XXIII.—*Note on the Liberation of Chlorine during the heating of a Mixture of Potassic Chlorate and Manganic Peroxide.*

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IN a paper published in the *Berichte*, **26**, 1790 (Abstr., 1893, ii, 454), O. Brunck states that the active substance evolved when potassic chlorate and manganic peroxide are heated together, and which has hitherto been supposed to be chlorine, is, in reality, ozone. This paper naturally interested me, for if chlorine is not evolved during the heating of the mixture, the explanation of this catalytic action which I ventured to suggest (Trans., 1889, **55**, 184) would be entirely erroneous; it seemed therefore desirable to make some further experiments on the subject.

I must plead guilty to some carelessness in not having directly proved that the active substance was chlorine, but the tradition of many decades had so impressed me with the idea that chlorine was evolved that it never crossed my mind to question it. It will be remembered that, in the experiments of 1889, the mixture of potassic chlorate and manganic peroxide was placed in a test tube and heated in mercury, or in the vapour of mercury, and the evolved gas passed through a U-tube containing a solution of potassic iodide; after acidifying the solution with hydrochloric acid, the liberated iodine was determined by a standard solution of sodic thiosulphate. The phenomena would obviously be the same if either chlorine or ozone had been produced. It was noticed that when about 10 per cent. of manganic peroxide was used there was more iodine liberated than when 1 per cent. was employed, and also that more iodine was found when precipitated manganic peroxide was substituted for the coarser native oxide.

In the recent experiments, an ammoniacal solution of argentic nitrate was placed in the U-tube, and after the gas had passed through it the solution was acidified with nitric acid.

In the first experiment, 3·1432 grams of powdered potassic chlorate and 0·3228 gram of granular manganic peroxide were placed in a test tube, which was then connected to a U-tube containing argentic nitrate, to which a sufficient quantity of ammonia had been added to dissolve the precipitate first formed; in order to prevent loss, another U-tube containing some of the same solution was attached to the first. To stop any potassic chloride from being carried over mechanically into the solution, some asbestos was placed in the connecting tube between the test tube and the first U-tube. The test tube was then heated in mercury vapour, and there was a rapid evolution of oxygen. In the first U-tube a considerable quantity of white fume was formed, there being, also, a small quantity in the second tube. On acidifying the contents of the U-tube with nitric acid, the liquid in the first tube gave a milkiness, and that in the second tube a slight turbidity. The liquids were mixed, heated to boiling, allowed to stand for 24 hours, and the precipitate collected, ignited, and weighed, when 0·0045 gram of argentic chloride was found, corresponding to 0·035 per cent. of chlorine on the potassic chlorate employed.

As there might be some uncertainty as to the complete removal of suspended potassic chloride by the small quantity of asbestos in the connecting tube, one of the U-tubes was filled with dry glass beads, the second U-tube containing ammoniacal argentic nitrate. 3·1563 grams of potassic chlorate and 0·3229 gram of granular manganic peroxide were heated in the test tube; the gas passed very rapidly, and a little of the solution was projected. The quantity of argentic chloride was 0·0028 gram, corresponding to 0·022 per cent. of chlorine on the chlorate used. These quantities of chlorine are not dissimilar from those given in the previous paper, when the determination was made by means of potassic iodide.

It appeared of interest to determine, if possible, at what stage of the process the chlorine is evolved, or whether the evolution occurs during the whole of the reaction.

In the previous paper, I suggested that chlorine is liberated owing to the formation of potassic permanganate, and that the latter is then decomposed into potassic manganate, manganic peroxide, and oxygen, and that, if any chlorine was produced later it would not pass off with the oxygen, but would decompose the potassic manganate with formation of potassic chloride, manganic peroxide, and oxygen. If this is the true explanation, the chlorine might be expected to be evolved only in the first stage of the action.

Many experiments were made to endeavour to settle this question. Mixtures of potassic chlorate and manganic peroxide were made in various proportions and heated in different ways, the chlorine evolved at the beginning, middle, and end of the process being determined, but the results were not definite. There was always more chlorine when the evolution of oxygen was rapid, and this happened even at the end of some of the operations. Perhaps these experiments were mere waste of time, for the appearance of the mixture, after heating, seemed to indicate that the action was complete at the part affected and the stopping of the heating at any stage of the decomposition merely left some portion of the mixture entirely unaltered.

In order to make sure that the whole of the chlorine reached the ammoniacal argentic nitrate, the apparatus was slightly modified, the test tube being replaced by a tube provided with a delivery tube sealed to its side, and down the axis of the tube a narrower one was fixed, through which air could be driven to sweep out the gas.

Brunck points out that if chlorine is evolved when potassic chlorate and manganic peroxide are heated together, the residue should be alkaline, which is not the case; the same statement is made in my previous paper (p. 191), although other observers have detected the alkaline character of the residue. I had always tested the aqueous extract of the residue with litmus paper, but without result. On considering, however, the very small quantity of chlorine that is liberated, one recognises how little potassic hydrate must be present in the extract of the residue, and if we further remember that only a very small fraction of this comes in contact with the test paper, it is not surprising that the alkalinity is not perceived. If, however, the solution is mixed with a measured quantity of solution of litmus and then compared with the same quantity of litmus diluted to a volume equal to that of the mixture, the alkalinity of the residue is at once perceptible, and can be determined by means of a centinormal solution of oxalic acid. 1 c.c. of such a solution, containing 0·00063 gram of oxalic acid, will neutralise 0·00056 gram of potassic hydrate, and be equivalent to 0·000354 gram of chlorine.

3·2416 grams of potassic chlorate and 0·3106 of manganic peroxide were heated together in a test tube surrounded by mercury vapour. The residue was extracted with water, the solution filtered and mixed with neutral solution of litmus. 1·18 c.c. of oxalic acid were required to bring the colour as near as could be judged to the same tint as a solution containing the same quantity of litmus. This corresponds to 0·000416 gram of chlorine, or 0·013 per cent. of the potassic chlorate used.

A tabular arrangement may show the result more strikingly, and also facilitate the comparison of the numbers obtained when the chlorine was determined by weighing the argentic chloride precipitated from the ammoniacal solution of argentic nitrate, and the amount calculated from the alkalinity of the extract of the residue.

Potassic chlorate, grams.	Manganic peroxide, grams.	Manganic peroxide, per cent. on chlorate.	Argentic chloride, grams.	Chlorine calculated from argentic chloride.		$\frac{N}{100}$ oxalic acid, c.c.	Chlorine calculated from alkalinity.	
				Grams.	Per cent. on chlorate.		Grams.	Per cent. on chlorate.
3·1432	0·3228	10·270	0·0045	0·0011	0·035	—	—	—
3·1563	0·3229	10·230	0·0028	0·00069	0·022	—	—	—
3·2416	0·3106	9·582	—	—	—	1·18	0·000416	0·013
1·4793	0·1657	11·201	0·0016	0·000396	0·027	0·5	0·000177	0·012
3·2458	0·7183	22·130	0·0057	0·001409	0·043	2·0	0·000708	0·022
3·8249	0·4089	10·690	0·0036	0·00089	0·023	2·51	0·000888	0·023

In the last case, the two numbers agree exactly; in the previous ones, the chlorine estimated as argentic chloride is about double that obtained from the alkalinity. This is no doubt partly due to insufficient washing of the very small quantity of the chloride, and partly due to the difficulty of obtaining the two solutions of the same tint during the titration.

When the residue is dissolved in water, small bubbles of gas are always seen to rise in the liquid; these may consist of gas that has been retained in the porous mass, or they might be formed by the decomposition of potassic peroxide by the manganic peroxide. Some of the residue, mixed with water, was immediately placed in a cylinder containing dilute sulphuric acid, potassic dichromate, and ether, but the production of perchromic acid did not take place, which would indicate that potassic peroxide is probably not formed.

I have made only one experiment to test for ozone in the gas evolved. A mixture of potassic chlorate with about 10 per cent. of manganic peroxide was placed in a tube, connected to the U-tube filled with beads which were saturated with a strong solution of sodic hydrate. The second U-tube contained a solution of potassic iodide. On heating the mixture by mercury vapour, gas was rapidly evolved, but there was no coloration of the potassic iodide on the addition of hydrochloric acid, so it would seem that, under these circumstances, ozone was not formed. The sodic hydrate was made from sodium, and was, therefore, not likely to contain any peroxide which might have decomposed the ozone.