

XXVII.—*On Limited Oxidation with Alkaline Permanganate.*

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## Preliminary Notice.

THE action of permanganic acid on organic bodies differs altogether according as it takes place in acid or in alkaline solutions.

If alcohol be treated with permanganate of potash and sulphuric acid, we obtain aldehyde and acetic acid, exactly as in the case of chromic acid. If however, we employ solution of crystallized permanganate, we obtain small quantities of aldehyde and acetic acid, together with various other bodies, and oxalic acid. If the permanganate be rendered strongly alkaline with potash, no aldehyde and no acetic acid whatever are produced, though the permanganate is almost immediately discoloured and binoxide of manganese is precipitated. If the solutions have been used hot, oxalic acid is the principal product; if cold, various other acids, probably identical with those obtained by Debus in his oxidation of alcohol by nitric acid, are produced. To obtain the oxalic acid, the alkaline solution is filtered, the filtrate rendered acid with acetic acid, and chloride of calcium added. Oxalate of lime was precipitated, and from it, all the reactions of oxalic acid may be obtained. It was analysed and proved to be pure.

In the case of lactic acid, similar results are obtained. With permanganate of potash, aldehyde, acetic acid, carbonic acid, and oxalic acid are all produced. With permanganate of potash and sulphuric acid, we obtain aldehyde, acetic acid, and carbonic

acid, exactly as when chromic acid is employed, and if we take permanganate and caustic potash, oxalic acid is produced, but no aldehyde and no acetic acid.

Oxalic acid itself appears to be totally unaffected by boiling with permanganate of potash and potash. I think the above facts will go far to explain the anomalous results obtained by M. Truchot in his oxidation of amylene. M. Berthelot has since oxidized amylene in a similar manner. He appears to have obtained acids of the acetic series and also bibasic acids. Had he employed alkaline solution of permanganate, he would have obtained no acetic acid whatsoever. Manganate is incapable of producing acetic acids. Manganic acid, however, in the free state is quite capable of producing these acids, and in fact produces no others.

If we consider what must take place when permanganate is reduced, we arrive at an explanation of these anomalies. If two solutions of permanganate, to one of which excess of caustic potash has been added, be reduced by the gradual addition of alcohol, totally different effects are observed. The alkaline solution rapidly becomes green, and for a considerable time no binoxide of manganese is deposited. The neutral solution, on the contrary, does not suffer this change of colour at all, but begins to deposit the binoxide at once. The neutral permanganate becomes green towards the end of the process only, and not even then, unless the reduction has been very slowly effected in a cold solution. The fact is, the neutral permanganate is, by the abstraction of 1 eq. of oxygen, in the presence of water, converted into 1 eq. of manganate of potash and the elements of 1 eq. of hydrated manganic acid. We say the elements, because hydrated manganic acid at once splits up into binoxide of manganese and oxygen. From this it appears that two-thirds of the available oxygen of the permanganate may be removed without in any way affecting the neutrality of the solution. But, as in this reduction acids are formed, an even larger quantity of oxygen may be removed from the permanganate before the solution has become really alkaline, and therefore before the decomposition has become perfectly regular. We have in fact, in this case, a most complicated series of actions; first, action in a neutral solution; secondly, action in a solution which may possibly have become acid from the products formed; and thirdly, action in an alkaline solution. All

these actions differ, and the result is, a complicated series of products.

Even in the case of the alkaline solution, we are not operating under one set of conditions; for some substances, citric acid for instance, will reduce permanganate under these circumstances to manganate, but have no action on the manganate so produced. From this it would appear that the only way to obtain a regular action is to employ manganate, and not permanganate. We may then hope to obtain definite and simple products, and shall in all probability find that they bear a definite and simple relation to the compounds from which they were produced.

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