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Abstract

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INVESTIGATION OF THE REACTIONS OF HYDROGEN PEROXIDE FORMATION DURING THE OXIDATION OF 2-ETHYLANTHYDROQUINONE AND ISOPROPANOL BY AN ISOTOPIC METHOD

The mechanism of the reactions underlying the industrial methods for obtaining hydrogen peroxide by oxidation of 2-ethylanthrahydroquinone (or its derivatives) and isopropyl alcohol with elemental oxygen (^{1}) has not hitherto been studied. In order to introduce a certain clarity into it, we studied these reactions by means of an isotopic method.

1. The oxidation of 2-ethylanthrahydroquinone and tetrahydro-2-ethylanthrahydroquinone was carried out under conditions close to industrial ones. A weighed portion of the quinone was introduced into a vessel containing a mixture of benzene and octyl alcohol, to which Raney nickel had been added. With constant shaking, dry hydrogen freed from oxygen was passed through the mixture for 20–40 min. After hydrogenation, the solution had a light-yellow color and slightly opalesced. Under excess pressure of H_2 it was filtered off from the catalyst into another identical evacuated vessel, through which, with shaking for 30–40 min, oxygen enriched in the heavy isotope O^{18} was then passed. After oxidation, the hydrogen peroxide was extracted from the homogeneous solution with water and decomposed in vacuo with potassium permanganate. The isotopic composition of the oxygen evolved in this process was determined with a mass spectrometer.

The results of experiments with 2-ethylanthraquinone, tetrahydro-2-ethylanthraquinone, and a mixture (1 : 1) of both (working mixture) are presented in Table 1. As is evident from this table, the oxygen of the hydrogen peroxide formed originates entirely from the elemental oxygen used for oxidation, without participation of the oxygen of the hydroxyl groups of the anthrahydroquinone or of the alcohol.

From the dependence of the oxidation kinetics on pH, Weisberger and co-workers (^{2}) concluded that analogous reactions with hydroquinone derivatives proceed with transfer of electrons from the hydroquinone anion to oxygen, for example, for durohydroquinone:

$$(CH_3)_4C_6(OH)_2 leftarrows (CH_3)_4C_6O_2'' \xrightarrow{+O_2} (CH_3)_4C_6O_2 + O_2''.$$

In the reactions we studied, such a mechanism is unlikely, since they proceed well in a neutral medium, and also in such a nonionizing solvent as benzene. The intermediate formation of transannular peroxides should likewise be excluded, since their rather high stability (^{3}) rules out the observed rapid course of the reactions. The data obtained by us are compatible with mechanisms involving intermediate formation of hydroperoxides, or radical mechanisms with abstraction of a proton from the hydroxyl of anthrahydroquinone.

To further elucidate the mechanism of the reactions under consideration, we introduced deuterium into the hydroxyl groups of 2-ethylanthrahydroquinone by exchange with methyl alcohol CH_3OD, in which the deuterium content in the hydroxyl was equivalent to an excess density of water of 12 450 γ.

(about 11.6% D). After distilling off the alcohol, 0.8 g of dry heavy 2-ethylanthrahydroquinone in 25 ml of benzene (which does not exchange hydrogen with anthrahydroquinone) was oxidized for 5 h by passing through oxygen containing no excess O^{18}. The hydrogen peroxide formed was extracted with 1.5 g of water, with which it very rapidly exchanges its deuterium.

Table 1

Substance	Charge, g	Solvent	Solvent	O^{18} content in mol. % above natural	O^{18} content in mol. % above natural
		benzene	octanol	in the initial O_2	in the O_2 liberated from H_2O_2
2-Ethylanthrahydroquinone (I)	1.8	25	25	0.966	1.04
Tetrahydro-2-ethylanthrahydroquinone (II)	1.8	25	30	0.966	0.956
Mixture (I)+(II)	3.2	40	50	0.936	0.936
2-Ethylanthrahydroquinone*	1.8	25	25	0	0

Substance	Charge, g	Solvent	Solvent	O^{18} content in mol. % above natural	O^{18} content in mol. % above natural
Isopropyl alcohol	3.2	–	–	0.936	0.936

* In this experiment, before oxidation, 2 ml of water containing 3 mol. % O^{18} was added to the reaction mixture.

After purification this water had an excess density of 448 γ, which, allowing for dilution, corresponds to a deuterium content in the hydrogen peroxide equivalent to 11 580 γ (or 10.8% D). After the benzene had been distilled off, the dry anthraquinone was burned and gave water with an excess density of 18 γ, i.e., it was practically free of deuterium. Thus, the hydrogen in the H_2O_2 obtained originates entirely from the hydroxyl groups of 2-ethylanthrahydroquinone. These data also make it possible to exclude the intermediate formation of a hydroperoxide with addition of the peroxide group at any position except 9 or 10, since such a mechanism would lead to transfer of deuterium into the nucleus and to transfer into the peroxide formed of only 50% of the hydroxyl deuterium, for example:

[structural scheme: deuterated 2-ethylanthrahydroquinone hydroperoxide] $\longrightarrow$ [structural scheme: 2-ethylant

Formation of hydroperoxides in positions 9 or 10 does not contradict our observations. Taking into account the known data on the mechanism of other, similarly well studied reactions of peroxide compounds ([1]), we consider the radical mechanism most probable, according to the scheme:

[hydroquinone structure]+$O_2 \longrightarrow$ [semiquinone radical structure]+$\dot{O}_2H \longrightarrow$ [quinone structure]+H_2O_2

with possible intermediate formation of 9- or 10-hydroperoxide:

[semiquinone radical structure] + $\dot{O}_2H \longrightarrow$ [hydroperoxide structure]

By means of potentiometric titration, Geake and Lemon ([4]) showed that the oxidation of anthraquinone and its derivatives by ferricyanide proceeds in two stages, with intermediate formation of semiquinone. However, in that study the oxidation was carried out in an alkaline medium.

At our request, V. V. Voevodskii, with the participation of N. N. Bubnov and N. I. Tikhomirova, recorded the electron paramagnetic resonance spectrum of a solution of 2-ethylanthrahydroquinone during its oxidation. In this case the semiquinone radical was not detected, which is possibly explained by its low stationary concentration. At higher concentrations in an alkaline medium, a distinct spectrum of the semiquinone radical ion was obtained. However, in this case its formation may also be ascribed to the reaction

$$\mathrm{C_2H_5C_{14}H_7O_2''} + \mathrm{C_2H_5C_{14}H_7O_2}\text{leftharpoons}\mathrm{2C_2H_5C_{14}H_7O_2''}.$$

The study of the paramagnetic-resonance spectra of the reacting systems considered in this work will be continued.

2. It is known that a number of secondary alcohols are readily oxidized by elemental oxygen, giving ketones and hydrogen peroxide in good yield. One practical method for obtaining the latter is such oxidation of isopropyl alcohol (5). We carried out this reaction with 3.2 g of alcohol, distilled into an evacuated ampoule made of molybdenum glass, which had previously been treated for a long time with a solution of boric acid and perhydrol. The ampoule was filled with oxygen enriched in O^{18} at one atmosphere and heated to 100° for 20 h. The yield of hydrogen peroxide reached 48%. Its isotopic composition is given in Table 1. In this case as well, all the oxygen of the hydrogen peroxide originates from elemental oxygen, without participation of oxygen from the alcoholic hydroxyl. The mechanism of this reaction is apparently analogous to that considered above for the oxidation of anthrahydroquinone with the participation of O_2H radicals.

Some further indications concerning the course of the oxidation reactions of isopropyl alcohol are given by the work of Westheimer and Nicolaides (6). For the oxidation of this alcohol with chromic acid, they found a large kinetic isotope effect upon replacement of secondary hydrogen by deuterium. It follows from this that, in the slow stage of the reaction, abstraction of the secondary hydrogen atom occurs, and not of the hydroxyl hydrogen. The totality of all the data presented above is in good agreement with the following two-stage mechanism:

$$\mathrm{(CH_3)_2CH(OH)} + \mathrm{O_2} \rightarrow \mathrm{(CH_3)_2\dot{C}} - \mathrm{OH} + \mathrm{\dot{O}_2H} \rightarrow \mathrm{(CH_3)_2C} = \mathrm{O} + \mathrm{H_2O_2},$$

with possible intermediate formation of hydroxy-hydroperoxide.

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