + ICl = CsIBrCl$ or $CsCl + IBr = CsIBrCl$, but it is destroyed by the excess of ICl: $CsIBrCl + ICl = CsICl_2 + IBr$.

(5) $KBr + 2ICl = KICl_2 + IBr$, the course of the reaction being exactly similar to the above.

(6) CsBr is quant. converted into $CsICl_4$ by an excess of ICl_3 vapour, but the exact nature of the reaction has not yet been established (possibly $2CsBr + 3ICl_3 = 2CsICl_4 + ICl + Br_2$).

Occurrence of Isomerism.—In all cases during the present investigation where any one polyhalide was prepared by more than one reaction or crystallised under different conditions, the product obtained was identical. This led us to reinvestigate critically those instances (apparently only three) in which isomerism has been reported, and we found in all cases that the facts could be explained without assuming the existence of isomerism or even dimorphism.

$CsIBr_2$ was described by Wells and Penfield (*Z. anorg. Chem.*, 1892, **1**, 83) as a dark cherry-red solid; Ephraim (*Ber.*, 1917, **50**, 1096) did not obtain crystals of this colour but of "bichromate-colour," so he suggested that the substance existed in two forms. We now find that the difference is merely one of the size of the crystals: the powder is always yellow, and large crystals are always deep red. Intermediate colours may be obtained, the red colour gradually changing to yellow as the material is ground; the yellow form is converted into the red on crystallisation or on fusion. There is no chemical difference between the two (*e.g.*, both may be obtained from CsI and Br_2 or from CsBr and IBr, and both give the same reactions), nor is there any difference between their m. p. or dissociation press. $KIBr_2$ and NH_4IBr_2, which are normally red, appear yellow when finely ground. Hence it would appear that there is no reason for postulating isomerism in $CsIBr_2$.

Because of a slight difference between two successive series of measurements of the dissociation press. of the same specimen of $RbBrCl_2$, Ephraim (*loc. cit.*) suggested that transformation into another form may have occurred during heating. The effect might, however, be attributed to a number of causes other than isomerism, *e.g.*, exptl. error, presence of impurities or H_2O of crystn. in the original material, or, most probably, failure to reach equil. Since the dissociation of $RbBrCl_2$ is more complicated than that of many polyhalides, owing to the dissociation of the BrCl formed initially: $RbBrCl_2 \rightleftharpoons RbCl + BrCl$; $2BrCl \rightleftharpoons Br_2 + Cl_2$, it is probable that considerable time is required for the attainment of equil., as in the dissociation of a dibromoiodide (cf. Cheesman and Martin, J., 1932, 588).

The other supposed case of isomerism is also illusory, although the evidence appears superficially more convincing. Wells and Penfield (*loc. cit.*) claimed to have obtained $CsICl_2$ in two forms, one rhombohedral and the other rhombic, but they do not appear to have analysed the latter, although Penfield carried out crystallographic measurements on both types. The rhombohedral form was obtained by crystallising $CsICl_2$ aq. and has since been prepared by

Wyckoff (*J. Amer. Chem. Soc.*, 1920, **42**, 1100), who examined its structure by the X-ray method. There can be little doubt as to the existence of this form, which, however, is not isomorphous with $CsIBr_2$ and other similar compounds. The supposed rhombic form of $CsICl_2$ was obtained by crystn. from $CsICl_2$ aq. containing a large excess of CsCl; Wyckoff was unable to obtain any evidence for the production of this form, and no confirmation of its existence has been reported. $CsICl_2$ is largely hydrolysed in aq. solution, forming CsCl, I_2, HIO_3, etc. (J., 1932, 2031), so it is difficult to obtain a pure specimen by crystn. from H_2O. CsCl and HIO_3 form a sparingly sol. compound, $CsCl,HIO_3$, which, in the presence of an excess of CsCl, would be very likely to separate. Wells and Penfield describe their crystals as badly formed, and as the cryst. form of the supposed rhombic $CsICl_2$ is closely similar to that of $CsCl,HIO_3$, it seems probable that the crystals were, in fact, this compound coloured orange by traces of mother-liquor. Penfield may have been deceived all the more readily because $CsCl,HIO_3$ happens to be similar in cryst. form to $CsIBr_2$.

It thus appears that the only three cases where isomerism has been supposed to occur are extremely doubtful. Even should dimorphism occur (and there appears to be little evidence for it), it is probably unaccompanied by any difference in the structure of the polyhalide ion. Considering the number of trihalides that are known, in which no isomerism is observed, isomerism seems very improbable among the trihalide anions.

The structure suggested on p. 182 would lead one to expect two forms for a compound such as KCl_2, *viz.*, $K^{\cdot}[\overset{-}{Cl}\text{–}\overset{+}{I}\text{–}\overset{-}{Cl}]'$ (I) and $K^{\cdot}[\overset{-}{I}\text{–}\overset{+}{Cl}\text{–}\overset{-}{Cl}]'$ (II). There is good reason for supposing that the compound actually known has the structure (I), and it is clear that the form (II) would be far less stable than (I), since the link between the I atom and the central Cl would be a semipolar bond, the I receiving a negative charge and the Cl a positive, which is contrary to their natural tendencies. Moreover, (I) is symmetrical. Again, from steric considerations, the form with the large atom (iodine) in the centre would be expected to be the more stable. Hence, it would be expected that whenever an ICl mol. attached itself to a Cl′ ion, it would do so by means of its I atom, forming (I), rather than (II). If (II) were formed in any reaction it would dissociate after the manner of all trihalides into KCl and ICl, which would recombine to form (I) of relatively low dissociation press. Hence the form (II) would change spontaneously into (I), and could only exist as a metastable substance.

Isomerism is similarly unknown among the higher polyhalides, and for similar reasons would hardly be expected to occur in the classes of compounds at present known. All attempts to prepare pentahalides of the type RIX_2Y_2 (*e.g.*, $CsIBr_2Cl_2$ from $CsICl_2$ and Br_2) have failed. Such compounds should show *cis-trans*-isomerism if the halogen atoms are coplanar, but none if the structure is tetrahedral. It might be possible to isolate both forms, since the difference in stability would probably be small. The NH_3 derivatives such as $NMe_4IBr_2(NH_3)_2$ (p. 182) may be compounds of this type, but no isomerism has been observed among them. A compound containing 4 different atoms grouped round an I atom $\left(e.g.,\ K^{\cdot}\left[\begin{matrix} F^- & & I^- \\ & I^+ & \\ Cl^- & & Br^- \end{matrix}\right]'\right)$ should exist in two optically active forms according to the tetrahedral arrangement, and in three forms, not optically active, if the structure is planar. The recent isolation of polyhalides containing F (CsIBrF, J., 1931, 2249; $CsICl_3F$, etc., see p. 185) suggests that it may be possible to obtain compounds of this type. The question whether the pentahalides have planar or tetrahedral structures might, however, be settled more simply by the X-ray method.

SUMMARY.

The action of various gases and vapours on solid polyhalides has been investigated, the following results being obtained:

(1) A stream of inactive gas tends to sweep away halogens, leaving a residue of monohalide.

(2) With stable dichloro- and dibromo-iodides, ammonia forms additive compounds (*e.g.*, $NMe_4IBr_2,2NH_3$); with less stable compounds, nitrogen tri-iodide is formed. Amines also form additive compounds with polyhalides.

(3) Ozone acts on potassium dibromoiodide thus: $KIBr_2 + O_3 = KIO_3 + Br_2$.

(4) The action of halogens and halogen halides on polyhalides has been investigated, and the general principles governing the replacement of one halogen in a polyhalide by another have been enunciated.

The velocity and mechanism of the reactions occurring between metallic monohalides and halogens or halogen halides have also been investigated.

The reported cases of isomerism among the polyhalides have been critically re-examined. There is no evidence that any of the polyhalide anions have yet been obtained in different isomeric forms. The types of isomerism which might be expected theoretically are discussed.

Throughout the study of the polyhalides described in the present series of papers, evidence has been accumulated, agreeing with the conclusions of other contemporary investigators, that the polyhalides have structures which may be illustrated by the following formula for potassium dibromoiodide: $K^{\cdot}[\overset{-}{Br}\text{–}\overset{+}{I}\text{–}\overset{-}{Br}]'$, the bonds between the halogen atoms being some type of semipolar bond, possibly single shared electrons. It is further concluded that the solid polyhalides dissociate spontaneously thus: $\underset{\text{(solid)}}{KIBr_2} \rightleftharpoons \underset{\text{(solid)}}{KBr} + \underset{\text{(vapour)}}{IBr}$; that in aqueous solution they yield complex anions (*e.g.*, $KIBr_2 = K^{\cdot} + IBr_2'$) which suffer partial hydrolysis (*e.g.*, $5IBr_2' + 3H_2O \rightleftharpoons 2I_2 + IO_3' + 10Br' + 6H^{\cdot}$) (those polyhalides which yield only iodine by dissociation are not appreciably hydrolysed), and that iodine cations are probably formed when methyl alcohol is used as solvent.

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