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chemical structural formulas labeled (II), (III), (IVa), and (IVb)

Figure 1: chemical structural formulas labeled (II), (III), (IVa), and (IVb)

Abstract

Full Text

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On the Oxidation of β-Naphthol and Some of Its Derivatives by Peroxide Compounds

Despite the considerable number of studies devoted to the oxidation of phenols by peroxide compounds, many details of the mechanism of this reaction remain unclear. For example, there are discrepancies in views concerning the participation of free radicals in this process ([1,2]). Even less studied is the mechanism of the reaction of peroxide compounds with naphthols.

In the present work, the action of several peroxide compounds (benzoyl peroxide, dicyclohexyl percarbonate, lead dioxide, and a series of hydroperoxides) on β-naphthol (I) and its derivatives—1,1′-dinaphthol-8,2′ (II) and 2-hydroxy-1,1′-dinaphthalin oxide-8,2′ (III)—was investigated by the method of electron paramagnetic resonance (EPR). It is shown that in this reaction intermediate radical products of various structures and stabilities are formed.

II and III were synthesized in accordance with works ([3]) and ([4]), with III being obtained by oxidation of the so-called "chinhydrone,"which apparently represents a molecular compound of the product of dehydrogenation of II by silver oxide with II ([4]). The investigation was carried out in the liquid phase (in solutions of benzene, toluene, chloroform); the EPR spectra were recorded on EPR-2 ([5]) and OKBA spectrometers and registered in the form of first derivatives of the absorption line on an EPP-09 self-recording instrument.

When peroxide compounds interact with I, radicals are formed that give a singlet spectrum with a distance between the points of maximum slope of 5 oersteds (Fig. 1). These radicals are probably produced by abstraction of hydroxyl hydrogen and are stabilized by conjugation of the unpaired electron with the π-bond system of the naphthyl ring. Nonequilibrium concentrations of radicals arose upon rapid heating of a mixture of the starting compounds to 100–120° followed by sharp cooling of the mixture to the temperature of liquid nitrogen. The observed concentrations were small and amounted to $\sim 10^{15}$ cm^{-3}. At room temperature the concentration of radicals rapidly decreases. It was not

Fig. 1. EPR spectrum of the radical formed in the interaction of peroxide compounds with β-naphthol

Figure 2: Fig. 1. EPR spectrum of the radical formed in the interaction of peroxide compounds with β-naphthol

Fig. 2. EPR spectrum of the radical formed in the interaction of peroxide compounds with II and III

Figure 3: Fig. 2. EPR spectrum of the radical formed in the interaction of peroxide compounds with II and III

possible to resolve the hyperfine structure of the EPR spectrum.

In contrast to I, its derivatives II and III, under the action of the peroxide compounds indicated above, already at room temperature form in large _generate concentrations, radicals differing from β-naphthoxy radicals in their stability. The EPR spectrum of the radicals obtained from II and III is identical to it (Fig. 2). A triplet with a component intensity ratio of 1 : 2 : 1 and a splitting between them of ~2.5 Oe arises due to interaction of the unpaired electron with two equivalent protons of the naphthyl ring. At high concentrations and in the presence of atmospheric oxygen the hyperfine structure of the EPR spectrum is smeared out. Upon dilution and in vacuum, and also upon cooling to −60°C (even in air), the hyperfine structure is well resolved.

Fig. 1. EPR spectrum of the radical formed in the interaction of peroxide compounds with β-naphthol

Fig. 2. EPR spectrum of the radical formed in the interaction of peroxide compounds with II and III

Identification of the radical formed in the reaction of II and III with peroxides is of considerable interest. In the oxidation of III with an alkaline solution of potassium ferricyanide, Pummerer and co-workers isolated a compound to which they assigned the structure of quinol ether IVa (4) and peroxide IVb (6). Upon dissociation of compound VI in solution, radicals were obtained that reacted mainly through the oxygen atoms. Later it was shown that IV in benzene and pyridine solution gives an EPR spectrum in the form of a triplet, which was assigned to the stable radical V (7). Comparison of the spectra obtained in (7) and by us (Fig. 2) reveals their identity. The results recently published by Rieche and co-workers (8) contradict the observations in (7). These authors found that in chloroform solution IV gives a complex, incom-

Fig. 3. EPR spectrum of an impurity radical in solutions of III

Figure 4: Fig. 3. EPR spectrum of an impurity radical in solutions of III

Fig. 4. Dependence of the logarithm of the equilibrium constant of dissociation of IV on reciprocal temperature

Figure 5: Fig. 4. Dependence of the logarithm of the equilibrium constant of dissociation of IV on reciprocal temperature

Fig. 3. EPR spectrum of an impurity radical in solutions of III

···a resolved spectrum, distinguished by its instability. To clarify the reason for such a discrepancy between the results in (7,8) and to obtain additional data that might help identify the radicals formed from II and III, we synthesized IV and studied the EPR spectrum of IV and of the compounds used for its preparation ("chingidrone," III).

It was found that in the crystalline state at room temperature "chingidrone" gives an intense EPR signal corresponding to a spin concentration of $\sim 2 \cdot 10^{20}$ spins/g. In solutions a spectrum of a stable radical is observed, identical to that shown in Fig. 2. When the temperature is lowered, the signal intensity decreases.

Upon oxidation of "chingidrone" according to (4), III was obtained. It was found that in the crystalline state III gives a weak signal. In solutions of III the radical concentration is also small ($\sim 10^{14}$ cm^{-3}), and their spectrum has a complex, poorly resolved structure, especially on the wings of the singlet (Fig. 3). We prepared III by another method–the decomposition of IV in light (4). No signal similar to that shown in Fig. 3 was detected. IV, obtained from III (6), gave a signal completely different from that found for III. In solutions of IV the spectrum is identical to the EPR spectrum of radicals formed from II and III (Fig. 2), and to the spectrum obtained in (7).

Fig. 4. Dependence of the logarithm of the equilibrium constant of dissociation of IV on reciprocal temperature

The facts presented make it possible to suppose that the EPR spectrum observed in (8) in a solution of IV (and also by us–Fig. 3) is due to the presence of impurity radicals arising in side processes during the preparation of IV and III.

Our data confirm the dimeric structure of IV. In the crystalline state at room temperature the degree of dissociation of IV is only $\sim 0.1\%$ (spin concentration $\sim 10^{18}$ spins/g). Upon dissolution the degree of dissociation increases sharply; for example, at a concentration of IV in benzene of $3 \cdot 10^{-3}$ g/cm^3, the degree of dissociation increases 30-fold (spin concentration $\sim 3 \cdot 10^{19}$ spins/g). With decreasing temperature, the degree of dissociation decreases. The temperature dependence of the degree of dissociation was studied quantitatively by us over the temperature range $-10 \div 60$°C in vacuum, in a solution of IV in toluene. The equilibrium concentrations of radicals formed upon dissociation of IV were measured by the EPR method. Equilibrium was always attained from both sides. The equilibrium constant of the indicated dissociation process has the form

$$K = \frac{(R)^2}{(M_0) - (R/2)},$$

where (R) is the equilibrium concentration of radicals, and (M_0) is the initial concentration of IV molecules. Since $(R) \ll (M)_0$ (by 3-4 orders of magnitude), the equilibrium constant was calculated from the equation

$$K = \frac{(R)^2}{(M_0)}.$$

Figure 4 presents the dependence of $\lg K$ on $1/T$. The equilibrium constant is expressed by the following formula:

$$K = 1.8 \cdot 10^{29} \exp(-16\,500/RT)\ \text{l/cm}^3.$$

On the basis of the foregoing, it may be concluded that the action of peroxides on II and III gives stable radicals identical to those into which IV dissociates. Their structure, in accordance with (7), may conventionally be described by formula V. We note that there is a great similarity between radicals V and Dimroth' s "oxygen radicals" (9,10) (but not with the radica-

[structural formulas labeled (V) and (VI)]

···of the type of 2,4,6-tri-*tert*-butylphenoxyl radicals (11), as indicated in (7). The features characteristic of Dimroth radicals and, in particular, of V—stability in air, reaction at this oxygen, the dimeric structure in the crystalline state, the presence in the ortho position to the oxygen atom of an aromatic ring whose protons do not interact with the unpaired electron—all this points to a profound analogy in the mechanisms of stabilization of these radicals.

The formation of the stable radical V under the action of peroxides on II possibly proceeds through an intermediate compound, which may be a radical or biradical with a lifetime too short for them to be detected by the EPR method. The assumption that intermediate products of this kind are present is supported by comparison of the spectra of solutions of IV and VI in benzene, toluene, and chloroform. VI, synthesized by us in accordance with (6), gave in the indicated solutions a triplet identical with that shown in Fig. 2. The same spectrum (see above) was observed in solutions of IV. This coincidence of spectra, also observed in (7), is explained by the fact that the "middle" part of VI either does not form a compound of radical type, or the radical (biradical) formed is unstable, which confirms the assumption made above concerning the mechanism of formation of V from II.

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