

CCXLIX.—*A Study of the Polyhalides. Part I.*
Methods of Preparation.

By HERBERT WILLIAM CREMER and DONALD RUSSELL DUNCAN.
PREVIOUS investigators of the polyhalides have dealt mainly with methods of preparation or some selected physical property; in fact, systematic knowledge of the group is lacking. The experiments

now described were initiated with the object of obtaining this knowledge and deal with various types of polyhalide, particular attention being given to the dibromiodides. These are readily obtained in a state of purity, and, whilst presenting no outstanding difficulties in manipulation, exhibit the more salient characteristics of the class. Attention is here directed to the most suitable methods of preparing these substances in a state of purity, with a view to examining their physical and chemical properties.

All the earlier investigators prepared their products by wet methods, crystallising their materials from aqueous or alcoholic solutions. Dry methods were employed successfully by Rae (J., 1915, **107**, 1286; 1918, **113**, 880) for the preparation of the dibromiodides and tetrachloriodides of the alkali metals, and the method has now been considerably extended. By employing dry methods of preparation, theoretical yields may be frequently obtained and the resultant materials are free from water and products of hydrolysis (such as iodate). The main disadvantage of dry methods is that they are usually slower than wet methods, but they frequently yield products which cannot be obtained by other processes. The general dry method of preparation consists in leaving the dry, finely powdered monohalide in a vessel containing a halogen or halogen halide, so that it may absorb the vapour evolved by the latter. In some cases absorption ceases when the theoretical gain in weight has occurred. In other cases an excess of halogen is taken up, owing to adsorption or to solution formation. The excess halogen may be removed by means of a current of dry air, by diminished pressure, by standing over alkali, or, in some cases, over iodine, or by washing with carbon tetrachloride or ether, according to the stability of the product and the volatility of the halogen.

Methods of Analysis.—When a metallic polyhalide is obtained by dry methods, the ratio of the mass of the product to that of the original monohalide directly gives the percentage of metal in the product, or the metal may be determined by conversion into monohalide by the action of heat. The percentage of metal or other kation may also be deduced from the volumetric determinations of the oxidising and total halogen. In the present investigations, the oxidising halogen (halogen in excess of that present in the monohalide) was determined by addition of a weighed quantity of the polyhalide to an excess of aqueous potassium iodide and titration with sodium thiosulphate solution. When iodate was present, it was determined by adding acid to the final solution and continuing the titration. The number of c.c. of *N*-thiosulphate equivalent to one gram of material provides a convenient constant for checking

the purity of products and this figure is recorded in connexion with the compounds to be described. The total halogen may be determined by reducing the polyhalide to monohalides by means of aqueous sulphur dioxide, destroying the excess of the latter by addition of hydrogen peroxide, and estimating the halides gravimetrically or volumetrically by means of silver nitrate. At least one analytical determination was carried out on each compound isolated, but, for brevity, figures will be recorded only in cases of special interest.

All the melting points given are temperatures at which melting begins when the materials are heated in a sealed tube.

Dibromiodides, RIBr₂.

Owing to their importance in the present research, the preparation of the compounds of this series will be discussed first and in greatest detail. The wet methods used by previous investigators have been carefully examined and, in the case of the less stable dibromiodides (such as those of the alkali metals), owing to their high solubility and to the formation of hydrolytic products, have been found inferior to dry methods. Extension of the latter to other cases has been investigated. Thus, by the action of bromine upon the iodides in question, quantitative yields of pure product have been obtained in the case of the dibromiodides of *monomethylammonium*, *monomethylammonium*, *tetraethylammonium*, and *isopropylammonium*, as well as evidence of the existence of dibromiodides of *n*-propylammonium and triethylammonium.

All the dibromiodides investigated form red crystals which are orange-yellow when finely powdered, and the possibility of isomerism suggested by Ephraim (*Ber.*, 1917, **50**, 1082) has not been confirmed.

Sodium dibromiodide. By the action of iodine bromide vapour on sodium bromide in a desiccator, a reddish-brown solid was produced, and a similar material was obtained by shaking sodium bromide with a solution of iodine monobromide in carbon tetrachloride for 5 months. Although it would appear probable that some compound of sodium, iodine, and bromine exists, it cannot be considered as established that the compound has the formula NaIBr₂.

The most suitable method for preparing the dibromiodides of potassium, rubidium, and caesium is a modification of that used by Rae (*loc. cit.*), in which the solid iodide is left in contact with bromine vapour or mixed with liquid bromine, excess of the latter being afterwards removed where necessary by standing in a desiccator over solid sodium hydroxide or iodine. The latter substance was found preferable, since it does not bring about decomposition

of the dibromiodide. The time required in the case of the potassium salt (m. p. 58°) was approximately 3 days, but this period is greatly prolonged by excessive drying. The rubidium salt (m. p. 225°) required 2 days, and the caesium salt (m. p. 247°) only 3 hours.

Ammonium dibromiodide has been prepared by a new method, viz., by dissolving ammonium bromide in a solution of iodine monobromide in absolute alcohol and leaving the solution to crystallise in a desiccator containing calcium chloride. The crystals were washed with alcohol and afterwards with carbon tetrachloride-ether. The m. p., not previously recorded, was 198° .

All the organic dibromiodides previously known appear to have been derived from completely alkylated bases—quaternary ammonium and phosphonium and tertiary sulphonium bases—or from bases containing cyclic nitrogen. Dibromiodides of primary, secondary, and tertiary amines have now been prepared: they are less stable and more soluble than the quaternary compounds.

Monomethylammonium dibromiodide was prepared in theoretical yield from the solid iodide and bromine vapour (Found: thiosulphate titration, 6.30 c.c. of $N\text{-Na}_2\text{S}_2\text{O}_3$ per g. $\text{MeNH}_3\text{IBr}_2$ requires 6.27 c.c.). It is deliquescent and unstable; m. p. 71° .

Dimethylammonium dibromiodide was prepared by precipitation, the correct quantity of bromine being added to an aqueous solution of the iodide. Yield, 50% (Found: thiosulphate titration, 6.00 c.c. $\text{Me}_2\text{NH}_2\text{IBr}_2$ requires 6.00 c.c.). M. p. 136° . Stable compound, readily soluble in alcohol, and exceptional in being soluble in ether, from which it can be recrystallised.

Trimethylammonium dibromiodide was precipitated when solutions of iodine monobromide and of trimethylamine in hydrobromic acid were mixed. Yield, 60% (Found: thiosulphate titration, 5.72 c.c. $\text{Me}_3\text{NHIBr}_2$ requires 5.77 c.c.). M. p. $67\text{--}68^{\circ}$. Readily soluble in alcohol.

Tetramethylammonium dibromiodide, Me_4NIBr_2 (Dobbin and Masson, J., 1886, 49, 848; Chattaway and Hoyle, J., 1923, 123, 654), was obtained by the former method in 80% yield after recrystallisation from alcohol. M. p. 190° .

Monoethylammonium dibromiodide was prepared in the dry way from the iodide and bromine. Yield, theoretical (Found: thiosulphate titration, 5.99 c.c. $\text{EtNH}_3\text{IBr}_2$ requires 6.00 c.c.). M. p. 49° . Deliquescent and unstable.

Diethylammonium dibromiodide was prepared in the same way as the trimethylammonium derivative (Found: thiosulphate titration, 5.62 c.c. $\text{Et}_2\text{NH}_2\text{IBr}_2$ requires 5.54 c.c.). M. p. $46\text{--}47^{\circ}$.

Triethylammonium dibromiodide, $\text{Et}_3\text{NHIBr}_2$, could not be

definitely isolated. Wet methods failed completely, and dry methods gave a red liquid, the composition of which agreed with the above formula. There is, however, reason to believe that this compound would melt below room temperature.

Tetraethylammonium dibromiodide (Chattaway and Hoyle, *loc. cit.*) was prepared in quantitative yield by the action of bromine on the solid iodide. M. p. 119°.

Ethyltrimethylammonium dibromiodide, $\text{EtNMe}_3\text{IBr}_2$, was prepared in the same way as the dimethylammonium salt. Poor yield. M. p. 145°. Very stable compound.

n-Propylammonium dibromiodide, $\text{Pr}^n\text{NH}_3\text{IBr}_2$, could not be obtained by wet methods. An impure product was obtained in the dry way from the iodide and bromine, but considerable difficulty was encountered, owing to the difficulty of removing the excess of bromine and to the extremely deliquescent nature of the product.

*iso*Propylammonium dibromiodide could be prepared without much difficulty by this method. Yield, theoretical (Found: thio-sulphate titration, 5.77 c.c. $\text{Pr}^i\text{NH}_3\text{IBr}_2$ requires 5.77 c.c.). M. p. 54°. Deliquescent, but more stable and easier to handle than the normal derivative.

The compound of pyridine and iodine monobromide, $\text{C}_5\text{H}_5\text{NIBr}$, was prepared by mixing alcoholic solutions of its constituents, as described by Mouneyrat (*Compt. rend.*, 1903, **136**, 1471; 1904, **139**, 1470). Yield, 60%. A larger yield can be obtained by using carbon tetrachloride as solvent. M. p. 115—117°. The product forms golden-yellow crystals, which are decomposed by water, and dissolves readily in methyl and ethyl alcohols, less readily in ether, and sparingly in carbon tetrachloride, the solubility in the last amounting to 0.297 g. per 100 c.c. of solution at 25°. This compound is not a dibromiodide, but was used for comparative purposes and for the preparation of the next compound.

Pyridinium dibromiodide, $\text{C}_5\text{H}_5\text{NHIBr}_2$, was prepared by cooling a solution of 5 g. of the above compound in 15 g. of hot concentrated hydrobromic acid (*d* 1.7) in ice and salt. The crystals which separated were washed with cold water and dried in a vacuum desiccator containing phosphoric oxide. Yield, 86%. M. p. 174°. It was first isolated by Trowbridge and Diehl (*J. Amer. Chem. Soc.*, 1897, **19**, 558), who prepared it in the wet way from bromine and the iodide, and obtained the m. p. 172—175°.

N-Methylpyridinium dibromiodide, $\text{C}_5\text{H}_5\text{NMeIBr}_2$, was obtained in the same way by Trowbridge and Diehl, who also prepared the ethyl homologue. M. p. of methyl derivative, 61—62°.

Hydrogen dibromiodide, HIBr_2 . During the present investigation, considerable evidence has been accumulated pointing to the

existence of the free acid, HIBr_2 , in aqueous solution. Although iodine monobromide is decomposed by water with separation of iodine, aqueous hydrogen bromide will dissolve an equivalent amount of iodine monobromide without liberation of iodine and with considerable absorption of heat. In this way a liquid of the composition 94% HIBr_2 , 6% H_2O , may be obtained. This 94% acid is a dark red, very dense, viscous liquid. It may be mixed with water in all proportions without separation of iodine, and behaves chemically as the compound HIBr_2 . Physical determinations will be described later in support of the view that the iodine is present in the same state as in an aqueous solution of potassium dibromiodide, suggesting that hydrogen dibromiodide is a strong acid ionising into H^+ and IBr_2^- . The dilute acid may be obtained free from an excess of iodine bromide or hydrobromic acid by decomposing potassium dibromiodide solution with the calculated quantity of fluosilicic acid : $2\text{KIBr}_2 + \text{H}_2\text{SiF}_6 = \text{K}_2\text{SiF}_6 + 2\text{HIBr}_2$. Perchloric acid acts similarly : $\text{KIBr}_2 + \text{HClO}_4 = \text{KClO}_4 + \text{HIBr}_2$. When hydrogen bromide gas, prepared very conveniently by dropping bromine into tetralin, was passed over iodine monobromide, no change occurred unless a trace of moisture was present, in which case a syrup was formed similar to that described above. The 94% acid gives no solid on cooling in ice and salt, and the anhydrous acid has not yet been isolated.

Bromodi-iodides, RI₂Br.

The only inorganic member of this series known is the caesium salt, CsI_2Br . The authors have prepared this compound by the method of Wells and Penfield (*Z. anorg. Chem.*, 1892, **1**, 83), and have confirmed the melting point as 208° . They have obtained definite evidence, which will be given later, that potassium bromide does not form any compound with iodine stable at 25° .

Chlorobromiodides, RClBrI.

No evidence could be obtained by the authors for the existence of sodium chlorobromiodide, NaClBrI .

Potassium chlorobromiodide has been obtained by exposing potassium chloride to the vapour evolved by iodine monobromide, in the manner already described (p. 1858) (Found : K, 13.87. KClBrI requires K, 13.90%. Thiosulphate titration : found, 7.10 c.c.; calc., 7.10 c.c.). Six months were required for the preparation, which, however, is considerably accelerated by evacuating the apparatus. A pure product was obtained by grinding potassium chloride and iodine monobromide together in the theoretical proportion, and leaving the mixture in a sealed vessel for slow com-

ination to take place. The compound does not melt sharply, but incipient melting occurs at 40° .

Rubidium and caesium chlorobromiodides were prepared by Wells and co-workers by wet methods, but the authors have found the dry method described under the potassium salt more suitable. The caesium salt may also be obtained by fusing together in a sealed tube an equimolecular mixture of caesium dibromiodide and dichloriodide: $\text{CsIBr}_2 + \text{CsICl}_2 = 2\text{CsIBrCl}$. By whichever method it is prepared, caesium chlorobromiodide melts sharply at 238° , which is also the melting point of the dichloriodide. These two compounds form a complete series of solid solutions, all melting sharply at 238° . Mixtures of the dibromiodide and chlorobromiodide melt less sharply at temperatures between 238° and 247° , the melting point of the dibromiodide. Rubidium chlorobromiodide melts at 205° .

Ammonium chlorobromiodide was prepared by Chattaway (J., 1915, 107, 105) by a wet method, and the authors have obtained quantitative yields by the dry method used for the alkali-metal salts, 2—3 months being required. M. p. $95-100^{\circ}$.

Hydrogen chlorobromiodide, HClBrI . The anhydrous acid is unknown, but the authors find that iodine monobromide is readily soluble in hydrochloric acid, it being possible to obtain a liquid of the composition 83% HIBrCl , 17% H_2O . Evidence will be given later for supposing that the red corrosive liquid so obtained contains the compound HClBrI in solution.

Dichloriodides, RICl_2 .

The dichloriodides form a series of compounds which differ from the dibromiodides in being yellow, less stable, more readily hydrolysed, and in combining with chlorine to form tetrachloriodides, no tetrabromiodides being known. They are, consequently, more difficult to prepare.

An orange compound, which is probably sodium dichloriodide, is formed when the vapour of iodine monochloride is absorbed by solid sodium chloride, but has not yet been obtained in a state of purity. It is very unstable and deliquescent.

The potassium salt was obtained by Ephraim (*Ber.*, 1917, 50, 1086) by crystallisation from water, but, owing to the ease with which it is hydrolysed, it is best obtained by dry methods. Thus, it is most readily obtained by grinding together potassium dibromiodide and tetrachloriodide in the proportion required by the equation $\text{KIBr}_2 + \text{KICl}_4 = 2\text{KICl}_2 + \text{Br}_2$, the bromine being removed by the methods already described for the removal of uncombined halogen. It is also prepared very conveniently by the action

of chlorine on dry potassium dibromiodide: $\text{KIBr}_2 + \text{Cl}_2 = \text{KICl}_2 + \text{Br}_2$. If the material be in a thin layer, this reaction is complete at the end of 5 minutes. Further absorption of chlorine takes place far more slowly: $\text{KICl}_2 + \text{Cl}_2 = \text{KICl}_4$. If, on analysis, the product be found to contain dibromiodide or tetrachloriodide, an equivalent quantity of tetrachloriodide or dibromiodide respectively may be added in order to convert the impurity into dichloriodide. Potassium dichloriodide begins to melt rather below 60° , but the melting point is far from sharp.

Rubidium dichloriodide has been obtained by a new method, *viz.*, crystallisation from a solution obtained by adding an excess of the aqueous acid, HICl_2 , to one of rubidium chloride. M. p. 208° .

The cæsium salt was prepared by the action of iodine monochloride vapour on solid cæsium chloride or bromide. Under experimental conditions, the action $\text{CsCl} + \text{ICl} = \text{CsICl}_2$ required 10 days, the action $\text{CsBr} + 2\text{ICl} = \text{CsICl}_2 + \text{IBr}$ only 7, for completion. M. p. 238° .

Ammonium dichloriodide was prepared in the wet way by Chattaway (*loc. cit.*). The authors have also employed the dry method, using ammonium chloride and iodine monochloride, but this was less satisfactory. M. p. 162° .

Earlier investigators have suspected the existence in solution of the free acid, HICl_2 ; further evidence will be put forward supporting its existence, although Philbrick (J., 1930, 2254) has recently expressed the contrary view. By dissolving iodine monochloride in hydrochloric acid, one may obtain a dark brown liquid of the composition 80% HICl_2 , 20% H_2O . This gives no solid on cooling in ice and salt. All attempts to prepare the anhydrous acid have been unsuccessful (see, however, Hannay, J., 1873, 26, 851).

Tetrachloriodides, RCl_4 .

The tetrachloriodides are a stable, well-defined, and easily obtainable series of pentahalides. Of the many methods available for the preparation of the potassium salt, one originally used by Filhol (*J. Pharm.*, 1839, 18, 457) has been found most satisfactory, *viz.*, by passing chlorine through a solution of potassium iodide acidified with hydrochloric acid. Yield, 70%. Excess of chlorine must be avoided, since, owing to the occurrence of the reaction $\text{KICl}_4 + \text{Cl}_2 + 3\text{H}_2\text{O} \rightleftharpoons \text{KIO}_3 + 6\text{HCl}$, the product tends to become contaminated with iodate (probably present as the compound $2\text{KIO}_3 \cdot \text{HCl}$). Hence, it is not advisable to crystallise it in a desiccator containing chlorine, as sometimes recommended. Absolute freedom from iodate, together with quantitative yield, may be ensured by the employment of dry methods, but these are generally

much slower. The action of chlorine on potassium dibromiodide forms the quickest dry method, only a few hours being needed for complete conversion. M. p. 110—115°.

Rubidium tetrachloriodide was prepared by the wet method just described for the potassium salt, but the yield was only 30%. M. p. 163°.

A quantitative yield of pure caesium tetrachloriodide was obtained by the action of iodine trichloride vapour on solid caesium bromide, a process requiring about a fortnight. M. p. 228°.

In the case of the ammonium salt, the standard wet method described above gave a 30% yield of product free from iodate, m. p. about 125°.

A solution of the free acid, HICl_4 , may be obtained by dissolving the theoretical quantity of iodine trichloride in hydrochloric acid. On cooling this solution in ice, a crystalline hydrate, $\text{HICl}_4 \cdot 4\text{H}_2\text{O}$, separates. This acid, which is the first and only solid hydrogen polyhalide to be isolated, was first obtained by Caglioti (*Atti R. Accad. Lincei*, 1929, 9, 563) by passing chlorine through an ice-cooled suspension of iodine in hydrochloric acid. The authors have also prepared it by passing chlorine through a cooled aqueous solution of hydrogen dichloriodide, this reaction being evidence that the compound HICl_2 exists in solution: $\text{HICl}_2 + \text{Cl}_2 + 4\text{H}_2\text{O} = \text{HICl}_4 \cdot 4\text{H}_2\text{O}$. By Caglioti's method the authors obtained a 26% yield. The orange-yellow plates obtained are very deliquescent and destructive to the skin, paper, etc. Hence the material is difficult to manipulate, but a specimen was dried on a porous plate, and a solution prepared and analysed. 0.5588 G. was made up to 100 c.c., so the solution should be 0.0163*M* in $\text{HICl}_4 \cdot 4\text{H}_2\text{O}$. It was found to be 0.0643*N* to thiosulphate (= 0.0161*M*), and 0.0817*N* to silver nitrate solution (= 0.0163*M*), confirming Caglioti's formula. The acid thus resembles its more unstable salts in crystallising with four mols. of water per atom of iodine. All attempts by the authors to prepare the anhydrous acid have been unsuccessful.

Polyhalides containing no Iodine.

Examination of the following compounds has confirmed the conclusions of previous investigators concerning their existence, composition, and properties, but it has been found preferable to employ dry methods in their preparation: caesium tribromide, caesium chlorodibromide, and caesium dichlorobromide. Careful investigation failed to yield evidence for the existence of any anhydrous polybromide of caesium other than CsBr_3 (compare Rae, this vol., p. 1578), or of any polychlorides of caesium or polybromides of

potassium. Rae's analytical data do not prove that his caesium tetrabromide is anhydrous; the break in the loss curve (p. 1580) is not very pronounced, and no corresponding break is noticeable in curves obtained by the authors.

Summary.

Methods are given for preparing the various types of polyhalide in a state of purity with a view to subsequent examination of their physical and chemical properties. The compounds investigated include the dibromiodides of the alkali metals, alkyl-ammonium and -pyridinium bases, but in the other series of polyhalides, only the alkali-metal salts have been examined. The existence of the acid $\text{HICl}_4 \cdot 4\text{H}_2\text{O}$ is confirmed, and the view is expressed that the acids HIBr_2 , HIBrCl , and HICl_2 exist in aqueous solution.

KING'S COLLEGE, LONDON.

[Received, May 20th, 1931.]
