THE

QUARTERLY JOURNAL

OF

THE CHEMICAL SOCIETY.

XVII.—*On a new method of preparing Hypochloric Acid or Peroxide of Chlorine.*

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We were recently led to study the action of chlorate of potash on oxalic acid, and found that when these two bodies were heated together, a yellow gas was produced, the composition of which we have studied. We think that it will be interesting to the Chemical Society to know that this substance, which has hitherto been so dangerous to prepare, on account of the violent action which sulphuric acid produces on chlorate of potash, can now be obtained without the slightest risk, by using the process and taking the precautions which we shall describe. Even when a large quantity of chlorate of potash is used relatively to the quantity of oxalic acid, no violent action ensues, unless a very strong heat is applied, when a deflagration takes place and the flask is generally broken; whilst, by employing excess of oxalic acid, regulating the temperature as described, and stopping the operation when ClO_4 ceases to be disengaged, no accident can happen, and this gas may be exhibited at a lecture, or prepared for any other purpose with as much facility as any other compound of chlorine and oxygen.

The gas was prepared by heating in an oil or water-bath to about 70°C. (158° F.), pure and well pulverized chlorate of potash and crystallized oxalic acid, when the gas is steadily given off accompanied by carbonic acid; when action ceases, raising the temperature above 70°C. does not cause a further evolution of hypochloric acid, as above this temperature the gas is decomposed and a mixture of chlorine and oxygen given off. We found that the addition of water to the materials diminished the amount of hypochloric acid produced.

It would appear at first probable that the reaction should consist in one equivalent of chlorate of potash oxidizing one equivalent of oxalic acid, and producing hypochloric acid, carbonic acid, and carbonate of potash; but we have not been able to effect this, as with these proportions, large quantities of both chlorate of potash and oxalic acid escape decomposition. We therefore increased the quantity of oxalic acid to 2, 3, 4 and 5 equivalents, but still could not entirely drive off all the chlorine of the chlorate of potash combined as ClO_4, though the quantity produced increased in the ratio of the additional number of equivalents of oxalic acid. This result is not due to want of intimate mixture, as towards the end of the operation the mixture becomes semi-fused, and also on repeating the experiment with the same quantities of materials, a constant quantity of ClO_4 was always obtained. As with six equivalents of oxalic acid, $\frac{2}{3}$ of the chlorine contained in the chlorate of potash employed was given off as ClO_4, we tried an experiment, using 9 equivalents, and found that $\frac{5}{6}$ of the chlorine of the chlorate of potash was given off as ClO_4, the remaining $\frac{1}{6}$ being in the residue in the flask as chloride of potassium. The latter proportions are those with which we have prepared the gas for various experiments.

From these results it appears probable that the formation of the ClO_4 is due to the liberation of the chloric acid, by formation of an acid oxalate of potash, the free chloric acid being afterwards decomposed by the excess of oxalic acid.

After several experiments, we found that the following process for analysing the gas gave the best results. A saturated aqueous solution of the gas being prepared, a stream of sulphurous acid was passed into the liquor until it was decolorised.

The liquid now containing sulphuric and hydrochloric acids was divided into four equal portions, and in two of these the sulphuric acid was determined as sulphate of baryta by boiling to expel excess of sulphurous acid and precipitating with chloride of barium. In the other two portions, the hydrochloric acid was determined as chloride of silver. From the weights thus obtained it was easy to calculate the formula of the gas; for, as one equivalent of chlorine would cause the oxidation of one equivalent of sulphurous acid, and as each equivalent of oxygen in the compound had a similar effect, each equivalent of chlorine should correspond to as many equivalents of sulphuric acid as there were equivalents of chlorine and oxygen together in the compound.

Thus, if the compound were ClO_4, there should be for each equivalent of chlorine 5 equivalents of sulphurous acid oxidized into sulphuric acid. The following figures will show how closely the results obtained coincide with those calculated from the formula.

	Chloride of Silver found.	Sulphate of Baryta found.	Sulphate of Baryta calculated supposing the compound to be ClO_4.
	grms.	grms.	grms.
No. 1	·192	·776	·780
No. 2	·221	·882	·865
No. 3	·235	·955	·955

In order that there may be no doubt as to the above being the composition of the gas, we give the quantity of sulphate of baryta which should be produced if its formula were ClO_3.

	Sulphate of Baryta found.	Sulphate of Baryta calculated supposing the compound to be ClO_3.
	grms.	grms.
No. 1	·776	·620
No. 2	·882	·705
No. 3	·955	·764

From the simplicity and accuracy of the above process, we think that it may be applied to the analysis of other compounds of chlorine and oxygen.

We have endeavoured to decide the question as to whether this substance possessed acid properties or not, but could not do so, as by this method of preparation, the hypochloric acid is accompanied by a large quantity of carbonic acid, which interferes with any attempt to combine it with bases.

The powerful oxidizing action of this gas, containing as it does both chlorine and oxygen, will probably render it a valuable agent in organic chemistry, now that it can be easily prepared.

We have also been examining the compound of chlorine which is formed in making oxygen from chlorate of potash and peroxide of manganese, and find that it is probably chlorous acid, ClO_3. We cannot, however, speak positively on this point, owing to the very small quantity which is produced. By using perfectly pure materials the oxygen is free from this compound, the quantity of which increases with the impurities of the chlorate of potash and peroxide of manganese, especially the latter. It is also more abundant when the oxygen is produced rapidly. The white fumes often perceived in oxygen rapidly prepared are composed of volatilized chloride of potassium.