

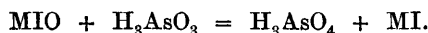
LXXV.—*Estimation of Hypiodites and Iodates and the Reaction of Iodine Monochloride with Alkalis.*

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SEVERAL characteristic properties of solutions of hypiodites have been recorded, that is, of solutions obtained by causing iodine (in the solid form or in solution) to react with solutions of alkalis.

The evolution of oxygen from hydrogen peroxide and barium peroxide, and the liberation of iodine from potassium iodide were noted by Schönbein (*J. pr. Chem.*, 1861, **84**, 385) and Seliwanow (*Ber.*, 1894, **27**, 1013); and the bleaching of indigo carmine and cochineal by Lunge and Schock (*Ber.*, 1882, **15**, 1883). The former reaction they attempted to apply quantitatively. Lonnes (*Zeit. anal. Chem.*, 1894, **33**, 409) found that sodium arsenite, and Péchard (*Compt. rend.*, 1899, **128**, 1453) that ferrous sulphate, were oxidised by these solutions.

The authors have used a modification of a method, proposed by Lonnes (*loc. cit.*), in which the oxidation of arsenite is employed to estimate the hypiodite, the reaction being represented by the following equation :



The iodate is estimated by acidifying the solution and titrating the iodine liberated by sodium sulphite or thiosulphate.

The solutions were prepared by mixing solutions of iodine in potassium iodide with alkalis, and from solutions of iodine monochloride in hydrochloric acid* and alkalis. The reaction of iodine monochloride with alkalis is shown to be represented by the equation.



Initially, no potassium iodide is formed as in the reaction of iodine and alkalis. As the presence of potassium iodide has a disturbing effect, a greater excess of alkali is necessary before the reaction of iodine with starch or chloroform ceases (compare Lonnes and Pechard, *loc. cit.*). In our experiments, sufficient alkali was always present to ensure the absence of any free iodine. The solutions prepared resemble those obtained from iodine; they have a characteristic odour

* A 3/10 to 4/10 *N* solution of iodine monochloride is easily made by gently warming 10 grams of iodine with a mixture of the calculated quantity (2·8 c.c.) of nitric acid of sp. gr. 1·4, and 30—40 c.c. of concentrated HCl of sp. gr. 1·15. When all the iodine has dissolved, the solution is diluted to 250 c.c. with water or dilute hydrochloric acid.

resembling that of iodoform or saffranine, and are pale straw-yellow. They oxidise arsenite, sulphite, and thiosulphate immediately. On standing, the hypoiodite disappears, and in most cases is not recognisable after 24 hours; ammonium hypoiodite, however, is much more stable and is not wholly decomposed after 2 weeks. When not too dilute, they give a precipitate of nitrogen iodide with ammonia. A trace of hypoiodite is readily recognisable, when no large quantity of alkali is present, by adding first sodium or potassium hydrogen carbonate and starch and finally potassium iodide. A blue colour immediately appears. If iodide is already present in quantity, the blue colour develops without the addition of potassium iodide (compare Taylor, this vol., 729).

Estimation of Hypoiodites and Iodate.

Excess of a standard solution of sodium arsenite is added to the alkaline hypoiodite. After standing for a short time, the alkali is removed by carbon dioxide,* and then the excess of arsenite estimated by standard iodine. Experiments have shown that under these circumstances the arsenite is not affected by iodate and iodide (compare Lonnes, *loc. cit.*). When ammonia is the alkali, it can be removed partly by boiling. The iodate is now estimated by adding a little dilute sulphuric acid, and titrating any iodine set free. A further quantity of sulphuric acid is added, and followed by addition of sulphite (or thiosulphate), and so on, until the solution is acid. This procedure avoids loss of iodine by the evolution of carbon dioxide, and further prevents the solution from ever becoming very acid, with the consequent interaction of the arsenate with the hydriodic acid. The following experiments show that this method is fairly trustworthy.

(1) To 100 c.c. of a solution containing 0.59 gram of potassium iodate and about 1 gram of potassium iodide, 10 c.c. of a 35 per cent. solution of potassium hydroxide were added, and then 26.6 c.c. of $N/10$ arsenious oxide. The solution was now saturated with carbon dioxide and allowed to stand 4 days. 26.6 c.c. $N/10$ iodine were required to oxidise the arsenite. The iodate was now estimated in an aliquot part. 0.5904 gram was found.

(2). 7.15 c.c. of $N/10$ arsenious oxide were added to a solution of ammonia ($3N$) containing 0.1 gram of potassium iodate. After partial removal of the ammonia by boiling and conversion into carbonate by carbon dioxide, 7.15 c.c. $N/10$ iodine were required to oxidise the arsenite, and 0.1003 gram of potassium iodate was found.

Similar experiments gave equally satisfactory results. As a rule, the amount of iodate found is slightly in excess of that taken.

* Lonnes only used such dilute solutions of alkalis that this operation was not necessary.

Solutions of Potassium and Sodium Hydroxide.

To a 4 per cent. solution of potash, the solution of iodine monochloride in hydrochloric acid was cautiously added. At intervals, 100 c.c. of hypoiodite solution were withdrawn and titrated as above. The temperature during the experiment was not absolutely constant, but about 15°.

Estimated by distillation with ferric alum and sulphuric acid after conversion of the iodate into iodide by sulphurous acid, the total iodine per 100 c.c. = 24.05 c.c. of *N*/10 iodine, or 0.3054 gram.

Time.	Percentage of iodine as hypoiodite.	Percentage of iodine as iodate and iodide.
5 mins.	78.96	21.4
45 „	35.5	64.2
60 „	26.0	73.8
24 hours	0.24	100.0

In a similar experiment in which 20 c.c. of *N*/10 iodine in a solution of potassium iodide was added to 100 c.c. of 4 per cent. potassium hydroxide, 77 per cent. of the iodine was present as hypoiodite after 5 minutes, 31 per cent. after 20 minutes, 21.2 per cent. after 30 minutes, and 14 per cent. after 45 minutes.

Many series of analyses similar to the above were made, both with caustic potash and soda, giving the same results. After 24 hours, the whole of the hypoiodite had practically disappeared at the temperature of the laboratory (about 15°). Light had little effect on the rate of transformation. Two exactly similar solutions were made up together—one kept in darkness and the other in diffused daylight. Each was titrated every half-hour. After 1½ hours, 50 c.c. of one oxidised 3.86 c.c., and of the other 3.75 c.c. of *N*/10 arsenious oxide.

With solutions of potash less concentrated than 3 per cent., the whole of the iodine can be found as hypoiodite for a very short time, but with more concentrated solutions some conversion into iodate and iodide had always taken place before the arsenite was added. Thus 5 c.c. of an iodine monochloride solution were added to 75 c.c. of 3 per cent. aqueous potassium hydroxide, and excess of *N*/10 arsenious oxide immediately run in, but only 98.4 per cent. of the iodine was present as hypoiodite.

Solutions of Calcium and Barium Hydroxide.

The solutions were made up by adding the acid solution of iodine monochloride to saturated solutions of the alkalis, and also, according to Lunge and Schock's directions, by grinding up iodine with calcium

hydroxide and water, filtering, and making up to a given volume. The solutions obtained by each of these methods were titrated with arsenite and standard indigo. In the latter case, after addition of the indigo, the solution was allowed to stand for 15 minutes, and then the excess titrated with bleaching powder.

(1) *N*/25 calcium hydroxide solution. Temperature about 15°. Total iodine per 100 c.c. = 1.92 c.c. of *N*/10 iodine, or 0.0244 gram.

Time.	Percentage of iodine as hypiodite.	Percentage of iodine as iodate and iodide.	c.c. of <i>N</i> /10 indigo bleached.
5 mins.	95.6	3.1	7.4
45 „	68.7	29.6	7.0
17 hours	8.4	91.1	6.0

(2) A solution made by Lunge and Schock's method, and containing iodine = 5.65 c.c. of *N*/10 iodine per 100 c.c. (= 0.0717 gram) after standing for 70 hours, did not oxidise arsenite, but bleached indigo. In two titrations, 100 c.c. bleached (a) 5.4 c.c., (b) 5.8 c.c. of *N*/10 indigo.

When iodine in potassium iodide is used, similar results are obtained. With iodine monochloride all the iodine has been found present as hypiodite for a short time.

The transformation into iodate and iodide is considerably slower than with potassium hypiodite. Thus, in 45 minutes, at about 15°, only 35 per cent. of hypiodite has disappeared; while with potassium hypiodite considerably more than 60 per cent. has disappeared in the same time. The indigo, bleached by a given solution, is seen to bear no relation to the arsenite oxidised, or, indeed, to the iodine present. The action on indigo decreases but little as the hypiodite diminishes, and is considerable with solutions which do not act on arsenite. This action is due to the alkali alone. Thus, after adding indigo to 100 c.c. of calcium hydroxide solution, and estimating the former after 15 minutes standing, 5.3 c.c. of *N*/10 indigo had disappeared. The bleaching effect observed by Lunge and Schock in their solutions, which had stood for 24 hours, is therefore probably due to the alkali, and not to hypiodite (compare Taylor, *Trans.*, 1900, 77, 729).

Solutions of Ammonia and Methylamine.

In the case of ammonia, only dilute solutions could be obtained, owing to the precipitation of nitrogen iodide on further addition of iodine monochloride. Admixture of iodine monochloride and methylamine solution (3*N*) produces a yellow solution, and only after a considerable quantity of iodine monochloride has been added does a precipitate of methyldiiodoamine, $\text{CH}_3 \cdot \text{NI}_2$, appear. The alkaline

solutions thus obtained in many ways resemble hypiodite solutions in their behaviour towards arsenite, and towards potassium iodide and sodium hydrogen carbonate, only they are far more stable. With ammonia, the formation of iodate and iodide is very slow, the change not being complete at the end of two weeks. With methylamine, the power of oxidising arsenite slowly diminishes, but in three weeks has not entirely disappeared. Iodate is only formed in very small quantity, and cannot be detected for the first few days. Iodide is produced in the solution from the product formed initially.

(1) 3*N* aqueous ammonia. Temperature 12–14°.

Total iodine per 100 c.c. = 0.9 c.c. of *N*/10 iodine = (0.0114 gram).

Time.	Per cent. of iodine as hypiodite.	Per cent. of iodine as iodate and iodide.
15 mins.....	99.5	0.0
24 hours.....	83.3	13.3
48 „	77.7	22.2
72 „	66.6	35.5
28 days	8.8	93.3

These titrations were carried out with 300 c.c. of the solution, using *N*/100 standard solutions.

(2) 3*N* methylamine solution. Temperature 15°.

Total iodine per 100 c.c. = 20.4 c.c. of *N*/10 iodine (= 0.259 gram).

Time.	Per cent. of iodine as hypiodite.	Per cent. of iodine as iodate and iodide.
15 mins.....	100.2	0.0
1 hour	99.2	0.0
19 hours.....	86.7	0.0
48 „	74.8	0.0
24 days	7.1	2.7

It was thought that possibly in the case of methylamine the arsenite was oxidised by iodate, but this was shown not to be the case by a blank experiment. Also the same amount of oxidation of arsenite took place when excess of concentrated sodium hydroxide was added to the methylamine solution before the arsenite was run in. It appears then that the initially formed product, whether methyldiiodoamine, $\text{CH}_3 \cdot \text{NI}_2$, or hypiodite, is fairly stable, and is only slowly converted into hydriodic acid (methylamine hydriodide) probably in oxidising some of the methylamine. This point will be further investigated.

Reaction of Iodine with Mercuric Oxide.

Köne (*Poggendorff's Annalen*, 1845, **66**, 302) and Lippmann (*Compt. rend.*, 1866, **63**, 968) have noticed the formation of hypiodous acid (or mercury hypiodite) when iodine is shaken up with water and mercuric oxide. In the presence of amylene, Lippmann observed the formation of an iodohydrin. We have estimated the amount of hypiodite and iodate in solutions prepared by shaking up finely-powdered iodine and mercuric oxide (precipitated) with water, alcohol being omitted owing to the action of hypiodite on it. The shaking was continued for a few minutes, and the solution then filtered through asbestos or hardened filter paper. The solutions were neutral or faintly acid, the latter being the case when the shaking was not prolonged. They were colourless and gave no reaction with starch paste on acidifying or on adding sodium hydrogen carbonate. For some hours (3—4), they gave the reaction for hypiodite with sodium hydrogen carbonate, starch paste, and potassium iodide. On addition of potassium iodide to the acidified solution, it became deep brown from the liberation of iodine, a reaction which points to the presence of iodate.

A solution prepared by shaking iodine with mercuric oxide for 5 minutes contained iodine per 100 c.c. = 2.3 c.c. of $N/10$ iodine, of which 48 per cent. was present as hypiodite, and the remainder as iodate.

In a similar experiment, after 15 minutes shaking, 4.4 c.c. of $N/10$ iodine were contained in 100 c.c., 13—14 per cent. of which was in the form of hypiodite. The filtering of the solution, &c., occupied some 10 minutes after the cessation of the shaking.

From these results, it would seem that the solutions obtained from iodine and mercuric oxide contain only a small quantity of hypiodite, and that the iodine is chiefly present as iodate. Iodide is only present in small quantity, owing to the low solubility of mercuric iodide.

No attempt was made to determine the velocity constant of these transformations of hypiodite. Schwicker (*Zeit. physikal. Chem.*, 1895, **16**, 303) has attempted to determine this constant for the transformation of potassium hypiodite, and found that it varied greatly with the variations in initial concentration of the hypiodite and the alkali. Excess of potassium iodide was present in the solutions. It is possible that the investigations of the solutions of calcium hypiodite or ammonium hypiodite (?) which undergoes transformation relatively slowly may lead to some elucidation of this point.

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