

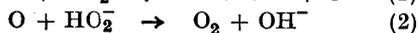
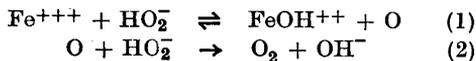
The Oxidation of Benzene by Means of Hydrogen Peroxide Catalyzed by Ferric Ions

V. STEN ANDERSEN

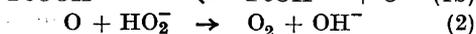
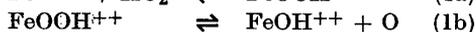
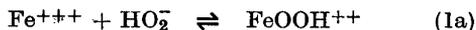
*Universitetets fysisk-kemiske Institut,
København, Denmark*

The oxidation of benzene by hydrogen peroxide and ferrous salt is mentioned by several authors, latest by Merz and Waters¹ who obtained beside phenols also diphenyl as oxidation products. Merz and Waters are of the opinion that the oxidizing effect in hydrogen peroxyd-ferrous salt solutions is due to the presence of free hydroxyl radicals.

In an earlier paper² I have shown that the decomposition of hydrogen peroxide catalyzed by ferric salts can be explained by the reaction mechanism:



or:



From this mechanism it would be expected that solutions of hydrogen peroxide containing ferric salt, due to the free oxygen atoms also would be able to oxidize many substances, which I have proved to be the case.

The following is a description of a qualitative experiment, of which, in 1948, I carried out several others with similar results.

500 ml of a saturated solution of benzene in water which was 0.003 *M* with regard to ferric nitrate and 0.01 *M* with regard to nitric acid and to which was added 5 g 30 % hydrogen peroxide (Perhydrol Merck) was allowed to stand at room temperature. In the course of about thirty minutes the

colour of the solution changed through reddish to dark brown, after which it turned more and more pale and finally became yellow. When the brown colour began to fade the hydrogen peroxide began to decompose with evolution of oxygen. From time to time a 10 ml sample was tested for phenols by bromine water.

The behaviour of the reacting mixture is shown in the following table:

Minutes after mixing	Colour of the solution	Reaction with bromine
10	Reddish	Weak opalescence
20	»	White turbidity
30	Brownish	» precipitate
35	Dark brown	»
40 *	Lighter brown	»
50	»	No
60	Yellow	»

The white precipitate formed by addition of bromine was isolated and identified as tribromophenol by its melting point. From the final solution oxalic acid could be isolated and identified as such by its equivalent weight and by the melting point of its derivative with benzylthio-carbamide. Furthermore it was found that the oxygen formed contained considerable amounts of carbon dioxide.

The oxidation process can be explained in the following way:

In the first stage oxygen atoms formed by reaction (1) in the above scheme oxidize benzene to phenol; thus reaction (2) is prevented and no free oxygen is formed. In the later stages phenol is oxidized to dark coloured compounds, probably quinones or quinhydrone which are finally decomposed to carbon dioxide and oxalic acid. When most of the oxidizable substances have disappeared, the evolution of oxygen according to reaction (2) commences.

Merz and Waters have, in their experiments, observed the formation of diphenyl in small yields. I have not tested my solu-

* Evolution of oxygen commences.