XCIV.—Studies of the Perhalogen Salts. Part. I. By CHARLES KENNETH TINKLER, B.Sc.

It has long been known that when iodine is dissolved in hydriodic acid or a solution of a metallic iodide, combination takes place between the iodine and iodide with the formation of a certain amount of periodide.

In 1877, a substance having the empirical formula KI_3 was isolated by Johnson (Trans., 1877, 31, 249) from an aqueous-alcoholic solution of iodine and potassium iodide, whilst other metallic reriodides have since been prepared. In addition a large number of periodides of organic bases have been described by Pelletier (*Annalen*, 1837, 22, 113), Herepath (Trans., 1853, 5, 177 and 1859, 11, 130), Tilden (Trans., 1865, 18, 99 and 1866, 19, 145), Jörgensen (*Ber.*, 1869, 2, 460), and others.

Evidence of the formation of metallic periodides in nitrobenzene solution was obtained by Dawson (Trans., 1902, 81, 524 and 1904, 85, 796), who found that by shaking a mixture of iodine and metallic iodide with nitrobenzene, the iodine and iodide were dissolved in proportions which showed that substances of the type KI_3 , BaI_6 , &c., were produced when the iodide was in excess, and substances of the type KI_9 , BaI_{18} when iodine was in excess. By substituting bromides and chlorides for iodides he obtained evidence of the formation of additive compounds of the halogen salt with iodine.

In connexion with an investigation on the state of iodine in various solvents, by an examination of the ultraviolet absorption spectra of its solutions, it was found that, whilst a N/1000 solution of iodine in water, chloroform, or alcohol shows no absorption band and very little general absorption in the ultraviolet when the thickness of layer photographed does not exceed 25 mm., on the addition of potassium iodide to N/1000 aqueous iodine the absorption spectra of the solution show very great general absorption and two absorption bands. Since potassium iodide itself in dilute solution has no characteristic absorption, the spectra of the solution of iodine in potassium iodide appear to be due to the presence of periodide. It thus appeared probable that the formation of these perhalogen salts in solution might be investigated by means of their ultraviolet absorption spectra.

(An account of the spectra of various iodine solutions is to be found in Kayser's *Handbuch der Spectroscopie*, **3**, 152 and 324.)

The spectra of N/1000 solutions of iodine in water containing excess of various iodides were photographed and were found in every case to be identical. In this connexion the iodides of sodium, potassium, barium,

magnesium, cadmium, and aluminium were employed. Exactly similar spectra were also obtained on the addition of hydriodic acid, ammonium and tetramethylammonium iodides to the aqueous solution of iodine. In all cases the addition of the iodide produces a change in the visible colour of the solution from reddish-brown to yellow.

Since on the addition of all the iodides mentioned above exactly the same spectra were obtained, it seems probable that all these solutions of iodine contain the same ion, probably (I_3) , as it has been shown by Janowkin (*Zeitsch. physikal. Chem.*, 1896, 20, 19) and Dawson (Trans., 1901, 79, 238) that a solution of iodine in potassium iodide contains the tri-iodide KI₃.

It was found by Dawson (Trans., 1904, 85, 805) that cadmium iodide did not dissolve with iodine when the two substances were shaken with nitrobenzene, so that cadmium periodide was probably not produced under these conditions. The addition, however, of cadmium iodide to the aqueous solution of iodine gives a solution, the spectra of which are identical with those of solutions to which any of the above-mentioned iodides is added. Cadmium tri-iodide thus appears to exist in aqueous solution.

By means of the formula given by Dawson (Trans., 1902, 81, 1090) it may be calculated that the amount of uncombined iodine in a N/1000solution of iodine, containing 0.5 per cent. of potassium iodide, amounts to only approximately 1/30th of the total amount of iodine present. The absorption curve of such a solution is shown in Fig. 1. By increasing the amount of potassium iodide above 0.5 per cent., only a slight change is observed in the character of the spectra, apart from the absorption due to the iodide itself, although with increasing quantities of the iodide more periodide is produced. It appears to be easier to trace a slight increase in the amount of periodide by means of the spectra of the solution when the total amount of periodide is small than when it is great, as in the case of a solution containing 0.5 per cent. of potassium iodide. A somewhat similar result was observed in the case of the estimation of the relative amounts of the two forms of cotarnine in a solution of the substance in a!kalis (Dobbie, Lauder, and Tinkler, Trans., 1904, 85, 127 and Plate III, Trans., 1903, 83, 605).

Fig. 1 shows the absorption curves of N/1000 solutions of iodine containing (i) 0.066 per cent. of potassium iodide and (ii) 0.5 per cent. of potassium iodide. By comparing the spectra of a solution of iodine containing a small quantity of an iodide with those of a solution containing an excess of the iodide, it is possible to estimate, although roughly, the amount of iodine in combination with the iodide. Thus, if the spectrum of a layer of a particular thickness of a solution of iodide containing a small quantity of an iodide is the same as a layer

of, say, 1/5th the thickness of a solution containing excess of the iodide, it is probable that in the first solution approximately 1/5th of the iodine is in combination with the iodide.

The examination of the spectra of a solution of iodine in water to which a soluble bromide is added affords evidence of the formation of compounds of iodine and the bromide.

By again employing N/1000 aqueous iodine, a layer 25 mm. of which shows no absorption in the ultraviolet, on the addition of



potassium bromide, spectra are obtained, which show one well marked absorption band and less general absorption than the spectra of iodine in a solution of an iodide. The same spectra were obtained by employing potassium bromide, magnesium bromide, cadmium bromide, hydrobromic acid, ammonium and tetramethylammonium bromides. The spectra are thus evidently characteristic of the same ion, which, owing to the large excess of bromide added and from analogy with the iodine additive compounds of iodides, is probably (BrI_2) .

Fig. 2 represents the absorption curves of N/1000 solutions of

iodine containing 0.24 per cent. of potassium bromide and excess of the salt respectively.

As in the case of the iodides, it is possible to estimate the amount of iodine in combination with the bromide, assuming that with excess of bromide the whole of the iodine is in combination, which is

FIG. 2.



extremely probable from the fact that when the solution contains a certain amount of bromide the addition of a further quantity causes no change in the absorption spectra. Thug, it will be seen from the curves, Fig. 2, a N/1000 solution of iodine containing 0.24 per cent. of potassium bromide gives spectra which are practically the same as those given by layers 2/5th the thickness when the solution contains

excess of the salt. It appears therefore that in the first case approximately 2/5th of the iodine is in combination with the bromide.

The addition of a soluble chloride to the aqueous solution of iodine also causes a complete change in the character of the absorption; the spectra showing a well-defined absorption band and less general absorption than those of a solution of iodine containing a bromide. Exactly the same spectra were obtained by employing an excess of the chlorides of lithium, sodium, potassium, calcium, strontium, barium, magnesium, and aluminium, and also by hydrochloric acid, ammonium and tetramethylammonium chlorides. It appears therefore that in all these cases the same ion is produced, which from analogy with the iodide compounds is probably (ClI₂).

The absorption curve of these chloroperiodides is shown in Fig. 3.

The amount of iodine in combination with a given quantity of chloride can be estimated as in the two previous cases.

The addition of either a bromide or chloride to the aqueous solution of iodine also produces a slight change in the visible colour of the iodine solutions. By estimating the amount of combined iodine, from the spectra of a solution containing a haloid salt, it was found that the addition of a small quantity of potassium iodide effected combination of a much larger proportion of the iodine than is brought about by an equivalent quantity of potassium bromide or chloride. Thus, whilst in N/1000 solution of iodine containing 0.03 per cent. of potassium iodide, approximately one-half of the iodine appears to be in combination with the potassium iodide, a solution containing an amount of potassium bromide or potassium chloride equivalent to this amount of potassium iodide shows that only a very small quantity of the iodine has combined with the bromide, and practically no combination had taken place in the solution containing the chloride. It appeared therefore of interest to determine in what way the iodine would be distributed by employing a mixture of the halogen salts.

By the addition of mixtures containing equimolecular quantities of potassium iodide and bromide, iodide and chloride, and bromide and chloride to solutions of iodine it appeared from the spectra that almost the whole of the iodine combined with the salt of higher molecular weight. From these experiments and from the results obtained in estimating the amount of iodine which combines with equivalent quantities of potassium iodide, bromide and chloride added to separate solutions of iodine, it appears that the compound KI₃ is more stable in aqueous solution than KBrI₂ and KCII₂, and KBrI₂ more stable than KCII₂. It was also found by Dawson (*loc. cit.*) that in nitrobenzene solution combination of iodine and an iodide took place more readily than combination of iodine and a bromide or chloride.

Since the stability of the periodides seems to increase with the increase in molecular weight of the halogen salt in combination with the iodine, it might be expected that iodine would be more soluble in a solution of an iodide than in a solution of the corresponding bromide

FIG. 3.





N/1000-Iodine in water + excess of KCl.

or chloride and more soluble in a solut[:] solution of the chloride. The results in this connexion appear to confirm of equimolecular solutions of potasare shaken with equal weights of n in **a** nents 98

the amounts of iodine dissolved by the respective solvents are greatest for the solutions of the iodide and least for the solutions of the chloride.

The same order of solubility was observed in the case of solutions of the corresponding ammonium salts, the solubility increasing with the stability of the perhaloid salt produced.

Since it was found that iodine combines more readily with an iodide than with either a bromide or chloride and with a bromide more readily than with a chloride, it might be expected that combination with a fluoride would take place less readily than with a chloride. By the addition of sodium, potassium, or ammonium fluorides no change is observed in the spectra, and it is probable that combination does not take place at all under the conditions of the experiment.

It is hoped to determine the relative stability of the iodine additive compounds of the various iodides in aqueous solution by the method previously described, and to apply the same method for determining the relative stability of the various bromoperiodides and of the chloroperiodides.

As already mentioned, it was found that by the addition of hydriodic, hydrobromic, or hydrochloric acids to the aqueous solution of iodine, the substances HI_3 , $HBrI_2$, $HCiI_2$ were probably produced; an investigation of the action of the corresponding gases on a chloroform solution of iodine was therefore undertaken in order to ascertain if such substances were formed in a non-ionising solvent. By passing dry hydrogen iodide into a N/1000 solution of iodine in chloroform, the colour of the solution changes from violet to yellow, and the ultraviolet absorption spectra of the solution obtained in this way are identical with those of a solution of iodine in water to which hydriodic acid or a soluble iodide has been added. It thus appears that the substance HI_3 is produced also in chloroform solution. A similar result was obtained by employing an alcoholic solution of iodine.

By passing a large excess of hydrogen iodide into the chloroform or alcoholic solution, the colour entirely disappears and the ultraviolet absorption spectra are again completely changed, spectra being obtained which show only slight general absorption. It is possible that under the influence of a large excess of hydrogen iodide the periodide reacts in some way with the solvent.

The spectra of a solution of indice in chloroform through which hydrogen bromide or chloride has been passed do not show the pressure of the correspondance of the correspondance of the stable than the substance HI_5 , as is the case the metallic salts in aqueous solution. (*Ber.*, 1887, 20, 688) that for the

(*Ber.*, 1887, 20, 688) that for the tarch iodide in the well known test odic acid or a soluble iodide should

be present with the reacting substances. He supposed that sufficient hydriodic acid is present in an aqueous solution of iodine for the production of a small quantity of starch iodide.

Meineke (*Chem. Zeit.*, 1894, 18, 157) found that the formation of the blue starch iodide was also facilitated by the presence of a large quantity of other salts, such as sodium or potassium sulphates, the chlorides of various metals, &c., whereas the addition of a minute quantity of potassium iodide caused a great increase in the intensity of the blue colour when starch and an aqueous solution of iodine are mixed together.

Lonnes (Zeitsch. anal. Chem., 1894, 32, 33) suggested in explanation of the formation of starch iodide in the presence of a chloride, that a chloroiodide is produced, which is then transformed by the starch into an iodide, and this in turn facilitates the production of the starch iodide.

The absorption spectra of solutions of iodine to which a large amount of sodium sulphate or potassium sulphate have been added, show the presence of a very small quantity of a periodide, such as is obtained by the addition of a minute quantity of potassium iodide to the iodine solution. It has been shown by the ultraviolet absorption spectra of a solution of iodine containing a chloride that the chloride and iodine are in combination; it seems possible, therefore, from these preliminary experiments, that the production of the blue starch iodide is dependent on the presence of a periodide, the formation of which, however, in the case of salts such as sodium or potassium sulphate it is difficult to account for. It is possible that sufficient iodide is present as impurity in the added salt to give the reaction, since it can be shown that the addition of one-millionth of a gram of potassium iodide causes a visible increase in the intensity of the blue colour of an aqueous solution of iodine containing starch. The absorption spectra of solutions of iodine containing an iodide are completely changed on the addition of starch solution, the two absorption bands characteristic of the periodide no longer being observed.

Some preliminary experiments on the combination of bromine with bromides and with chlorides in aqueous solution have given results similar to those obtained in the case of iodine.

It is hoped to examine more fully, by this method, the formation of perhalogen salts and to investigate the effect of temperature on the stability of the compounds; all the experiments mentioned in this paper were carried out under the ordinary conditions, no special precautions being taken to ensure that the temperature of the various solutions was the same.

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