XXVIII.—*The Peroxidic Compounds of Copper.*

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PEROXIDIC compounds of copper of two distinct types have been described by several investigators, a series of yellowish-brown to olive-green precipitates of neutral character obtained by the action of hydrogen peroxide on cupric hydroxide, and a number of so-called cuprates of the alkalis and alkaline earths obtained by the oxidation of alkaline suspensions of cupric hydroxide by means of chlorine and presumably containing a higher oxide of copper with acidic properties. Preparations of the former class probably all consist of mixtures in varying proportions of cupric oxide and hydroxide with a yellow, gelatinous peroxide of formula CuO_2 , as has been shown by the work of Osborne (*Amer. J. Sci.*, 1886, [iii], 32, 334), Moser (*Z. anorg. Chem.*, 1907, 54, 121), and E. Müller (*ibid.*, 1907, 54, 418). The analytical results of these investigators,

whilst approximating in many instances to the formula ascribed to the peroxide, always showed a deficiency of peroxidic oxygen. This deficiency might be due either to the instability of the compound or to the inclusion of unaltered cupric hydroxide. In view of the latter possibility, it was considered desirable to attempt the preparation by other methods, using as the starting material, not a solid compound of copper like the hydroxide, but a solution. Neither solutions of simple copper salts nor strongly alkaline solutions such as Fehling's solution, ammoniacal solutions, or the colloidal suspension of copper hydroxide in sodium hydroxide described by Justin-Mueller (*Compt. rend.*, 1918, **167**, 779) could be used, since no precipitate is produced by hydrogen peroxide in solutions of simple salts, whilst the presence of large concentrations of hydroxyl ion leads to the rapid decomposition of the compound. It seemed probable that the solutions of the double carbonate of sodium and copper, recently investigated by one of us (Applebey and Lane, T., 1918, **113**, 609), might prove suitable, since their alkalinity was very slight indeed. The investigation of this reaction was the primary object of the present experiments. In the course of the work, however, the effect of other oxidising agents on various copper solutions was tried, with the result that some further information has come to light with respect to reactions which had previously been studied by other workers. The experiments to be described fall into three sections :

- (1) The action of hydrogen peroxide on carbonate solutions ;
- (2) The action of chlorine and of hypochlorite on Fehling's solution ;
- (3) The cuprates.

(1) *The Action of Hydrogen Peroxide on Carbonate Solutions.*

The solutions of sodium copper carbonate used in the preparations were made by adding to a solution saturated with sodium carbonate and bicarbonate at the room temperature varying quantities of dilute copper acetate solution with constant stirring. Such solutions are comparatively stable, but deposit the crystalline double carbonate on standing over-night if they contain more than 0.15 gram of copper per litre. It was found that any such solution, when treated in the cold with hydrogen peroxide, gave immediately a precipitate of the peroxide of a yellowish-brown colour, the greater part of the copper being removed from solution in this form. The precipitate is, however, not only unstable, but also very gelatinous, so that the preparation of a specimen for analysis presents great difficulties. All ordinary methods of filtration failed

to give a sufficiently rapid separation from the mother-liquor; the best results were obtained after many failures by the use of a filter-bed of powdered and graded glass contained in a Gooch crucible to which a light suction was applied. Such a device only retains the larger particles of the suspended gelatinous solid, but has the advantage of working very quickly. The precipitate collected in this filter was thoroughly washed with ice-cold water and analysed by dissolving it on the filter in a known amount of standard ferrous sulphate solution acidified with sulphuric acid. Estimation of the ferrous ion remaining and of the copper in the solution gave the required ratio of copper to peroxidic oxygen. The results obtained were very variable and gave clear evidence of the occurrence of rapid decomposition of the peroxide during the necessary manipulations. The most highly oxidised products were obtained by the use of excess of hydrogen peroxide at a low temperature. They contained more oxygen than corresponds with the formula Cu_2O_3 , but never reached an oxygen content corresponding with CuO_2 . Variation in the concentration of copper in the original solution had little influence on the composition of the precipitate except that there was always noticeable an increase in peroxidic oxygen as the quantity of precipitate to be dealt with diminished. This is simply a consequence of the greater rapidity with which smaller quantities can be handled. These observations, together with the colour of the products, indicate that the pure peroxide is produced by the reaction studied, but suggest that even the small concentration of free alkali present in the solutions reduces the stability to a degree which, combined with the intractable character of the precipitate, renders its separation in the pure state practically impossible.

(2) *The Action of Chlorine and of Hypochlorite on Fehling's Solution.*

When chlorine is passed through or hypochlorite solution added to Fehling's solution, a curious reaction occurs leading to the reduction of the solution with the precipitation of yellow to orange-red cuprous oxide. This reaction, which was first observed by Millon (*Compt. rend.*, 1862, **55**, 513), was attributed by him to the oxidation of the tartrate by the chlorine, with the formation of a reducing agent. The explanation is probably correct, although little can be said about the exact identification of the reducing agent.

Many experiments have been devised by the authors with the view of separating and identifying the unknown intermediate product. The passage of chlorine through strong solutions of Rochelle salt leads to oxidation with evolution of carbon dioxide,

but no products other than sodium carbonate could be separated from the solutions,* although slight reducing properties (to Fehling's solution) could be detected in partly oxidised solutions. It is therefore clear that the intermediate product, as would be expected from its reducing properties, is very rapidly destroyed by chlorine and does not accumulate in the solution. The only clue to its nature is the formation of a faint violet coloration on addition of ferric chloride to such solutions, similar in appearance to the coloration produced by the same reagent in presence of dihydroxymaleic acid, which Fenton has shown to be a product of the oxidation of tartaric acid by hydrogen peroxide. The reaction with sodium hypochlorite is similar but more vigorous, a great evolution of heat and violent liberation of carbon dioxide taking place when strong hypochlorite is employed.

The authors are unable to confirm the statement made by Millon (*loc. cit.*) that the precipitate formed in the early stages of the reaction of hypochlorites with Fehling's solution differs in any essential particular from that produced in the later stages. Millon states that the product first obtained with calcium hypochlorite is pale yellow and shows the reactions of "a double salt of calcium carbonate and cuprous formate." Exactly what analytical reactions were used by Millon is not stated, but the authors have convinced themselves by repeated tests that no trace of carbon dioxide is evolved from the properly washed precipitate with dilute acids, and concentrated sulphuric acid gives no carbon monoxide. There is no doubt that the precipitate is simply the finely divided form of cuprous oxide which frequently occurs in the early stages of reduction of Fehling's solution and that Millon's statement arose from inclusion in the precipitate of mother-liquor containing tartrate and carbonate. It may perhaps be added that the precipitate bears no resemblance in appearance or reactions to the colourless cuprous formate described by Angel (T., 1906, 89, 345).

In the course of the experiments on the action of hypochlorite on Fehling's solution a somewhat remarkable time-reaction has been observed, the further examination of which may possibly throw some light on the course of the reactions involved. When a small quantity of strong hypochlorite is added to Fehling's solution, the precipitate of cuprous oxide does not appear immediately but only after the lapse of about half a minute. If a further small quantity of hypochlorite be now added, the first effect is to produce complete and rapid re-solution of the precipitate present; only after another period of waiting the precipitate reappears. This may be repeated

* Potassium hydrogen tartrate crystallises out during the chlorination owing to the hydrochloric acid formed in the oxidation.

many times, the precipitate dissolving after each addition of hypochlorite and coming down again after a short time. The reaction produces heat, and the times necessary for precipitation after each addition gradually diminish owing to the rise in temperature, unless precautions are taken. Presumably the changes described are to be explained as follows. The first effect of each addition of hypochlorite is to oxidise the cuprous oxide to cupric oxide, which dissolves in the excess of tartrate present in the Fehling's solution. The remainder of the hypochlorite then reacts with tartrate, forming the unknown reducing agent and therefore causing a further precipitation of cuprous oxide. The comparative slowness of the latter change enables the two stages of the reaction to be observed.

(3) *The Cuprates.*

Krüger (*Pogg. Ann.*, 1844, **62**, 445) first observed the formation by the chlorination of alkaline suspensions of cupric hydroxide of pink solutions which he supposed to contain salts of an acidic peroxide of copper. Other investigators have failed to repeat the preparation, so that Krüger's cuprates have been regarded with some suspicion. In the course of the present work we have occasionally obtained similar pink solutions by the chlorination of solutions of sodium copper carbonate, and the examination of the conditions of reaction has led us to the view that Krüger's cuprates are simply dilute solutions of permanganate produced by traces of manganese present as impurity in the solutions. The grounds for this view are as follows:

(a) When materials free from manganese and chlorine from a cylinder are used, the pink colour never appears.

(b) When chlorine prepared from manganese dioxide is used, the colour is obtained, but not if an efficient wash-bottle is used.

(c) The addition of a small trace of manganese salt to the solution to be chlorinated ensures the formation of the colour.

(d) The absorption spectrum of the pink solutions is identical in every respect with that of a permanganate solution of similar tint.

(e) The pink colour is obtained equally well or even better if the solution contains no copper at all, provided that the necessary trace of manganese is present.

All the above statements have been verified in respect to the solutions obtained from alkaline suspensions of cupric hydroxide as well as in respect to the chlorination products of the double carbonate solutions, and leave no doubt that the so-called cuprates of the alkalis have no real existence.

The cuprates of the alkaline earths, which have been described

by Krüger (*loc. cit.*), Crum (*Annalen*, 1845, **55**, 213), and Osborne (*loc. cit.*), are insoluble substances produced by the addition of dilute solutions of copper salts to a suspension of bleaching powder. The precise formulæ and compositions of these reddish-purple precipitates have never been satisfactorily settled, since all preparations undoubtedly contain unchanged bleaching powder, but it is interesting to note that they are obtained even when bleaching powder prepared from pure calcium oxide and cylinder chlorine is used. They are therefore real substances and are not, like the alkali compounds of Krüger, due to impurities.

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