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Abstract

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STUDY OF THE OXIDATION OF BENZENE AND PHENOL BY PERNITROUS ACID AND OF SALICYLALDEHYDE BY FENTON' S REAGENT

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Earlier, with the aid of O^{18}, it was established (^{1,2}) that during the hydroxylation of phenol by hydrogen peroxide, Fenton' s reagent ($H_2O_2 + Fe^{2+}$), or persulfate, and of salicylaldehyde by hydrogen peroxide, the oxygen from the oxidant enters the hydroxyl group formed. Further investigation showed that, in the oxidation of benzene and phenol by pernitrous acid, and also of salicylaldehyde by Fenton' s reagent, the reaction products formed also contain oxygen from the peroxide. The conditions and results of our experiments are given below. Isotopic analysis of organic substances (^{3}) and H_2O^{18} (^{4}) was carried out by the methods described earlier. Its accuracy, taking into account errors in sample preparation, was 5%.

Oxidation of benzene by pernitrous acid

To an emulsified mixture of 1.28 mole of benzene and 0.15 mole of hydrogen peroxide in 350 cm^3 of 0.1 N HCl in H_2O^{18}, containing in two experiments 0.92 and 0.97 atom % O^{18}, a solution of 0.11 mole of sodium nitrite in 150 cm^3 of 0.1 N HCl in H_2O^{18} with the same O^{18} content was added dropwise at room temperature. Since nitrous acid rapidly exchanges its oxygen with water at room temperature (^{5}), the $NaNO_2$ solution in acidified H_2O^{18} was first allowed to stand for several hours for isotopic equilibration. The benzene layer was extracted with dilute alkali solution. From the alkaline extracts, after acidification, the *o*-nitrophenol formed was steam-distilled. The purified product with m.p. 45° contained 1/3 of its oxygen from water (0.30 and 0.35 atom % O^{18})* . The entry of oxygen from water into *o*-nitrophenol is explained as follows: upon the formation of pernitrous acid from H_2O_2 and HNO_2, preliminarily isotopically equilibrated with H_2O^{18}, the peroxide oxygen passes entirely into the peracid formed,

$$\mathrm{HOO[\;H + H^{18}O\;]NO^{18}} \longrightarrow \mathrm{HOO^{18}NO + H_2O^{18}},$$

whose subsequent cleavage at the O—O bond gives a nitro group containing one half of the label from water; addition of the labile hydroxyl from the same acid dilutes this label to 1/3.

Oxidation of phenol by pernitrous acid

To a solution of 0.2 mole of phenol and 0.3 mole of hydrogen peroxide in 200 cm^3 of 0.1 N HCl in H_2O^{18}, containing 0.97 atom % O^{18}, at 40° and with vigorous stirring, a solution of 0.07 mole of $NaNO_2$ in 100 cm^3 of 0.1 N HCl in H_2O^{18} was added dropwise over 30–40 min. The brown mixture was extracted with ether. After removal of the ether and of unreacted phenol from the residue by fractional distillation in vacuo, pyrocatechol and hydroquinone were isolated. The purified pyrocatechol with m.p. 104° contained no excess O^{18} (in two experiments, 0.03 and 0.03 atom % O^{18}). Hydroquinone, after purification, contained 0.50 and 0.59 atom % O^{18}. It is known that phenol, nitrophenol, and pyrocatechol ([6,7]) do not exchange their oxygen with water at room temperature. Such exchange is observed only above 100°. In hydroquinone the exchange proceeds faster and is strongly accelerated by acids ([6]).

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* In experiments in which sodium nitrite was not preliminarily equilibrated with H_2O^{18} (0.93 atom % O^{18}), the *p*-nitrophenol obtained contained only 0.14–0.15 atom % O^{18} from water.

To determine the extent of exchange of hydroxynone under the conditions of our experiments, its exchange with H_2O^{18} in 0.1 N HCl was studied in the presence of H_2O_2 and $NaNO_2$, and in their absence. In these experiments, for 0.009 mole of hydroxynone, the amounts of hydrogen peroxide, sodium nitrite, and H_2O^{18} were taken to be five times smaller than in the experiments on phenol oxidation. After 3 hours at 40° in 0.1 N HCl, no exchange of hydroxynone was detected (0.02 at.% O^{18}). In the presence of H_2O_2 in H_2O^{18} with 1.07 at.% O^{18}, the unreacted hydroxynone isolated after 10 min. likewise contained no excess O^{18} (0.03 at.% O^{18}). Hydroxynone isolated 40 min. after the start of the reaction from water containing 0.83 at.% O^{18} contained 0.45 at.% O^{18}. In the presence of H_2O_2 and $NaNO_2$ in water with 1.10 at.% O^{18}, the hydroxynone isolated after 20–25 min. had exchanged by 37% (0.41 at.% O^{18}). On the basis of these data it may be concluded that, in the oxidation of phenol, transfer of oxygen from water into the hydroxynone formed occurs as a result of exchange. Pyrocatechol under similar conditions does not undergo such exchange. The mechanism of the exchange of hydroxynone with water in the presence of H_2O_2 and $NaNO_2$ is unclear and requires further study.

Oxidation of salicylaldehyde with Fenton' s reagent. To an emulsified mixture of 0.016 mole of salicylaldehyde with 0.1 g of $FeSO_4 \cdot 7H_2O$ in 50 cm^3 of H_2O^{18} (1.24 at.% O^{18}), acidified with 2–3 drops of 60% $HClO_4$, a 5% solution of H_2O_2 in 100 cm^3 of H_2O^{18} containing 1.24 at.% O^{18} was added dropwise with ice cooling. After all the peroxide had been added, the mixture was stirred at room temperature for another hour and extracted with ether. After the ether reaction scheme

Figure 1: reaction scheme

was distilled off, pyrocatechol was isolated from the residue in the form of the lead salt, which was then decomposed with HCl. The purified product with m.p. 104-105° contained no excess O^{18} (in two experiments, 0.02 and 0.03 at.% O^{18}).

The data obtained show that, in the oxidation of benzene and phenol with pernitrous acid and of salicylaldehyde with Fenton's reagent, the oxygen of water does not participate in the formation of the hydroxyl groups of the reaction products. For oxidation with pernitrous acid, this eliminates on this basis the mechanism of hydroxylation by NO_2 radicals (^{8,9}). According to this mechanism, the NO_2 radicals formed in the decomposition of pernitrous acid

$$HOONO \to HO + ONO,$$

should add to the aromatic nucleus through the oxygen atom, with intermediate formation of an ether of the type $X—C_6H_4—ONO$, where $X = H$ or OH, followed by its hydrolysis with cleavage of the $O—N$ bond. Such a path of hydrolysis was confirmed by us in (^{1}) for the diacetate and the monosulfuric acid esters of hydroxynone.

In this case, as is readily calculated, pyrocatechol would contain one fourth, and *o*-nitrophenol one half, of their oxygen from water, which contradicts the results obtained. They can be reconciled with the Halpern and Robinson (^{10}) mechanism of direct oxidation of the aromatic nucleus by OH and NO_2 radicals according to the scheme:

if it is assumed that the hydroxyl radicals, which according to literature data should very rapidly exchange their oxygen for the oxygen

water (^{11,12}), react with it more slowly than with the substance being oxidized. Our data are also consistent with a mechanism involving an intermediate complex of type A between the substance being oxidized and pernitrous acid, without its preliminary decomposition into radicals:

(schematic structure of complex A)
(A)

However, the facts reported in the literature concerning the initiation of methyl acrylate polymerization by an acidified solution of sodium pernitrite or by a mixture of H_2O_2 with $NaNO_2$, as well as the formation of dimerization products in the oxidation of organic substances by pernitrous acid, etc. (^{10}), make it possible to prefer a free-radical pathway for the reaction. The absence of oxygen from water in pyrocatechol obtained in the oxidation of salicylaldehyde by Fenton' s reagent, which is a powerful source of OH radicals, permits the assumption that the rate of interaction of hydroxyl radicals with water is also, in this case, lower than with the substance being oxidized. We do not dwell on the details of the radical scheme of the reaction, since our data add nothing new to it. The results obtained also do not exclude an ionic mechanism of the reaction through the intermediate formation of hydroperoxide and its subsequent decomposition with the Criegee rearrangement ([2,13]). We are continuing our study of the participation of radicals in these reactions.

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