The Mechanism of the Kolbe Reaction

IT has been observed by us that a variety of substances which are good catalysts for the decomposition of hydrogen peroxide produce a marked deviation of the anodic processes occurring during the electrolytic oxidation of thiosulphate[1] and of sulphite[2], and in the liberation of halogens[3]. We have now found that in the electrolysis of acetate solutions, relatively small amounts of plumbous, manganous, cupric, ferrous or cobaltous ions have a profound influence on the course of the Kolbe reaction. For example, the addition of 0·001 *M*-lead acetate to a solution containing *N*-potassium acetate and *N*-acetic acid reduces the efficiency for ethane formation at a platinum anode from about 70 per cent almost to zero, when using a current density of 0·025 amp. per sq. cm.

The effects of the ions mentioned are in the order $Pb^{\cdot\cdot} > Mn^{\cdot\cdot} > Cu^{\cdot\cdot} > Co^{\cdot\cdot} = Fe^{\cdot\cdot}$, and an independent consideration of their catalytic influence on the decomposition of hydrogen peroxide, under the conditions prevailing at the anode during the electrolysis of an acetate solution containing acetic acid, has led us to arrange these ions into the groups $(Pb^{\cdot\cdot}, Mn^{\cdot\cdot}) > (Cu^{\cdot\cdot}, Co^{\cdot\cdot}, Fe^{\cdot\cdot})$. This parallelism suggests the possibility that hydrogen peroxide is the effective agent in the formation of ethane by the Kolbe reaction, just as it appears to be in the other anodic oxidation processes we have studied.

A comprehensive investigation of the mechanism of the Kolbe synthesis was commenced some time ago, but as a period is likely to elapse before the final conclusions are ready for publication, we consider it desirable to make a preliminary announcement of the important observations relating to the effect of catalysts for hydrogen peroxide decomposition.

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Jan. 5.

[1] *J. Chem. Soc.*, 2345, 2800; 1932.
[2] *ibid.*, 829; 1933.
[3] *ibid.*, in the press.

Possible Chemical Nature of Tobacco Mosaic Virus

IN a recent issue of NATURE[1] Barton-Wright and McBain give results of experiments on the precipitation of virus from infected tobacco juice. The method they used was that of Vinson and Petre, which consists essentially of the precipitation of the protein and other materials from the plant juice with basic lead acetate and the subsequent removal of the virus by elution with potassium-hydrogen phosphate solution. Barton-Wright found that if the mixed phosphate eluate be acidified to a *p*H of 5 (which means, in effect, the conversion of the alkaline to the acid phosphate, KH_2PO_4) and 2 volumes of acetone added, a precipitate is thrown down, which is partly colloidal and partly crystalline. The colloidal material is largely protein in nature and is rich in virus. The crystals also contain virus.

I have been working on similar lines for the past two years, and I am in agreement with Barton-Wright and McBain up to this point. Barton-Wright and McBain, however, claim that they have been able to purify the crystals by repeated recrystallisation until they contain no nitrogenous material but still contain virus, and that no crystalline material was formed from healthy juice similarly treated. My experience may be of interest in this connexion. I have determined the presence of virus in the crystals quantitatively as well as qualitatively, using the N. glutinosa method. In the original crystals there is a small virus content and some protein. As the crystals are washed and reprecipitated, virus appears in the supernatant liquid, and at each recrystallisation the amount of virus in the crystals is reduced. After repeated treatment the crystals still contain a little virus, much less than originally, and they still contain a trace of organic nitrogen on microanalysis. Nitrogen-free virus-containing crystals have not been obtained. I have found no evidence that the crystals contain virus except as an impurity.

That the crystals have no specific relation to the virus is easily demonstrable. If the K_2HPO_4 eluate from healthy tobacco tissue be acidified as was that of the infected material and two volumes of acetone added, a crystalline as well as a colloidal precipitate is obtained, despite the statement of Barton-Wright and McBain. The amount of this crystalline portion of the precipitate depends on the concentration of the phosphate solution used in the elution of either the healthy or the infected juice. If an *M*/1 K_2HPO_4 solution be used, the precipitate of crystals is very large.

It can readily be shown that the crystals are due to the presence of KH_2PO_4 by the fact that the addition of two volumes of acetone to one of *M*/1 KH_2PO_4 in aqueous solution results in a heavy white precipitate of rhombic crystals, indistinguishable in outline from those obtained in the experiments recorded above.

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Jan. 23.

[1] NATURE, 132, 1003, Dec. 30, 1933.

Activity of Crystalline Preparations of Vitamin B_1

IN an important letter, Dr. van Veen[1] describes the isolation of a vitamin B_1 preparation from rice polishings more potent by rice bird tests than our own. At the same time he mentions that his activity reaches 500,000 units per gm. It is well to realise that some of our most potent specimens have shown this activity by pigeon test[2], so that a final judgment upon the question must await further work.

In addition to the strong probability that most vitamin B_1 crystals contain inactive vitamin, we must reckon with the further complication of different analytical figures. Dr. van Veen's new crystals have the same analytical figures as previously, whereas repeated work shows that analysis of our crystals differs significantly and constantly from his (and others) in several respects, for example, C 42·2 per cent instead of 40·7 per cent. Hence active torulin (from baker's yeast) appears to be different from active oryzanin. At present these differences cannot be reconciled with the published results of X-ray analysis[3].

We acknowledge with gratitude a specimen of Dr. van Veen's B_1, which is now under test.

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Jan. 27.

[1] NATURE, 133, 137, Jan. 27, 1934.
[2] *Biochem. J.*, 27, 232; 1933.
[3] NATURE, 131, 911, June 24, 1933.