

OXIDATION OF THE AMINO ACIDS: II. ALANINE AND TYROSINE.

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In a previous communication¹ I have given an account of the oxidation of glycocoll and cystine with alkaline potassium permanganate; the work has been continued along the same lines and in the present paper are recorded the results obtained by the oxidation of two other of the more common amino-acids—alanine and tyrosine.

Oxidation of Alanine with Alkaline Potassium Permanganate.

Two grams of Kahlbaum's alanine dissolved in 50 cc. of water were oxidized with 500 cc. of a solution containing 10.8 grams of potassium permanganate and 37.0 grams of potassium hydroxide (30 molecules). Vigorous oxidation took place at once and the temperature of the mixture rose to 37° C. After standing for forty-eight hours at room temperature complete decolorization had taken place; the products of oxidation were then isolated and quantitatively determined by the methods previously described.

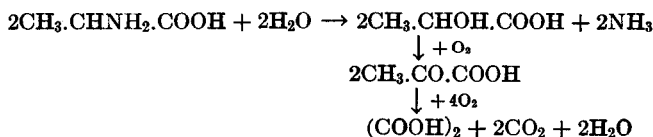
From the above mentioned 2 grams of alanine I obtained 1.45 grams of carbon dioxide, 0.37 gram of ammonia, 1.9 grams of oxalic acid melting at 101° and volatile acids equivalent to 10 cc. of decinormal sodium hydroxide.

The volatile acid fraction was found on the application of qualitative tests to consist of a mixture of acetic and nitric acids.

Regarding the intermediate products it would seem most probable that the greater part of the alanine on oxidation with alkaline

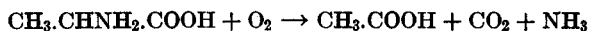
¹ This *Journal*, ix, p. 365, 1911.

permanganate would first undergo a transformation into lactic acid with subsequent oxidation to pyruvic, oxalic and carbonic acids.



However in a number of experiments in which alanine was oxidized under various conditions with an insufficient amount of alkaline permanganate solution I was unable to obtain qualitative proof of the presence of pyruvic acid.

The isolation of a minute quantity of fatty acid would seem to indicate that a small portion of the alanine is transferred directly into acetic and carbonic acids.



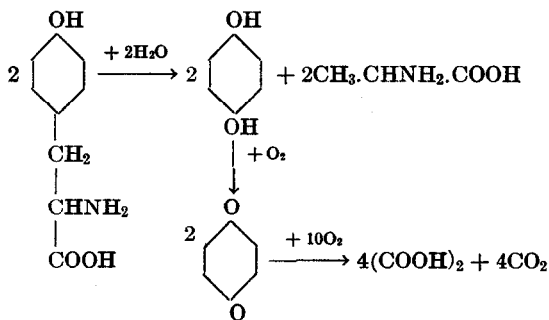
Oxidation of Tyrosine with Alkaline Potassium Permanganate.

The tyrosine used in this work was prepared from silk by hydrolysis with 20 per cent sulphuric acid. To 2 grams of tyrosine suspended in 50 cc. of water were added 600 cc. of a mixture containing 19.0 grams of potassium hydrate (30 molecules) and 17.0 grams of potassium permanganate. Vigorous oxidation began at once and the mixture was allowed to stand at room temperature for two days, as a small amount of the permanganate still remained unreduced. The solution was then heated for an hour on the boiling water bath; ammonia, carbon dioxide, oxalic acid and volatile acids were determined by the methods previously described. In this way I obtained from the above mentioned 2.0 grams of tyrosine 0.18 gram of ammonia, 2.02 grams of carbon dioxide, 2.1 grams of oxalic acid, volatile acids equivalent to 16.00 cc. of decinormal sodium hydrate. The volatile acids were found to consist of 0.03 gram of acetic acid, and some nitric acid; in the early part of the distillation a small amount of a white crystalline body was driven over, this substance which is probably *p*-oxybenzoic acid was formed in such minute quantities that a positive identification was impossible.

The oxalic acid obtained was identified by its melting point, 99°C ., rising after desiccation over sulphuric acid to 189° , and by the properties of its calcium salt.

From these results it is apparent that in the oxidation of tyrosine by alkaline permanganate approximately four carbon atoms are utilized in the formation of carbon dioxide while the remaining five carbon atoms go to the production of oxalic, acetic, and probably *p*-oxybenzoic acids.

The ease with which the benzene ring is broken would seem to point to the intermediate formation of quinone compounds with the tearing apart of the side chain and benzene ring.



In order to obtain proof of this theory I have oxidized hydroquinone by exactly the method used for tyrosine.

Two grams of hydroquinone suspended in 50 cc. of water were treated with 600 cc. of a mixture containing 32.2 grams of potassium hydrate (30 molecules) and 18.6 grams of potassium permanganate; after standing for two days at room temperature decolorization of the permanganate was almost complete, the mixture was then heated for half an hour on the boiling water bath to obtain complete reduction. In this way I obtained 2.56 grams of oxalic acid, 2.52 grams of carbon dioxide and on distilling after acidifying the solution a small amount of a white crystalline acid body condensed in the receiver which had the same properties as the substance obtained in a similar way on the oxidation of tyrosine; no volatile fatty acids could be detected in the distillate.

SUMMARY.

1. The products produced by the oxidation of alanine with alkaline potassium permanganate were shown to be ammonia, carbon dioxide, oxalic, acetic and nitric acids.

2. On oxidation of tyrosine with alkaline potassium permanganate the oxidation products were found to consist of ammonia, carbon dioxide, oxalic, acetic and nitric acids, together with traces of an acid which was thought to be *p*-oxybenzoic acid but which owing to the minute amounts available was not positively identified.