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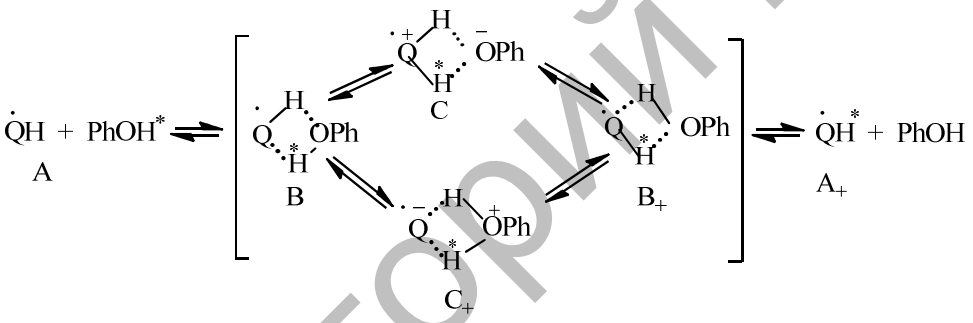
Investigation of intermolecular proton exchange 3,6-di-tert-butyl-2-hydroxyphenoxyl with phenol by ESR spectroscopy method

The intermolecular proton exchange reactions was study between radical 3,6-di-tert-butyl-2-hydroxyphenoxyl and melt of phenol by ESR spectroscopy method. Kinetic parameters of the intermolecular proton exchange reactions was presented. Phenol has been weaker protolytic reactivity than of carboxylic acids and phenol as a medium slows intermolecular proton exchange were shown.

Key words: ESR-spectroscopy, spin probe, semiquinone radical, phenol, 3,6-di-tert-butyl-2-hydroxyphenoxyl, OH-acids, proton exchange reactions, Bloch equation.

The stable semiquinone radical 3,6-di-tert-butyl-2-hydroxyphenoxyl (I), was used as acid spin probe (QH) for investigations of protolytic ability of different acids and bases such as: carbonic acids, alcohols, tertiary amines, alkaloids, nitrogen heterocycles etc in medium of organic solutions [1].

We was investigated system radical I — phenol. The reaction of intermolecular proton exchange is represented by the following scheme:

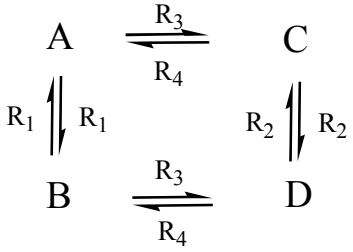


(1)

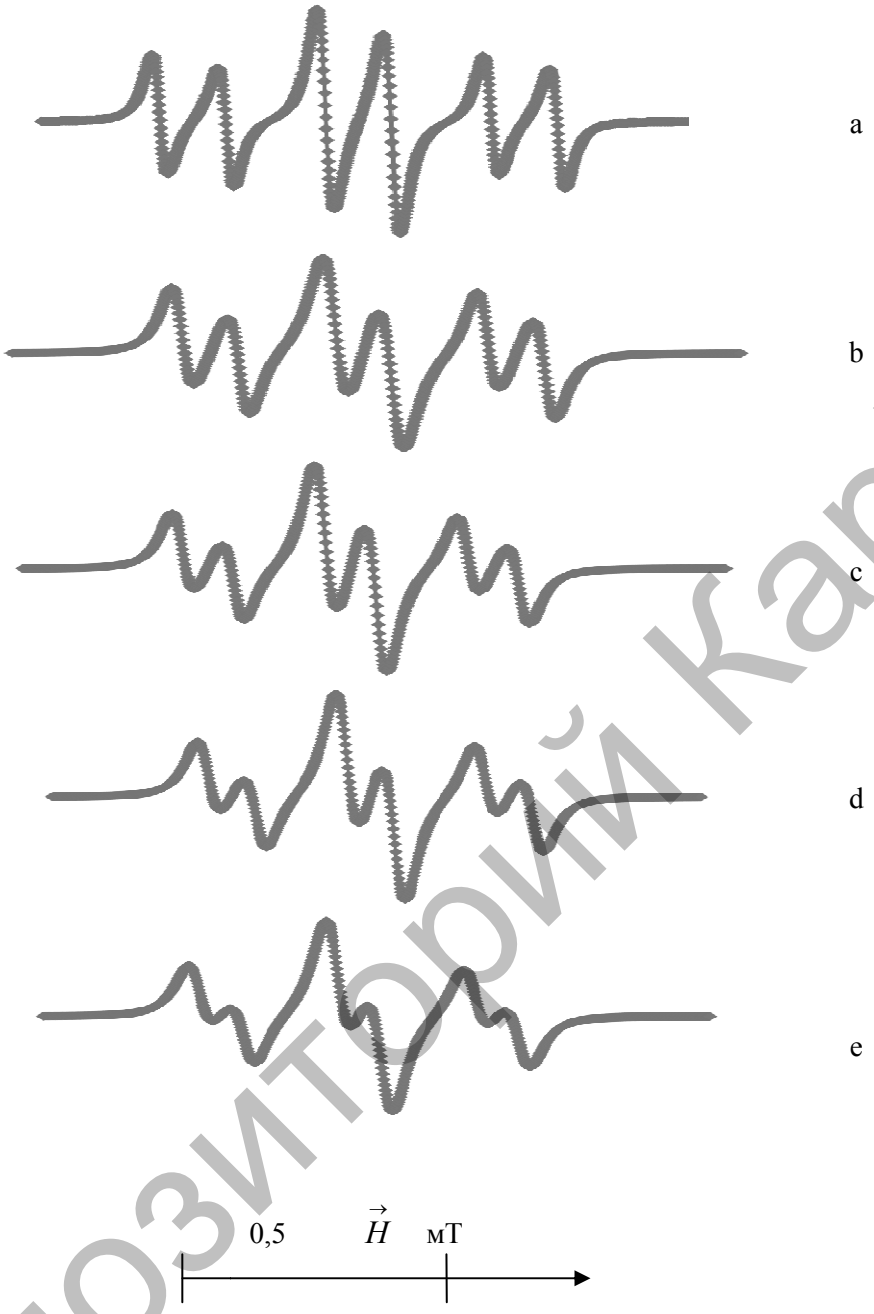
where QH — radical; PhOH — phenol; A and A_+ denote various forms of semiquinone radical differing spin of the hydrogen atom.

The ESR spectra of the spin probe — stable semiquinone radical 3,6-di-tert-butyl-2-hydroxyphenoxyl presented triplet of doublets. Figure gives the ESR spectra of the radical I in the melt of phenol (PhOH concentration 10.6 mol/l) as a function of the temperature. As can be seen from figure 1, each component of the triplet (aH = 0,39 mT) due to interaction of the unpaired electron with the ring protons and split into a doublet (aHOH = 0,162 mT) on account of the proton of the OH group, is broadened, the broadening increases with increasing temperature. An analogous dependence is observed in the ESR spectra of the investigated radical and in the presence others acids. In accord with the theory, such broadening of the lines in the ESR spectra is accompanied by a decrease in the hyperfine interaction [2]. The ESR spectrum of the radical undergoes a characteristic broadening of the lines corresponding to the intermolecular proton exchange, broadening increases with increasing temperature.

The protolytic processes of intermolecular proton exchange in non-aqueous solutions with various proton donors, with given the radical intramolecular processes can be described by the following scheme:



(2)



Temperature, K: *a* — 347; *b* — 396; *c* — 448; *d* — 473; *e* — 498; concentration of PhOH — 10.6 mol/l

Figure 1. ESR spectra of 3,6-di-tert-butyl-2-hydroxyphenoxyl in the melt of phenol

Four-jump model and the modified Bloch equation is the basis of the developed program for the simulation of the ESR spectra of the radical and comparison with experimental data [3–5]. System of equations derived from the modified Bloch equations

$$\begin{cases} 0 = -\langle G_A \rangle (\alpha_A + R_1 + R_3) + \langle G_B \rangle R_2 + \langle G_C \rangle R_4 - i\gamma_e H_1 M_0 P_A \\ 0 = -\langle G_B \rangle (\alpha_B + R_2 + R_3) + \langle G_A \rangle R_1 + \langle G_D \rangle R_4 - i\gamma_e H_1 M_0 P_B \\ 0 = -\langle G_C \rangle (\alpha_C + R_2 + R_4) + \langle G_A \rangle R_3 + \langle G_D \rangle R_1 - i\gamma_e H_1 M_0 P_C \\ 0 = -\langle G_D \rangle (\alpha_D + R_1 + R_4) + \langle G_B \rangle R_3 + \langle G_C \rangle R_2 - i\gamma_e H_1 M_0 P_D \end{cases}$$

where R_1, R_2 — rates tautomeric transfers; R_3, R_4 — rates intermolecular proton exchange; $\alpha_A = 1/T_2 + i(\omega - \omega_A)$, $\alpha_B = 1/T_2 + i(\omega - \omega_B)$, $\alpha_C = 1/T_2 + i(\omega - \omega_C)$, $\alpha_D = 1/T_2 + i(\omega - \omega_D)$; ω, ω_A, ω_B, ω_C, ω_D — angular

frequency and angular frequences corresponding particles A, B, C, D; T_2 — time relaxation, γ_e — magnetogyric ratio; H_1 — external magnetic field; M_0 — bulk magnetization; P_A, P_B, P_C, P_D — probabilities particles A, B, C, D.

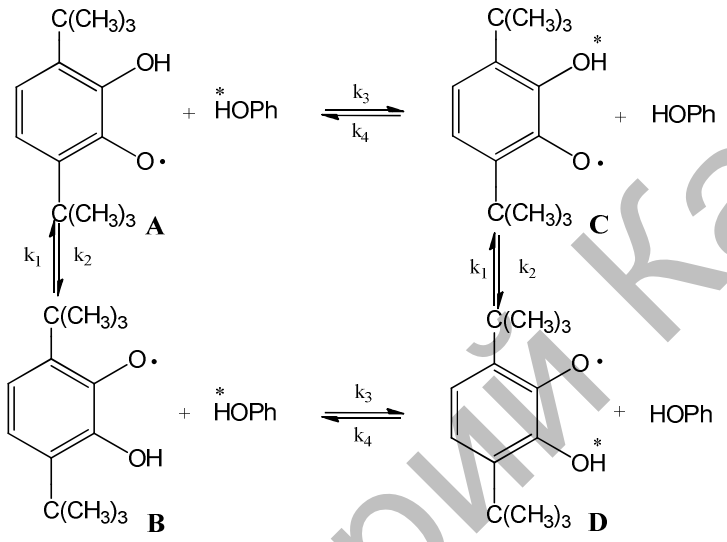
The total complex transverse magnetization G is then given by

$$\left\langle \bar{G} \right\rangle = \left\langle \bar{G}_A \right\rangle + \left\langle \bar{G}_B \right\rangle + \left\langle \bar{G}_C \right\rangle + \left\langle \bar{G}_D \right\rangle . \quad (3)$$

The intensity of absorption is proportional to the imaginary part of G:

$$I(\omega) \infty \mathrm{Im}(G). \quad (4)$$

Intermolecular proton exchange 3,6-di-tert-butyl-2-hydroxyphenoxyl with phenol taking into account tautomeric transformations can be represented by the following scheme, where A, B, C, D denote same forms of radical I differing spin of the hydrogen atom.



(5)

Kinetic parameters intermolecular proton exchange 3,6-di-tert-butyl-2-hydroxyphenoxyl with phenol were calculated using the program in the algorithmic language Fortran presented in Table.

T a b l e

Kinetic parameters of the fast intermolecular proton exchange reactions between radical I and various OH-acids

H-acid	Solvent	k_{exch} (293 K), l/mol·s	E_a, kJ/mol	pK_a
Formic	Toluene	$(4,5 \pm 0,2)\cdot 10^7$	7,1±0,3	3,75
Acetic	Toluene	$(5,1 \pm 0,7)\cdot 10^7$	13,4±0,4	4,75
Succinic	Toluene	$(8,4 \pm 0,5)\cdot 10^6$	11,1±0,6	4,21
Abietic	Toluene	$(2,2 \pm 0,1)\cdot 10^8$	7,7±0,3	–
Phenol	Phenol	$(1,0 \pm 0,5)\cdot 10^6$	13,1±0,9	–

EPR-spectroscopic kinetic data represented in Table show that that phenol OH-acids have weaker protolytic reactivity than carboxylic acids.

Comparising of the kinetic data obtained for intermolecular exchange with acids, we can conclude has weaker protolytic properties as the medium significantly reduces the reaction rate.

References

1 *Masalimov A.S., Nikolskiy S.N., Tur A.A., Prokof'ev A.I.* EPR-spectroscopy of the proton exchange fast reactions in solutions // Physics and Chemistry of Elementary Chemical Processes: The Proceedings of VIII International Voevodsky Conference. — Novosibirsk, 2012. — P. 144.

2 *Masalimov A.S.* EPR spectroscopy of fast protolytic reactions // Materials of I[st] Russian-Kazakhstan International Conference on Chemistry and Chemical Technology. — Tomsk, 2011. — P. 553–558.

3 Investigation of Rates and Mechanism of Reactions / Ed. by G.Hammes. — New York: Wiley and Sons, 1974. — P. 627.

4 *Weil J.A., Bolton J.R.* Electron Paramagnetic Resonance, Elementary Theory and Applications. — New York: John Wiley & Sons, 2007.

5 CRC Handbook of Chemistry and Physics. 86th Edition. — New York, 2006. — P. 8–42.

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3,6-Ди-үш.бутил-2-гидроксифеноксилдің фенолмен молекулааралық протон алмасуын ЭПР-спектроскопия әдісімен зерттеу

Мақалада ЭПР-спектроскопия әдісі арқылы 3,6-ди-үш-бутил-2-гидроксифеноксилдің фенолмен молекулааралық протон алмасу реакциялары зерттелді. Молекулааралық протон алмасу реакцияларының кинетикалық өлшемдері ұсынылды. Карбон қышқылдарымен салыстырғанда фенолда орта әсерінен молекулааралық протон алмасудың баяулауына байланысты протондану реакциялық қабілеттілігі төмен екендігі көрсетілді.

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Исследование межмолекулярного протонного обмена 3,6-ди-трет.бутил-2-гидроксифеноксила с фенолом методом ЭПР-спектроскопии

В статье методом ЭПР-спектроскопии изучена межмолекулярная реакция протонного обмена между радикалом 3,6-ди-трет-бутил-2-гидроксифеноксилом и фенолом. Представлены кинетические параметры межмолекулярной реакции протонного обмена. Показано, что фенол обладает меньшей протолитической реакционной способностью, по сравнению с карбоновыми кислотами, и как среда замедляет межмолекулярный протонный обмен.