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## Abstract

## Full Text

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# STUDY OF THE MECHANISM OF OXIDATION OF HYDROXYBENZALDEHYDES BY PEROXIDES WITH THE AID OF $O^{18}$

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In the action of alkaline solutions of hydrogen peroxide and peracids on aromatic aldehydes, diatomic phenols are formed in quantitative yield (the Dakin reaction ([1])). This reaction serves as a preparative method for obtaining hydroquinone, pyrocatechol, and their derivatives. Its mechanism has not yet been definitively established. The use of the heavy isotope of oxygen, $O^{18}$, may help to elucidate it. In the present work the oxidation of salicylaldehyde by hydrogen peroxide in alkaline and acidic media, of methoxysalicylaldehyde in alkaline medium, and of salicylaldehyde by benzoyl hydroperoxide in alkaline medium was studied. The label was introduced into the peroxide or into the water. The results of typical oxidation experiments are given below. To an alkaline solution of 0.01 *M* salicylaldehyde in light water was added an equimolar amount of a 1% solution of hydrogen peroxide enriched with $O^{18}$ to 1.18 atom %. The solution darkened and self-heated. After extraction with ether and removal of the latter, pyrocatechol was precipitated with lead acetate in the form of the lead salt, which was then decomposed with dilute hydrochloric acid. The pyrocatechol isolated and purified by sublimation contained, in the newly formed second hydroxyl group, all the oxygen from the hydrogen peroxide (in two experiments, 1.20 and 1.16 atom % $O^{18}$). In experiments with heavy-oxygen water (1.60 atom % $O^{18}$), carried out under analogous conditions, the pyrocatechol obtained contained no excess $O^{18}$ (0.01; 0.01 atom % $O^{18}$).

In the oxidation of salicylaldehyde (0.02 mole) with 26% hydrogen peroxide (0.02 mole) in the presence of 0.01 mole of acetic acid ([2]) in heavy-oxygen water (1.51 atom % $O^{18}$), the pyrocatechol isolated as in the preceding experiments likewise contained no excess of the heavy oxygen isotope (0.06 atom % $O^{18}$). In all experiments the pyrocatechol melted at 104°.

Oxidation of methoxysalicylaldehyde (0.02 mole) with 26% hydrogen peroxide (0.025 mole) ([3]) in a solution of $KO^{18}H$ (1.26 atom % $O^{18}$) gave bis-(4-methoxypyrocatechol), isolated by the method described in ([3]), with a melting point of 264–265°, containing no excess $O^{18}$ (0.03; 0.03 atom % $O^{18}$).

(Figure: structural formula)

In the oxidation of salicylaldehyde (0.0025 mole) in a solution of $KO^{18}H$ (1.11 atom % $O^{18}$) with an excess of benzoyl hydroperoxide (about 0.01 mole), the pyrocatechol obtained contained 92% $O^{18}$ from the water in the newly formed second hydroxyl group (1.04; 1.00 atom % $O^{18}$). Isotopic analysis of water ([4]), hydrogen peroxide ([5]), and organic substances ([6]) was performed by the

methods described in the literature. Its accuracy, allowing for purification and preparation of the samples, was 5%. All data are given in atomic fractions in excess of natural abundance.

The results presented show that in the oxidation of hydroxyaldehydes by hydrogen peroxide in alkaline and acidic media, the oxygen of the hydroxyl group replacing the aldehyde group comes only from the peroxide. This excludes the participation of free hydroxyl radicals in the reaction, since the latter rapidly exchange their oxygen with water ([7]), and exchanged oxygen would have entered the pyrocatechol. The formation of the dimer, bis-(4-methoxypyrocatechol), in the oxidation of methoxysalicylaldehyde apparently cannot serve as sufficiently convincing evidence of a radi–

cal mechanism of hydroxylation of aldehydes, since the formation of dimers through cyclic transition complexes is possible without the direct participation of free radicals.

The addition of the hydroxyl group containing oxygen from hydrogen peroxide is consistent with the mechanism of Criegee ([8]) and Fries ([9]), proposed for the oxidation of carbonyl compounds by peroxides and demonstrated for these reactions in ([10]), as well as with the aid of $O^{18}$. According to this mechanism, the peroxide adds to the double bond of the carbonyl, with subsequent rearrangement to an ester and hydrolysis of the latter. In an acidic medium the reaction apparently begins with the addition of a proton to the oxygen of the carbonyl, while in an alkaline medium the attacking agent is the anion $HO_2^-$.

$$\text{o-hydroxybenzaldehyde} + HO_2^- \longrightarrow (I)$$
$$(I) \longrightarrow (II)$$
$$(II) + H_2O \longrightarrow \text{pyrocatechol} + HCOOH + (^*OH^-)$$

The entry into the newly formed second hydroxyl group of oxyphenol of oxygen from the peroxide shows that, during the hydrolysis of (II), the bond of the ether oxygen with the carbonyl carbon is broken. In the oxidation of certain aldehydes and cyclic ketones, peroxide compounds of type (I) have been isolated ([11]).

Various proposals ([12], [13]) have been made concerning the detailed mechanism of the rearrangement of (I) into (II); we shall not dwell on them, since the data of the present work do not add further clarity to this controversial question. Earlier ([14]) another mechanism was proposed, according to which the peroxide OH group replaces the hydrogen of the hydroxyl group at the ring, after which this introduced OH group exchanges places with the neighboring aldehyde group. We do not consider this mechanism, since there are insufficient experimental data in its favor. In the oxidation of an alkaline solution of salicylaldehyde with benzoyl hydroperoxide, only oxygen from water entered into the newly formed hydroxyl group of pyrocatechol. This can be explained either by the participation in the reaction of free hydroxyl radicals and exchange of their

oxygen with water, or by such exchange in some intermediate compounds formed during the course of the reaction. Further study of the mechanism of these reactions is being continued by us.

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*Note: Figure translations are in progress. See original paper for figures.*