CXLIII. *On the Action of Bleaching Powder on the Salts of Copper and Lead.* By WALTER CRUM, Esq., F.R.S.

IN February 1843 I read to the Philosophical Society of Glasgow an account of a rose-coloured oxide of copper which I had obtained by the action of bleaching powder and lime upon nitrate of copper. Although I had then made numerous analyses of this substance, prepared under a variety of circumstances, I had been unable to obtain from it the full amount of oxygen which a definite compound must contain, and delayed therefore to make it further known until I should have the opportunity of producing it in a purer form. In the mean time the rose-coloured substance was observed, and correctly described, by Krüger of Berlin, as a combination of the oxide of copper, or, as he calls it, cupric acid, with lime. Having completed my experiments on this subject as far as my leisure will permit, I shall now state the results I have obtained.

When the hydrated oxide of copper is added to a solution of bleaching powder it changes colour and becomes brown. Oxygen gas is then plentifully disengaged, and the effervescence continues till the whole of the hypochlorite of lime is decomposed. The brown precipitate suffers no change during this decomposition. When separated from the soluble matters, it is found to contain no chlorine and no excess of oxygen. It is anhydrous oxide of copper. Hypochlorite of soda produces the same effect.

If we add nitrate of copper to a solution of bleaching powder containing a considerable quantity of lime, and previously cooled to below the freezing-point of water, a bluish-green precipitate is formed. When the precipitate subsides, we find the solution of a fine blue colour and containing copper; but in what state I have not examined. As the heat advances to the ordinary temperature, the copper in solution, as well as

the precipitate, changes colour, and both at last become an insoluble purplish black powder. Oxygen gas is disengaged during the latter part of this process, and continues for some time to prevent the precipitate from subsiding; but after twenty or twenty-four hours the evolution of gas nearly ceases, the particles having united into larger grains sink to to the bottom of the vessel into moderate bulk, and may then readily be separated from the soluble matters, by repeated mixing with cold lime-water and drawing off the clear liquid with a syphon. The precipitate thus obtained is, as I have said, nearly black; but by triturating upon a piece of glass it is seen that its real colour is rose-red.

Exposed to the action of boiling water oxygen gas is disengaged from this substance, and brown anhydrous oxide of copper is left behind. Acids dissolve it, with the liberation of oxygen gas, mixed with the carbonic acid taken down by the lime. The solution in nitric acid gives no precipitate with nitrate of silver. Exposed to the air the substance is speedily changed into the green carbonate. In attempting to press and then to dry it *in vacuo* over sulphuric acid, a large proportion was changed into the brown oxide mixed with carbonate. It can only therefore be examined in the moist state and newly prepared. I shall describe the process by which I have obtained the best results.

Twenty grains of black oxide of copper, prepared by calcining the nitrate, are dissolved with the assistance of heat in 70 grs. of nitric acid, specific gravity 1.35. Fifty grains of fresh hydrate of lime, sifted through fine calico, are mixed with 1 lb. solution of bleaching powder of specific gravity 1.06, and added to the solution of copper. When the precipitate becomes granular, as already described, it is quickly washed, and decanted until the lime water comes off nearly pure. The precipitate is then put into a wide tube over mercury, an excess of sulphuric acid added to it; and, after pouring out as much as possible of the solution which is thus formed, caustic soda is added to absorb the carbonic acid. In six experiments made in this way, 20 grs. of oxide of copper produced a compound which yielded of oxygen gas, after the necessary corrections,—

1.875

1.886

1.748

1.915

1.795

1.747

Mean . . 1.828 grain.

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By calculation 20 grains CuO changed into Cu_2O_3 ought to yield, by Berzelius's numbers, 1.98 grain of oxygen. A nearer approximation than in the foregoing results is scarcely to be expected; for although there was no perceptible disengagement of gas during the washing of the precipitate in these experiments, it is certain that oxygen always escapes during the time so employed.

The quantity of lime necessary to the production and stability of this oxide is not more than 1 equivalent after saturation of the nitric acid: 1 atom of lime to 3 of copper gave only 0.558 gr. of oxygen gas instead of the mean quantity of 1.828; 2 atoms to 3 of copper yielded 1.295. I conceive the rose-coloured powder then to be a compound of an oxide of copper with lime, in which the copper exists in the state of sesquioxide, Cu_2O_3 .

I have not succeeded in producing this oxide by means of the hypochlorites of potash or soda, even with the alkali in great excess; but by adding caustic soda to a solution of hypochlorite of lime, and afterwards nitrate of copper, we obtain the calcareous compound (lime being precipitated along with the copper) in a state of division so fine as to show the rose colour as soon as it is formed. This method, however, does not serve for the purposes of analysis, for the powder never becomes granular, and remains therefore too bulky to be washed.

It will now be observed that the dehydrating action of the hypochlorites upon oxide of copper must depend upon the momentary formation of a sesquioxide in which the oxygen has replaced the previously combined water.

The solution of bleaching powder in which the sesquioxide has been formed is of a fine but very pale pink colour, and contains so small a proportion of the colouring ingredient, that the nature of that body can scarcely be discovered by analytical means. The second washing of the oxide is colourless; but if a very minute portion of sulphate of manganese be added, the pink colour is restored. When manganate of potash is dropped into nitric acid, the well-known red colour of permanganic acid is produced. In lime water the colour is bluish green; but in bleaching liquor, even with excess of lime, we have the peculiar amethystine colour of the solution in which the sesquioxide of copper has been produced. Bleaching powder has long been said to contain manganese, and to this I at first attributed the pink colour of the original solution; but I afterwards found that it could be reproduced from pure Irish limestone which I employed. Even marble gives a pink solution in the same circumstances.

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The vessel in which the sesquioxide has been produced, is lined with a beautiful rose-coloured deposit, which remains attached to the glass when the other matters are washed out; but it fades away in a few hours, particularly when exposed to light, and cannot even be long preserved in the solution which forms it. Dissolved in dilute nitric acid, copper is found in the solution and no manganese. There can be no doubt that, like the precipitate, it is the sesquioxide of copper in combination with lime.

The red oxide of iron has also the power of decomposing the hypochlorites. This fact, as well as the formation of a superoxide of copper, was observed many years ago by Mr. Mercer of Oakenshaw, and stated by him to the British Association in 1842, in a paper containing some interesting speculations on these and other weak affinities which give rise to many of the phenomena of catalysis.

When a solution of bleaching powder is mixed with nitrate of copper, a light bluish-green powder precipitates, the bulkiness of which renders it somewhat difficult to wash. This powder is very slightly soluble in water, and scarcely changes colour in boiling. Heated in a glass tube over a spirit-lamp, chloride of copper sublimes into a cooler part of the tube, and water escapes. The residue consists of black oxide of copper mixed with a quantity of chloride, which may be separated from the oxide by washing. Professor Graham, who suggested to me this experiment, remarked the analogous effect of boiling water in separating water from a hydrate. It proved to be a hydrated oxichloride of copper, the substance known by the name of Brunswick green, and formed in a variety of other circumstances. Analysis gave me nearer 3CuO , CuCl than 4CuO , CuCl ; but the presence of carbonate in the specimen left me in doubt upon this point, and I could not resume the inquiry. In this reaction the whole of the hypochlorous acid is set free.

Peroxide of lead is often produced by passing a stream of chlorine through a solution of sugar of lead. The chloride which accompanies it in this way may be also converted into peroxide by employing a solution of bleaching powder instead of chlorine. The peroxide produced by these means has a light brown colour, although washed with dilute nitric acid and boiling water. I have succeeded, by the following process, in forming a compound, nearly colourless, of *peroxide of lead and lime*. Dissolve in water 1 lb. of nitrate of lead,

and add it, along with 3 equivs. of lime, to 16 pounds of a solution of bleaching powder of sp. gr. 1.08. Heat the mixture gradually to 160° Fahr. and stir it frequently during five hours. Pour off the clear liquid, add 16 pounds more of the same solution, and continue the heat three hours longer. The combination is obtained white with only a slight brown tinge. It is quite insoluble in water, and when dried does not alter in the air. Nitric acid, by dissolving the lime, leaves the peroxide of a deep black colour, and therefore much deeper than that obtained by any of the processes usually employed.

I have had no means of determining the proportion of lime contained in this plumbate. With less than two equivalents to one of oxide the compound is not white; and an excess of lime cannot afterwards be dissolved away by an acid without discolouring the salt.

I found it convenient in these experiments to prepare a quantity of cream of lime, by dropping newly-burnt lime into boiling water, stirring up, allowing the sand and the grosser parts to subside, and pouring off the superstratum. When this again had subsided for some time, the water was poured away, and the cream of lime which remained corked up in small bottles for use. By this means I had always at hand a quick lime, whose equivalent I knew, free from sand and free from carbonate. Marble, of course, answers the best for this purpose.

Manganese, again, appears in the nitric acid which has been employed to decompose the plumbate, in the state of a pink-coloured permanganic acid. When this solution is poured off and more water and nitric acid added to the peroxide that is left, a small quantity of sulphate of manganese restores the colour. Peroxide of lead, prepared by the same or by other means, when dried, does not yield the pink colour without the application of heat.