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Abstract

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FREE RADICALS IN THE OXIDATION OF PHENOLS IN THE PRESENCE OF COMPLEX CATALYSTS

The oxidation of organic compounds by oxygen in the presence of homogeneous catalysts Cu^{2+}—amine and Cu^{+}—amine has recently attracted wide attention. These catalysts have been used in the oxidation of phenols and naphthols as a model of the enzyme tyrosinase ([1]), in the polymerization of phenols by oxidative dimerization ([2]), and in the oxidation of primary amines and hydrazo compounds ([3]), benzoin and its derivatives ([4]). The oxidative dimerization of acetylenic compounds proved to be very important ([5,6]). Most authors assumed that free radicals formed from the organic compound (phenoxyl, ethynyl, amine radicals) participate in the oxidation process; however, this assumption had not received direct experimental proof.

In the present work an attempt was made to detect radicals and to investigate their role using as an example the oxidation of 2,4,6-tri-*tert*-butylphenol (I) by oxygen with the aid of a complex catalyst. Phenoxyl radicals had previously been detected in the oxidation of sterically hindered phenols by potassium ferricyanide or by peroxide compounds, for example ([7,8]). Under other conditions (oxidation by oxygen in an alkaline medium) the process proceeds through the phenoxy anion ([9]).

The catalyst— "complex A" —was prepared by saturating a solution of Cu_2Cl_2 in pyridine with oxygen. For one mole of Cu_2Cl_2, 0.5 mole of oxygen was consumed.

$$(I) \quad \rightleftarrows \quad (II) \quad \longrightarrow \quad (III) + \equiv C(CH_3)_3$$

By the method of electron paramagnetic resonance (e.p.r.) we showed that free radicals arise during the oxidation of I. The number and magnitude of the splitting of the components of the hyperfine structure of the spectrum (3 components with an intensity ratio of 1 : 2 : 1 and a splitting between them of 1.7 oersted) indicate that these free radicals are 2,4,6-tri-*tert*-butylphenoxyl radicals II ([10]) (Fig. 1).

Fig. 1. E.p.r. spectra of the radical formed during the oxidation of
2,4,6-tri-tert-butylphenol.

Figure 1: Fig. 1. E.p.r. spectra of the radical formed during the oxidation of 2,4,6-tri-tert-butylphenol.

Fig. 2

Figure 2: Fig. 2

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10 oersted.

We then attempted to determine whether these radicals take part in the process or whether their presence is due to side reactions. For this purpose we studied both the oxidation of I and the separately prepared, in accordance with (^{7}), II. The principal product of the oxidation of I is 2,6-di-*tert*-butylbenzoquinone III (60-70% yield). In addition to III, IV was isolated in small and variable yield. In the oxidation of I at the expense of the oxygen contained in the catalyst, the reaction proceeds only as far as the stage of formation of radical II, identified by the e.p.r. method. Most of I remains unchanged. In the oxidation of I by oxygen in the presence of "complex A," 0.7 mole of O_2 is absorbed per mole of phenol. When the amount of catalyst is increased from $0.125 \cdot 10^{-4}$ to $0.5 \cdot 10^{-4}$ mole, the rate, measured by absorp—

of O_2 increases. After the molar ratio of Cu_2Cl_2 to phenol reaches 0.5, the rate becomes maximal and remains constant upon further increase in the amount of catalyst. The kinetic curves have a maximum until the molar ratio of catalyst to phenol reaches 0.5 (compare curves 1 and 3, Fig. 2).

By the EPR method, the change in the concentration of radicals II during oxidation of I was studied. At catalyst-phenol ratios less than 0.5, the radical concentration passes through a maximum (curve 2, Fig. 2). At a ratio of 0.5 and higher, the curve has no maximum (curve 4, Fig. 2). The bulk of the radicals disappears at $\sim$ 40-50% conversion of I; some radicals remain for a certain time after the absorption of O_2 has already ended. By the end of the reaction the catalyst is completely regenerated, as confirmed by the EPR spectrum of "complex A" and by the fact that oxidation of a new portion of I proceeds on the used catalyst at the same rate as on the fresh complex.

Fig. 2. Kinetics of oxidation of 2,4,6-tri-*tert*-butylphenol by "complex A." 1, 3—dependence of the rate of O_2 absorption on time (ΔV/min); 2, 4—change in the concentration of free radicals II with time, measured by the EPR method; 1, 2—molar ratio $Cu_2Cl_2/I = 0.025$; 3, 4—molar ratio $CuCl_2/I = 0.5$.

The induction period in the oxidation of I is absent. Additions of hydrogen peroxide in a molar ratio of 0.3 to I did not change the rate of absorption or the shape of the curves. This indicates that H_2O_2 does not participate in the process, in contrast to the oxidation reaction of I to *o*-benzoquinone (^{1}). Addition of benzene and methyl methacrylate, which are acceptors of unstable free radicals (^{11}), in ratios from 0.16 to 0.33 to I did not decrease the rate of the process.

During oxidation of II, 0.5 mole of O_2 is absorbed, and V is formed in quantitative yield:

$$\mathrm{II} + \frac{1}{2}O_2 \longrightarrow \mathrm{V} + \mathrm{C(CH_3)_3}.$$

The induction period or an increase in rate during the reaction was not observed. Increasing the amount of "complex A" decreased the oxidation rate; the highest rate was observed without the complex. This interesting result is apparently associated with the stabilization of II upon its entry into the complex.

The facts presented indicate that oxidation of I occurs when it enters a catalytic complex containing one oxygen atom (see the schematic representation). The hydrogen of the hydroxyl group of I participates in the formation of a bond between the complex and I and passes from I to the complex, modifying the latter. The anion of I reduces the catalyst, being converted into a radical that reacts in the quinoid form IIb while located in the modified complex. This stage requires the presence of molecular oxygen, which is consumed in oxidizing the catalyst and the split-off *tert*-butyl group. Conversion of II in the complex evidently proceeds through IV. Separately prepared IV, upon oxidation with oxygen in the presence of "complex A," indeed gave III, although the rate of the process and the yield varied greatly.

$$[\mathrm{Cu^+}, \mathrm{Py}] \xrightarrow{\mathrm{O_2}} [\mathrm{Cu^{2+}}, \mathrm{Py}, \mathrm{O}] \xrightarrow{\mathrm{I}} [\mathrm{I} \cdots \mathrm{Cu^{2+}}, \mathrm{Py}, \mathrm{O}] \longrightarrow$$

$$\longrightarrow \left[\begin{array}{c}\text{phenoxy radical}\\ \mathrm{Cu^{2+}}, \mathrm{Py\ OH}\end{array}\right] \longrightarrow [\mathrm{II}^a, \mathrm{Cu^+}, \mathrm{Py}, \mathrm{OH}] \longrightarrow$$

$$\longrightarrow [\mathrm{IV}, \mathrm{Cu^+}, \mathrm{Py}] \xrightarrow{\mathrm{O_2}} \mathrm{III} + [\mathrm{Cu^{2+}}, \mathrm{Py}, \mathrm{O}].$$

The oxidation of II, taken as the starting compound, proceeds when it enters into a complex with the unmodified catalyst, which determines a different direction of the process:

$$2\,\mathrm{II}^b \xrightarrow{2[\mathrm{Cu^{2+}},\mathrm{Py},\mathrm{O}]} 2[\mathrm{II}^b, \mathrm{Cu^{2+}}, \mathrm{Py}, \mathrm{O}] \longrightarrow \mathrm{V} + 2[\mathrm{Cu^{2+}}, \mathrm{Py}].$$

The entry of $\mathrm{II}^{\cdot}$ into the unmodified complex stabilizes the radical.

Fig. 3. Dependence of catalyst activity on the pyridine:methanol ratio. Effect of benzene additions. Solid curve—oxidation by the catalyst Cu2Cl2—pyridine—CH3OH; dashed curve—oxidation by the catalyst Cu2Cl2—pyridine—CH3OH with addition of benzene (in a molar ratio of 0.33 to I).

Figure 3: Fig. 3. Dependence of catalyst activity on the pyridine:methanol ratio. Effect of benzene additions. Solid curve—oxidation by the catalyst Cu2Cl2—pyridine—CH3OH; dashed curve—oxidation by the catalyst Cu2Cl2—pyridine—CH3OH with addition of benzene (in a molar ratio of 0.33 to I).

By changing the catalytic system one can create conditions under which the process takes place outside the complex. The catalyst for this purpose was prepared by oxidizing Cu_2Cl_2 in methanol ("complex B"). In the oxidation of I by oxygen in the presence of "complex B," additions of benzene and methyl methacrylate lower the rate of oxidation (Fig. 3). When pyridine is added to "complex B," even small additions of pyridine increase the oxidation rate and change the mechanism of the process in such a way that benzene and methyl methacrylate do not affect its rate.

Fig. 3. Dependence of the activity of the catalyst on the pyridine:methanol ratio. Effect of benzene additions. Solid curve—oxidation by the catalyst Cu_2Cl_2 —pyridine—CH_3OH; dashed curve—oxidation by the catalyst Cu_2Cl_2—pyridine—CH_3OH with addition of benzene (in a molar ratio of 0.33 to I).

As in carrying out the reaction in pyridine, so also when methanol is used, the product of oxidation of I proves to be III. The totality of the data obtained permits the assumption that the factor determining the direction of oxidation of I is modification of the catalyst under the action of the substrate. Such modification is reversible. It contributes to the selectivity of the process. The indicated phenomenon, which may be called the phenomenon of "automodification," is possibly one of the principles of the catalytic action of enzymes, ensuring selectivity by means of double control (through the initial catalyst and the catalyst modified under the action of the reaction).

Experimental Part

I was obtained by alkylation of phenol with isobutylene (12). II was prepared from I according to (7). IV was synthesized in accordance with (8,13). The catalyst was obtained by shaking a solution of 0.01 g (0.00005 mole) of Cu_2Cl_2 in 50 ml of pyridine (methanol or the corresponding mixture of pyridine with methanol) in an oxygen atmosphere for 30 min at room temperature. Oxidation was carried out in a rapidly rocking "duck," connected to a gas burette. EPR spectra were recorded on an EPA-2 spectrometer.

The reaction mixture was acidified with dilute hydrochloric acid and extracted with ether. The ether extracts were dried over $CaCl_2$, and the ether was distilled off.

III was isolated from the residue by sublimation in vacuum and recrystallization from methanol and petroleum ether.

Found, %: C 76.85; H 9.5
$C_{14}H_{20}O_2$. Calculated, %: C 76.16; H 9.3

The melting points of I and of its derivatives—2,6-di-*tert*-butyl-benzoquinone-1,4-phenylhydrazone-4 and the quinol—are, respectively, 63-65°; 100-101°; 101-102° (without depression), which agrees with the literature data (^13, ^14). The IR spectra coincide with those given in the literature (^13). IV was isolated by fractional recrystallization, m.p. 131-132° (without depression with a sample obtained by independent synthesis). V was isolated by recrystallization from ethanol, m.p. 148° (without depression with a sample prepared according to (^8)). The IR spectra coincide with those given in the literature (^7, ^13).

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