A NOTE ON THE REDUCTION OF ALKALINE COPPER SOLUTIONS BY SUGARS

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Anyone who has used Fehling's solution for the detection of dextrose in the urine is familiar with the different coloured precipitates obtained under various conditions, as products of the reduction of this reagent. Thus the precipitate obtained may be red, yellow or even green. The commonly accepted explanation of the different appearance of these precipitates has been that the red compound consists of cuprous oxide, Cu_2O , while the other precipitates represent hydrated forms of this compound. In a recent paper Maclean,¹ on the contrary, maintains that in each case the precipitate obtained is the cuprous oxide, the colour of the precipitate being dependent merely upon the state of division in which this substance exists. The red precipitate is the least finely divided, the yellow one consists of smaller particles, while the green one is in a *still finer state* of division. The evidence on which Maclean bases his explanation is briefly as follows:— (1) Microscopic examination of the different precipitates shows coarsely granular particles in the case of the red substance, while the other precipitates consist of smaller particles. (2) The green and yellow precipitates settle with much greater difficulty than does the red one. (3) If the red suboxide be dried and finely ground in a mortar it becomes somewhat yellowish in appearance.

Interesting as are these observations, the fact that the yellow and green precipitates are made up of smaller particles than the red

1. Maclean, *This Journal*, Vol. II, p. 156, 1907.

one, is not convincing evidence that the same compound is involved in each case. Cupric oxide separates from a suspension in water in large masses much more rapidly than does the hydroxide; yet this is no evidence that they are the same chemical substances.

In Maclean's work comparisons are made of the colour of the precipitate obtained in the case of urine containing 0.4 per cent. dextrose and that yielded by pure sugar solutions of equal concentration. The solution of the sugar in urine gave yellow or green precipitates while the pure solution in every case yielded a red product as a result of the reduction. Maclean points out that the substance determining this difference in the character of the precipitate is creatinin, and holds that this causes the precipitation of the suboxide in a finer state of division than occurs when creatinin is absent.

If one is unwilling to admit the validity of Maclean's explanation, the question of the relative dehydrating action of the various solutions used is at once raised. Since the action of creatinin in modifying the colour of the precipitates is quite obscure, it may be well to ask to what extent variations in the dehydrating power of the solutions used may effect the character of the reduction product obtained in pure sugar solutions. Some light may be thrown upon this question by using pure solutions of known different dehydrating powers, and then noting the colour of the precipitates obtained under these conditions. If Maclean's explanation is correct, there should be little if any difference found here; or if a difference be found, we should hardly expect, in view of his explanation, that the results would be exactly parallel with those produced by the urine.

In a recent paper, the use of copper solution in which the alkalinity is secured by means of carbonate instead of hydroxide was suggested for the detection of sugars.¹ In that same paper it was further pointed out that the yellow or green precipitates are obtained

1. Benedict, *Journ. of Biolog. Chem.*, Vol. III, p. 101, 1907. The carbonate reagent mentioned is made up from two solutions prepared according to the following formulae:

Solution A: Crystallized copper sulphate, 69.3 grams.; distilled water to 1,000 c.c.

Solution B: Pure Rochelle salt, 346 grams.; anhydrous sodium carbonate, 200 grams.; distilled water to 1,000 c.c.

For use these solutions are freshly mixed in equal proportions and the resultant mixture diluted with an equal volume of distilled water.

with the carbonate reagent much more *frequently than with* Fehling's solution, and the explanation was suggested that this is due to the much stronger dehydrating action of the hydroxide solution than that of the carbonate. The following further experiments throw light upon the problem. When one half volume of one per cent. pure dextrose solution is added to the carbonate reagent and the mixture warmed to boiling a distinctly green precipitate is first obtained, which, upon further heating, becomes bright yellow. This precipitate will then slowly become reddish in tinge, and may become distinctly red. By substituting Fehling's solution for the carbonate reagent a bright red precipitate is obtained almost at once. In these instances the less strongly dehydrating reagent shows changes in colour of the precipitate as might be explained by assuming that the first products are the hydrated oxides which then gradually lose water. A much stronger dehydrating agent would not permit these changes to be seen so distinctly if at all, hence the much more rapid formation of the red suboxide with Fehling's reagent. The concentration of sugar is the same in both cases, and no disturbing factor such as creatinin is present. The following experiment is also of interest in this connection. If to a few cubic centimetres of the carbonate reagent is added one half to one volume of 0.1 per cent. dextrose solution and the mixture heated to boiling, the *precipitate formed* will remain distinctly greenish-yellow for some minutes. Just after the solution has reached vigorous boiling it is divided into two equal portions. To one of these is added an equal volume of distilled water and to the other an equal volume of ten per cent. potassium hydroxide solution. Both are now heated to vigorous boiling. The one containing the excess of hydroxide rapidly becomes bright red in colour, while the other remains yellow for some minutes. The potassium hydroxide serves in this case to convert the yellow precipitate into the red substance. When it is remembered that potassium hydroxide solution of this strength is a strong dehydrating agent the probable explanation appears to be that the red compound represents a dehydrated form of the yellow one. It might be assumed that the alkali acts here simply as an electrolyte to cause the smaller

particles, possibly in a semi-colloidal state, to unite to form larger masses. But if saturated sodium chloride be used in place of the hydroxide, the change in colour of the precipitate from yellowish-green to red does not occur.¹ It appears more likely that the excess of hydroxide exerts a dehydrating action than to assume that by purely physical action the solid particles already out of solution are brought together into larger masses.

There is no apparent reason for assuming a different explanation for the colour phenomena in the urine reaction and *those obtained with* pure sugar solutions. In view of the comparable reactions obtained with the latter solutions it seems premature to give up entirely current conceptions regarding the nature of the coloured precipitates formed by the reduction of alkaline copper solution by means of sugars.

1. For suggesting the possible objection that the hydroxide might act here simply as an electrolyte and the use of sodium chloride solution as a control test, I am indebted to Professor L. B. Mendel.