

LII.—*The Interaction of Iodine, Water, and Potassium Chlorate.*

By HENRY BASSETT.

HAVING occasion some three or four years ago to prepare some quantity of iodic acid, I made use of the excellent method given by Millon at the beginning of his elaborate paper on iodic acid and iodates (*Ann. Chim. Phys.* [3], **9**, 400, 1843); but the results of the first trial were so widely different from his description as to necessitate further experiments. The usual accounts of the process, repeated pretty uniformly in most books, represent the action as a direct displacement of the chlorine by an equivalent of iodine; but my experiments lead to such a different interpretation as to induce me to bring them before the Society.

The directions given by Millon are as follows:—

80	parts of iodine,
75	„ potassium chlorate,
1	„ nitric acid,
400	„ water,

“are placed in a flask of sufficient capacity. The flask is heated to boiling, and removed from the lamp as soon as the chlorine begins to be abundantly liberated.”

In the first experiment made, 75 grams of potassium chlorate were dissolved in 400 c.c. of water with 1 c.c. of nitric acid, and heated to

about 80°. Then the prescribed 80 grams of iodine were added, not all at once, but by degrees. Under these circumstances, the iodine dissolved slowly at first, but quicker and quicker at each addition till the whole had disappeared, but without any evolution of chlorine beyond a very slight indication at the last, when the liquid was nearly boiling. At each addition of iodine, a peculiar greenish-yellow colour appeared in the liquid, which very soon vanished—no doubt, due to chlorous acid.

Finding that the liquid would still take up iodine, I added gradually 30 grams more, when it became of a permanent orange-yellow colour. Then added more chlorate till the colour disappeared, the quantity required being 14 grams. The total proportions used were, therefore, 110 grams of iodine and 89 grams of chlorate.

On cooling, a large quantity of well-crystallised biniodate of potassium was deposited. On boiling down the mother liquor from this, a steady effervescence of chlorine began when somewhat concentrated, accompanied when getting nearly dry by brownish vapours of iodine chloride.

The salt dissolved in water, and precipitated hot by barium nitrate, gave a large quantity of crystalline barium iodate. I must here mention a very curious fact already noticed by Gay-Lussac in his magnificent research on iodine (*Annalen*, **91**, 5, 1814). The barium iodate, after drying over sulphuric acid, when heated in the water-oven, loses 1·8 per cent. of hygroscopic water, and when taken out and exposed to the air, the crystals are seen under a magnifier to be in a state of violent agitation and disruption, throwing up a fine powder, which settles all round the mass, looking as if a sublimate had condensed there. Gay-Lussac refers to this as occurring during drying, but it really happens on cooling after drying, and is accompanied by an increase of weight, and in some hours all the original loss is made up. Some specimens do not behave in this way at all, and others only in a less degree.

The next experiment was made with—

6	grams of iodine,
6	„ chlorate,
30	„ water,
0·03	„ iodic acid,

mixed all at once, and heated up gradually to 50—60°, when solution began—kept at 65° till all the iodine dissolved, which took about two hours, the action being very slow at this temperature. No chlorine was given off.

Next day the solution was poured off, and the crystalline deposit washed with a little water. The solution was found to be very

strongly acid. Neutralised with barium hydrate, filtered from the small quantity of barium iodate precipitated, and made up to 200 c.c.

20 c.c. precipitated with silver nitrate gave 0.475 gram AgCl.

20 c.c. evaporated to dryness, and heated strongly to complete decomposition, redissolved in water, and precipitated with silver nitrate, gave 0.566 gram AgCl.

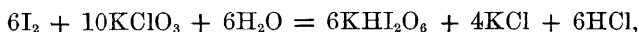
Now  $566 : 475 :: 6 : 5.04$ , indicating that one-sixth of the potassium chlorate remains in excess unacted upon by the iodine used. This was confirmed by saturating filter-paper with the solution, and drying, when it burnt with deflagration.

#### *Experiment 3.*

6 grams of iodine,  
5     ,,     chlorate,  
30    ,,     water,  
1 drop of nitric acid,

mixed all at once, and heated to  $80^{\circ}$ . The iodine rapidly dissolved without evolution of chlorine, and the resulting solution was colourless. Then added 0.1 gram of iodine, which dissolved with yellow colour, which soon disappeared. Another decigram of iodine gave the same result, and again a third, but, on adding more, the yellow colour was permanent.

The equation indicated by these experiments is—



which leads exactly to the proportions—61 parts iodine to 49 parts potassium chlorate, which are confirmed by the quantities arrived at in the first experiment by a purely tentative method, viz., 110 grams of iodine and 89 grams of chlorate.

Now  $61 : 49 :: 110 : 88.4$ .

#### *Experiment 4.*

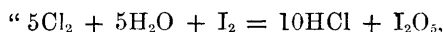
6.1 grams of iodine,  
4.9     ,,     chlorate,  
30     ,,     water,  
1 c.c. of dilute nitric acid,

mixed, and heated to  $80^{\circ}$  in a long-necked flask. Colourless solution formed with no evolution of chlorine. Added water, and made up to 250 c.c. when cold. 50 c.c. of this gave on titration numbers corresponding to 2.548 grams  $\text{Na}_2\text{CO}_3$  for the whole solution, that is, for the product from 4.9 grams of potassium

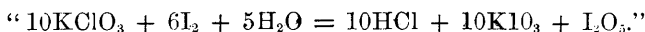
chlorate (allowing, of course, for the 1 c.c. dilute nitric acid). The equation above requires 2.544 grams.

After the above experiments were finished, I happened to refer to the account of the process given in Schützenberger's *Traité de Chimie Générale*, which concludes as follows:—

“If, instead of heating, we operate in the cold, we may succeed in dissolving all the iodine without liberation of chlorine. In fact, the displaced chlorine oxidises the iodine in presence of water, yielding iodic and hydrochloric acids—

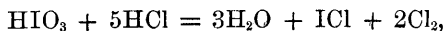


from which it follows that we may diminish the proportion of chlorate, for we have—



It will be seen that this equation amounts to much the same thing as that previously given, and I was at first under the impression that there was perhaps nothing new in my results. Finding, however, on making the experiment that no action whatever happened in the cold even after several weeks, I last year determined to look into the matter more fully.

In order to account for the evolution of chlorine which Millon must undoubtedly have observed, some experiments were made exactly as described, that is, by mixing the ingredients all at once, and heating to boiling. Under these circumstances, when using quantities of 40 or 50 grams of iodine, it was found that at a certain point a violent action was set up, with evolution of some quantity of chlorine, accompanied, of course, by much vapour of iodine and iodine chloride; but this only occurred after a considerable quantity of iodine had been dissolved, and is, doubtless, owing to the rapid formation of iodic and hydrochloric acid in the dense mass of iodine at the bottom of the flask causing a secondary action:—



This action was soon checked on reducing the temperature by dipping the flask in water for a short time, but the dissolution of the iodine still went on rapidly without further evolution of chlorine.

This is an important point, as it is obvious that if the evolution of chlorine were due to direct displacement by the iodine as usually represented, it would begin and continue concurrently with the more or less rapid solution of the latter.

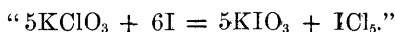
At the commencement of Millon's paper, already referred to, he mentions incidentally a former paper on the subject, which does not seem to be so well known. This is “On the Action of Iodine on

Potassium Chlorate" (*Compt. rend.*, **12**, 258, 1841), and I make the following short extracts from it:—

"Potassium chlorate is dissolved in three or four times its weight of water, and heated to boiling. Iodine then added dissolves in considerable quantity, the solution remaining colourless so long as not much more than one equivalent to one of chlorate is added. After this point, the liquid becomes yellow, then brown. The final result is neutral potassium iodate, and more or less iodised chloride of iodine. Evaporation to dryness gets rid of the latter, leaving pure potassium iodate."

Then follow some details, and a very curious explanation of the probable action, concluding:—

"The reaction may be represented thus—



He then refers to "the interesting modification of the reaction induced by the addition of a few drops of acid to the mixture . . . .

an action much more lively than that occurring between iodine and chlorate alone . . . . . at the same time, an abundant disengagement of chlorine takes place, and on afterwards evaporating to dryness a very pure potassium iodate is obtained."

Further on, he says, "the chloride of iodine which is an essential product of the first reaction . . . . . is scarcely formed at all under the influence of the nitric acid, so rapid is the evolution of chlorine."

Lastly.—"To prove the exactness of these reactions . . . . . 10 grams of dry potassium chlorate, treated by a sufficient quantity of iodine and a drop of nitric acid, and evaporated to dryness, gave a residue of 17·3 grams of perfectly white potassium iodate—theory requiring 17·4 grams.

"1·805 grams of this decomposed by heat gave 1·389 grams potassium iodide—theory requiring 1·399."

No equation is given for the modified reaction.

Experiments were then made without the addition of acid, and the first point noticed was that in many cases, but not always, the iodine coloured the liquid brown without any further action taking place for a considerable time, even when boiled. In one case, no change occurred for more than an hour at 80°, but then the liquid became suddenly colourless, and the solution of the iodine went on rapidly. The introduction of the least possible trace of acid, however, always caused instantaneous decolorisation.

Experiments made side by side, with and without addition of acid, showed no difference in behaviour after the action was once started.

I then proceeded to the examination of the results obtained by evaporating the solution to dryness. A number of preparations were made, using always 6.1 grams of iodine, 4.9 grams of chlorate, and about 40 c.c. of water (without any addition of acid).

These mixtures were placed in bulb-tubes, the necks drawn off and sealed, and then heated in a water-bath at from  $80^{\circ}$  to  $100^{\circ}$  with occasional agitation, till all iodine had disappeared, and the solutions were nearly or quite colourless. On cooling, a considerable quantity of white salt was deposited. In no case was any chlorine found on opening the tubes. The contents of each bulb were then dissolved in cold water, and made up to 500 c.c.

Three of these original solutions were titrated cold with sodium carbonate, using methyl-orange as indicator, and gave numbers corresponding to 2.536, 2.533, and 2.538 grams of  $\text{Na}_2\text{CO}_3$  for the whole solution, confirming the first experiment for the total acidity.

All subsequent analyses were calculated in the same way to correspond to 4.9 grams  $\text{KClO}_3$ .

The solutions were evaporated to dryness on the water-bath in flat dishes, in quantities of 50 or 100 c.c. When approaching dryness, chlorine was given off, and also some chloride of iodine, which gave a yellow colour to the residue. On the addition of a few drops of water, again drying, and repeating this process 5 or 6 times, a perfectly white, odourless residue was obtained, which was dried in the water-oven till the weight was constant.

Fifteen experiments, of which the extreme results only varied 1 per cent., the majority being much closer, gave a mean weight of 9.919 grams for 4.9 grams  $\text{KClO}_3$ .

Supposing the residue to be pure potassium iodate, it should weigh 8.566 grams, but on examination it was found to be acid, and to contain chlorine.

On titration, seven closely agreeing experiments gave a mean result corresponding to 1.160 grams  $\text{Na}_2\text{CO}_3$  for 4.9 grams  $\text{KClO}_3$ .

The chlorine and iodine were determined as follows:—

To a dilute solution, pure sodium bisulphite was added gradually to slight excess, that is, till the iodine, liberated at first, disappeared. Then added silver nitrate and a sufficient quantity of nitric acid and heated moderately with stirring. The resulting precipitate of  $\text{AgI} + \text{AgCl}$  was then washed, dried, and weighed.

Two experiments gave weights corresponding to 12.857 grams and 12.900 grams for 4.9 grams  $\text{KClO}_3$ .

Further experiments were then made as follows:—

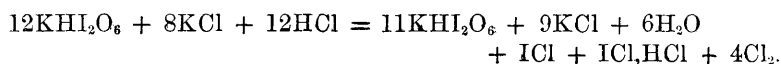
The mixed precipitates obtained as above were, after washing, rinsed into a beaker, and digested at a gentle heat with hydrochloric acid and potassium chlorate for an hour or two. Then added hot water,

boiled for a few minutes, and allowed to stand till next day, when the liquid was quite bright. Then washed, dried, and weighed the residue of  $\text{AgCl} + \text{AgCl}$ .

Three experiments gave weights corresponding to 8.871 grams, 8.865 grams, and 8.900 grams for 4.9 grams  $\text{KClO}_3$ .

The method is very satisfactory with a little care; the most important precaution being to avoid making the reduction in a strong light, for reasons to which I need not now refer.

These results lead to the following equation, expressing the decomposition on evaporating the original solution to dryness:—



The theoretical numbers calculated from this for 4.9 grams  $\text{KClO}_3$  are:—

	Grams.	Mean found. grams.
Weight of the residue $11\text{KHI}_2\text{O}_6 + 9\text{KCl}$ ...	9.921	9.919
$\text{Na}_2\text{CO}_3$ required to neutralise do. ....	1.166	1.160
Mixed silver salts from do. = $22\text{AgI} + 9\text{AgCl}$	12.923	12.879
Do. after chlorination = $22\text{AgCl} + 9\text{AgCl}$ ..	8.897	8.879

The next step was to try the effect of higher temperatures on the residue from the water-bath. It was found impossible to arrive at any definite results by heating in dishes on a sand-bath, and an air-bath at a uniform temperature of  $250^\circ$  was then tried, but the heat was not sufficient.

Several experiments were then made in bulb-tubes plugged with asbestos. The decomposition showed three well marked stages. At first the bulb was filled with brown vapours of chloride of iodine, soon replaced by violet iodine vapour, which in its turn was expelled by large quantities of oxygen.

On examination of the final residue it was found invariably to contain about 3 per cent. of potassium chloride, the separation of the iodine being made directly by palladium so as to avoid any doubt which might arise from the employment of an indirect method. I refrain from giving any symbolical expressions for these final decompositions, though I believe that the analytical results obtained give reasonable indications of such expressions; but they are rendered inexact by several causes, among which I may mention the corrosion of the glass by the fused salt, which was found to contain silica, and also by a secondary action of which I obtained distinct evidence, and to which I hope to have occasion to refer in a future communication.

My best thanks are due to Mr. E. Fielding for his able assistance in the earlier experiments, and to Mr. F. A. Manning for the use of his laboratory.

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