ESR study of the effect of water on the kinetics of proton transfer and exchange in solutions of semiquinone radicals

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The interaction of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl with triethylamine in the reaction of proton transfer is catalyzed by water. However, the rate of proton exchange with diethylamine is independent of water admixtures in the reaction medium. ESR showed that the complexing of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl with water leads to redistribution of the spin density.

Key words: 3,6-di-*tert*-butyl-2-hydroxyphenoxyl; triethylamine; diethylamine; complexing; ESR.

In kinetic studies of fast acid-base interactions in nonaqueous media the occasional presence of water in a system is the main cause of uncertainty in the interpretation of the experimental data obtained. Also, water is a unique solvent and the investigation of the effect of its presence on the reactivity of organic compounds of a different nature is a separate interesting problem.[1—3] Recently similar kinetic studies have been carried out by the dynamic NMR method.[4] The ESR method has an advantage over NMR and is more suitable for following the course of faster protolytic reactions in nonaqueous media.

Figure 1 shows the ESR spectra of semiquinone radical, 3,6-di-*tert*-butyl-2-hydroxyphenoxyl (**1**), in a mixture of tetrahydrofuran (THF) with water at different temperatures. The choice of the organic solvent—water mixture is due to the poor solubility of sterically hindered ortho-quinone and pyrocatechol (the starting materials in the synthesis of **1**) in water. The ESR spectra were registered using a RE-1306 spectrometer equipped with a thermostatting system.

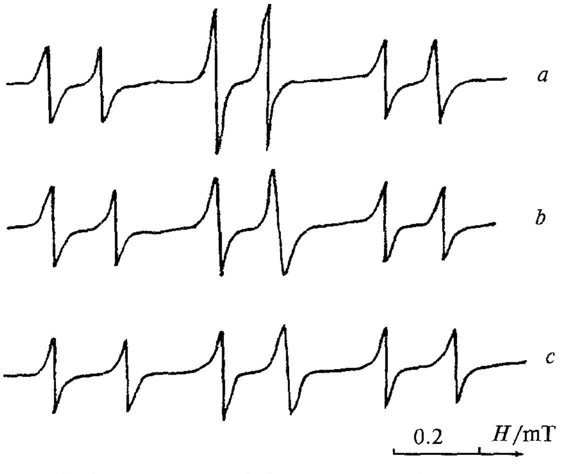

Fig. 1. ESR spectra of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl dissolved in a mixture of water with tetrahydrofuran at temperatures (K): (*a*) 383, (*b*) 366, and (*c*) 349; $[H_2O]$ = 0.56 mol L^{-1}.

In the high-temperature range (330 K and above) the ESR spectrum of radical 1 in tetrahydrofuran is a triplet of doublets with the following constants of hyperfine interaction (HFI): 0.39 mT and 0.16 mT for the ring and the hydroxyl protons, respectively.[1] The magnetic equivalence of the ring protons results from the fast prototropic rearrangement in radical **1**. As can be seen from Fig. 1, when the water—ether solution is heated, the splitting by the hydroxyl group decreases, which is characteristic of intermolecular exchange.[1—3] This exchange is manifested less here than in solutions of carboxylic acids and secondary amines but it allows the one to estimate the kinetic parameters of the reaction on the basis of the modified Bloch equation:

$$\dot{Q}H + \overset{*}{H}X \rightleftharpoons \dot{Q}H^* + HX \qquad (1)$$

The rate of proton exchange, ν_{exch}, is connected with the effective constant of HFI with the hydroxyl proton of radical **1** ($\tilde{a}$) by the relation[5]

$$\nu_{exch} = \frac{\gamma_e a_o}{2\sqrt{2}}\sqrt{1-\left(\frac{\tilde{a}}{a_o}\right)^2} \qquad (2)$$

where γ_e is the gyromagnetic ratio for an electron, a_O is the HFI constant for a hydroxyl group of radical **1**

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in anhydrous THF. The reaction rate constant $k_{exch} = 4\,\nu_{exch}/[H_2O]$ estimated by this means is $6.1 \cdot 10^5$ L (mol s)$^{-1}$ and the activation energy of the process is E_{act}=38.9 kJ mol^{-1}. Because of the limited solubility of water in toluene, we could not obtain the similar information for this system.

As a result of the complexing of compound **1** with the molecules of THF *via* hydrogen bonding, the rate of proton exchange in the semiquinone radical decreases and the ring protons become magnetically nonequivalent (Fig. 2). The ESR spectrum of this complex at 233 K is a doublet of doublets with a_H = 0.78 mT and $a_H{}^{OH}$ = 0.165 mT.[6] The central component of the above triplet of doublets becomes registered at high temperature significantly broadened or disappears completely. When the low-temperature ESR signal of the **1**—H_2O—THF system is registered at a high gain, a complex multiplet is observed along with the ESR spectrum of the radical-ether complex. The hyperfine structure (HFS) of this multiplet with a_H = 0.66 mT is characteristic of *tert*-butyl protons. A doublet of doublets with HFI constants equal to 1.58 and 0.24 mT can be seen in this spectrum. In pure THF and in other anhydrous organic solvents similar ESR spectra are not observed and, therefore, the latter doublet may be assigned to the complex of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl with water molecules, which appears to be an intermediate determining the proton exchange between radical **1** and water. A comparison of the ESR spectra of the complexes of **1** with ether and water shows considerable redistribution of the spin density in the latter complex. The doublet with a_H = 1.58 mT may be ascribed to the HFI with the ring proton of **1** in the para position to the radical center.[7] The doublet with a_H = 0.24 mT is, apparently, the result of the splitting of the Zeeman levels of the unpaired electron by the proton in the *ortho* position. This suggestion is confirmed by the fact that the ESR spectrum of the complex under consideration remains unchanged when the hydroxyl proton of the semiquinone radical is replaced by deuterium in the CD_3OD medium (see Fig. 2, *b*). The absence of splitting by the hydroxyl group of the complex of **1** with water is evidently due to the rupture of the five-membered chelate bridge $^{\cdot}$OCCOH in the radical, because the hydroxyl proton is strongly bonded with water and the hydroxyl group is forced out of the benzene ring plane. This, in turn, may lead to the well-known effect of compensation for the negative constant of HFI with the hydroxyl proton of **1** by the positive contribution of hyperconjugation to the spin polarization of the OH bond.[8—10] Similar ESR spectra of complexes of **1** with water are observed only in media that can stabilize them through specific solvation; *i.e.*, in ethers and alcohols, but not in toluene, hexane, *etc.*

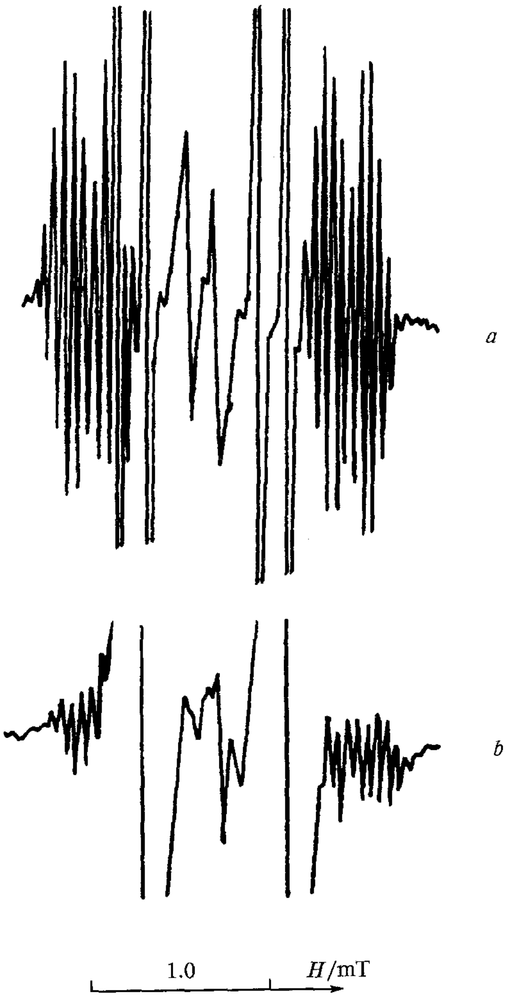
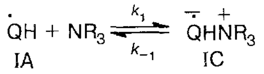


Fig. 2. ESR spectra of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl in (*a*) THF—H_2O mixture at 233 K and (*b*) CD_3OD—THF mixture at 253 K.

Toluene is known to dissolve water, the content of which can be as high as 0.02 % at saturation.[11] It was of interest to reveal the effect of water admixtures in an organic solvent on the kinetics of the transfer and exchange of a proton between semiquinone radicals (SR) and amines. The parameters of the transfer of a proton from SR **1** to triethylamine in toluene saturated with water were estimated from the dynamic ESR spectra:[12]



$$\underset{\text{IA}}{\dot{Q}H} + NR_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{IC}}{\overset{\cdot - \ +}{QHNR_3}} \qquad (3)$$

The experimental data are as follows: K_{eq}(293 K) = 13.5 L mol^{-1}, ΔH = −43.1 kJ mol^{-1}, k_1(293 K) = $1.6 \cdot 10^9$ L (mol s)$^{-1}$, E_1 = 22.4 kJ mol^{-1}, E_{-1} = 65.2 kJ mol^{-1}, and k_{-1} (293 K) = $1.1 \cdot 10^8$ s^{-1}. For comparison, the analogous parameters of reaction (3) in anhydrous toluene are: K_{eq} (293 K) = 9.7 L mol^{-1}, ΔH = −107.8 kJ mol^{-1}, k_1 (293 K) = $7.7 \cdot 10^8$ L (mol s)$^{-1}$, E_1 = 10.5 kJ mol^{-1}, k_{-1} (293 K) = $8.7 \cdot 10^7$ s^{-1}, E_{-1} = 48.1 kJ mol^{-1}.

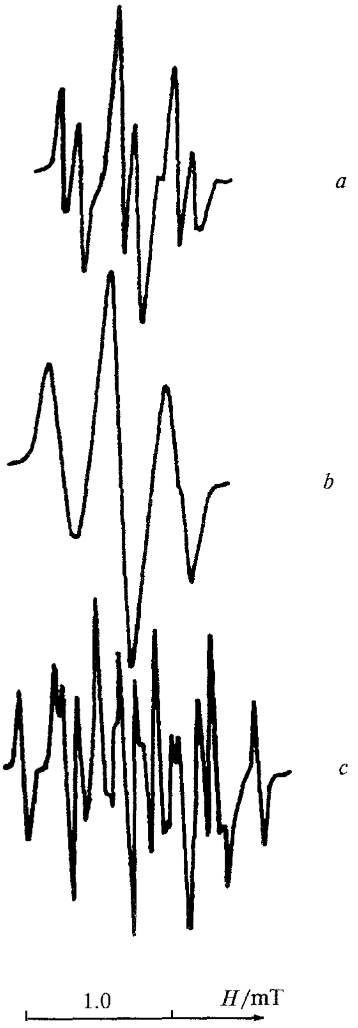


Fig. 3. ESR spectra of semiquinone radical **1** in the mixtures: (*a*) toluene—water—triethylamine at 283 K, [TEA] = $2.0 \cdot 10$ mol L^{-1}; (*b*) toluene—water—diethylamine at 333 K, [DEA] = $5.0 \cdot 10$ mol L^{-1}; and (*c*) diethylamine—water (4:1) at 353 K.

The ESR spectra of the **1**—toluene—triethylamine—H_2O system (Fig. 3, *a*) show that the presence of water does not lead to notable loosening of the ion pairs of 3,6-di-*tert*-butyl-ortho-semiquinone with triethylammonium cations, which occurs in the tributylphosphate medium.[12] It may be concluded that the water admixtures in this acid-base mixture result mainly in the polarization of the OH bond in **1**, which brings about an increase in the kinetic acidity of the semiquinone radical. In other words, water catalyzes the proton transfer. Additionally, water solvates the molecules of the reacting partners and the ion pair produced, which leads to an increase in the activation barriers and to a shift of the equilibrium of reaction (3) to the right. The kinetic parameters of proton exchange between SR **1** and diethylamine in the water-toluene mixture

$$\dot{Q}H + \overset{*}{H}NR_2 \rightleftharpoons \dot{Q}H^* + HNR_2 \qquad (4)$$

are: k_{exch} (293 K) = $4.7 \cdot 10^9$ L mol^{-1} and E_{exch} = 1.3 kJ mol^{-1}. The analogous parameters of reaction (4) in anhydrous toluene are: k_{exch} (293 K) = $3.1 \cdot 10^9$ L mol^{-1} and E_{exch} = 4.3 kJ mol^{-1} (see Ref. 2). It follows that the effect of water on the rate of proton exchange is less pronounced than its effect on the kinetics of protolysis of semiquinone radicals. This difference may be explained by the fact that the exchange proceeds in the relatively stronger complexes formed through two cyclic type hydrogen bonds.[13] However, when the system is heated the ESR spectrum shows the HFS lines characteristic of a loose ion pair consisting of a semiquinone anion-radical with a diethylammonium cation, which are shifted upfield compared to the signal of the neutral radical (see Fig. 3, *b*). The loosening of the ion pair and the preceding rupture of the cyclic complex with the hydrogen bonds inhibit the "fast" reaction of intermolecular proton exchange between SR **1** and the secondary amine. When SR **1** is heated in a mixture of diethylamine and water (4:1) at 80 °C for 15 min, its ESR spectrum shows a triplet split by the nitrogen atom and by one of the NH protons of the ammonium cation (Fig. 3, *c*); the HFI constants are 0.38 and 0.23 mT, respectively. There is also a triplet from two ring protons of the semiquinone radical with a_H = 0.28 mT. This ESR spectrum apparently belongs to the contact ion pair of 3,6-di-*tert*-butyl-ortho-semiquinone with a diethylammonium cation solvated by water molecules. HFS from counter ions has frequently been observed earlier for ion pairs of different anion-radicals with cations of alkali metals and ammonium[14].

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