

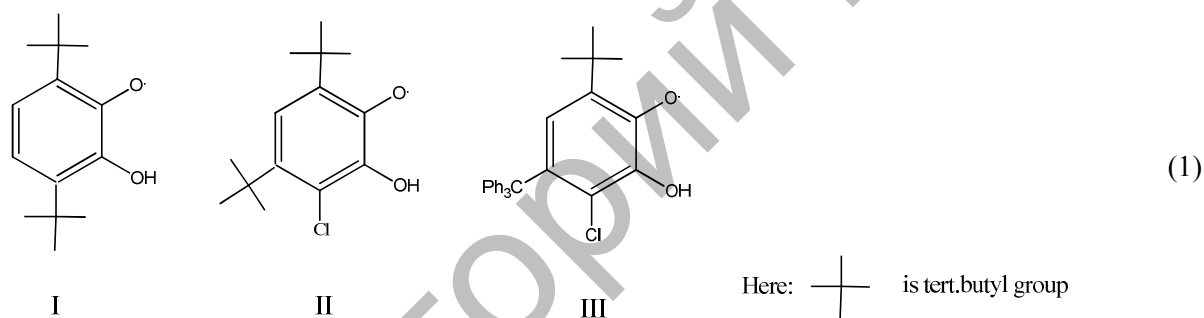
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(E-mail: masalimov-as@mail.ru)**EPR-spectroscopy of the fast proton exchange reactions in solutions**

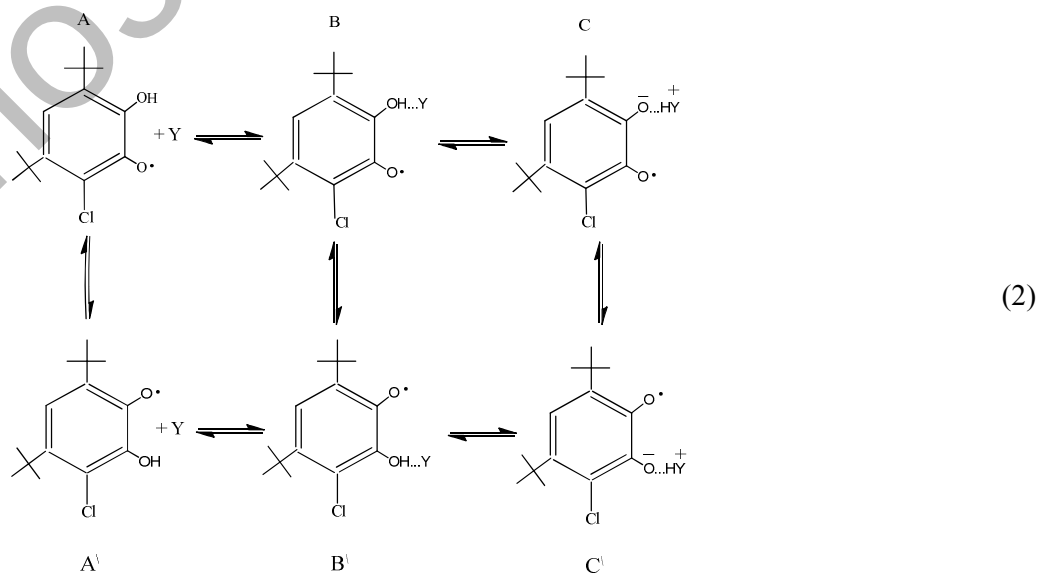
Kinetic parameters of the fast intermolecular proton exchange reactions between radical 3,6-di-tert.butyl-2-oxyphenoxyl and different H-acids in toluene solutions obtained by ESR spectroscopy method are presented. NH-acids have more protolytic reactivity than carboxylic acids. Values of various physico-chemical properties for some H-acids, such as ionization potential, electron affinity, proton affinity and energy of deprotonation were obtained by quantum chemical calculations in the program «Gaussian-2009».

Key words: EPR-spectroscopy, semiquinone radicals, H-acids, proton exchange reactions, quantum-chemical investigations.

The stable semiquinone radicals were used as acid spin probes (XH) for EPR-spectroscopic determination of the rate constants of fast intermolecular proton transfer (IPT) and exchange (IPE) reactions in solutions [1]. For example, stable semiquinone radicals: 3,6-di-tert.butyl-2-oxyphenoxyl (I), 4,6-di-tert.butyl-3-chlorine-2-oxyphenoxyl (II) and 4-triphenylmethyl-6-tert.butyl-3-chlorine-2-oxyphenoxyl (III) generated by mixture corresponding to orthoquinone and pyrocatecol in EPR glass-tube, containing organic solution of investigated chemical systems [2, 3].



It is necessary to say that the high intramolecular mobility of hydroxyl hydrogens atom in semiquinone radicals I – III determine nanosecond homolytic tautomerism. Therefore radicals I – III have property of the dual protolytic reactivity. With a glance of tautomerism the general scheme of intermolecular proton transfer reactions for spin semiquinone probes represents as:



Here: Y is the molecule of proton-acceptor, for example, tertiary amine

The computation of kinetic parameters like this fast IPE reactions in liquids was made in accordance with modified F.Bloch equations for several magnetic resonance line broadening effects, connecting with chemical protons spin exchange processes [1].

$$v_{ex} = \frac{\gamma_e \tilde{a}_H^{OH}}{2\sqrt{2}} \left[1 - \left(\frac{\tilde{a}_H^{OH}}{a_H^{OH}} \right)^2 \right]^{1/2} \quad (5)$$

Simulation of dynamic EPR spectra was made by the use of fortran program of N.Hirota, adapted for our IPE-reactionary system (2)–(4) [1, 5]. It should be said that short-lived intermediates of IPE-reaction B, B₊ and C, C₊ do not appear and dynamic EPR spectra (see figure 1) contains summarized kinetic information about two-channel IPE-reaction (4).

Table 1

Kinetic parameters of the fast IPE-reactions between radical I and different H-acids in toluene solutions

H-acid	k_{ex} (293 K) l/mol·s	E_a kJ/mol	pK _a
Formic	$(4,5 \pm 0,2) \cdot 10^7$	7,1±0,3	3,75
Acetic	$(5,1 \pm 0,7) \cdot 10^7$	13,4±0,4	4,75
Succinic	$(8,4 \pm 0,5) \cdot 10^6$	11,1±0,6	4,21
Abietic	$(2,2 \pm 0,1) \cdot 10^8$	7,7±0,3	–
Diethylamine	$(3,1 \pm 0,7) \cdot 10^9$	4,0±0,4	10,93
Diethylamine	$(2,3 \pm 0,1) \cdot 10^9$	3,7±0,5	11,01
Ethylenediamine	$(6,8 \pm 0,1) \cdot 10^9$	10,4±0,2	–
Hexamethylenediamine	$(7,2 \pm 0,1) \cdot 10^9$	8,7±0,9	–
Ephedrine	$(3,7 \pm 0,2) \cdot 10^9$	2,3±0,5	–
Pseudoephedrine	$(4,6 \pm 0,2) \cdot 10^8$	26,0±0,5	–
Anabasine	$(8,7 \pm 0,1) \cdot 10^8$	5,3±0,3	–

EPR-spectroscopic kinetic data represented in table 1 show that NH-acids have more protolytic reactivity than carboxylic acids. For explanation of this kinetic effect we have studied several physicochemical properties of known molecules presented in table 2 by ab-initio method contained in quantum chemical programs packet «Gaussian-2009» [6–11].

Table 2

The physicochemical properties of different simple acids and bases, obtained by UHF 3–21G ab-initio method

H-acids	–IP, eV	–EA, eV	PA, eV	–DPE, eV
HOH	10,2881	5,8816	8,3070	19,5200
CH ₃ OH	9,0160		8,8956	18,3197
ĈH ₂ OH	7,0663	2,4965	8,3747	17,4008
CH ₃ CH ₂ OH	8,7268		9,0871	18,1611
ĈH ₂ CH ₂ OH	8,0106	2,1823	9,1255	18,1082
CH ₃ CH ₂ CH ₂ OH	8,6453		9,1468	18,0965
ĈH ₂ CH ₂ CH ₂ OH	7,8003	2,4527	9,1064	17,9920
HCOOH	9,4855	2,6624	7,5833	16,2066
CH ₃ COOH	8,8767	2,7611	8,1016	16,3585
CF ₃ COOH	10,3745	0,9973	6,9294	15,0084
CCl ₃ COOH	12,0497			14,6575
HCl	11,8418		4,9062	14,0372
HNO ₃	10,2874	–0,3313	7,2328	14,7820
H ₃ PO ₄	8,1912	1,7598	8,0519	15,3807
H ₂ SO ₄			7,3467	14,1206
NH ₃	8,0530	6,5410	9,8411	20,0334
CH ₃ NH ₂	7,2285	6,3192	10,2776	19,4600
(CH ₃) ₂ NH	6,6263		10,5609	18,9794

For calculation of indicated physicochemical data known formulas were used, for example: the value of ionization potential of molecule (IP) is equal to

$$IP = E_M - E_{M^+}, \quad (6)$$

where E_M — molecules' total energy; E_{M^+} — total energy of correspondent cation of this molecule. The value of proton affinity (PA) is equal to:

$$PA = E_M - E_{MH^+}. \quad (7)$$

Here: E_{MH^+} — total quantum-chemical energy of protonated molecule. Electron affinity (EA) presented with the following expression:

$$EA = E_M - E_{M^-}. \quad (8)$$

The energy of deprotonation (DPE) of H-acid molecules (MH) is equal to:

$$DPE = E_{MH} - E_{M^-}. \quad (9)$$

It seems from scheme (4) that the fast IPE reaction is the cooperative concerted process going in four-centered cyclic complex with 2 hydrogen bonds. It is naturally to suppose that molecular dynamic in hydrogen bridge with more strong acid-base pair will be determine the value of common rate of the fast IPE reaction in liquid medium. For example in case of mixture I — secondary amine the strength of hydrogen bridge OH...N higher than in acid-base system I – OH-acids and the first tunneling of acid proton inside OH...N-bridge involves next return the proton of conjugate acid to more slow second acid-center. The calculated data presented in table 2 show that the proton-acceptor ability of basic molecules depends on values of ionization potentials: the lowest value of IP the more value of PA of bases [10].

The amino-alcohol ephedrine exchange in IPE-reaction its NH-proton and produce ionic pair C_+ on cooling reactive mixture. The ionic pair C generate in reactions radical I with more stronger H-acids. The difference between kinetic values for alkaloids ephedrine and pseudoephedrine may be explained with availability of intramolecular hydrogen bond in threo-isomer of 1-phenyl-2-methylaminopropanol-1. The necessity of destruction this hydrogen bond bring to increasing activation energy and decreasing the rate constant of IPE reaction for pseudoephedrine in regard to ephedrine. The values of experimental by EPR derived kinetic data for irreversible IPT-reaction between spin probe I and pseudoephedrine were obtained: $k_1(293K) = 1.8 \cdot 10^9$ l/mol·c, $E_1 = 28,0$ kJ/mol.

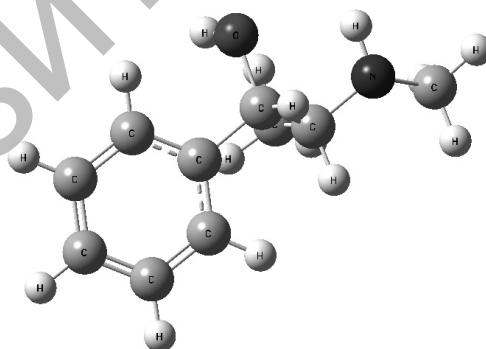


Figure 2. Ab-initio (3–21G)-structure of pseudoephedrine molecule with intramolecular hydrogen bond

Due to the presence of intramolecular hydrogen bond pseudoephedrine molecule may be display the nature of tertiary amines i.e. realize fast irreversible reaction of proton transfer according to schemes (2) and (3).

Alkaloid anabasine has two basic centers, but in protolytic reaction only morpholinyl substituent with NH-group participates. The dynamic EPR spectra of fast IPE reaction between spin probe I and anabasine shown in figure 1. Under cooling of reactionary system form the contact ionic pair with hyperfine splitting on nitrogen's atom of ammonium cation.

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Ерітінділердегі жылдам протон алмасу реакцияларының ЭПР-спектроскопиясы

ЭПР-спектроскопия әдісі арқылы алынған толуол ерітінділеріндегі әр түрлі Н-қышқылдарының 3,6-ди-үш.бутил-2-оксифеноксил радикалымен молекулааралық жылдам протон алмасу реакцияларының кинетикалық өлшемдері көрсетілген. Карбон қышқылдарымен салыстырғанда NH-қышқылдары жоғары протондану реакциялық қабілеттілігіне ие екендігі көрсетілген. «Gaussian-2009» бағдарламасында кванттықхимиялық есептеулер көмегімен кейбір Н-қышқылдар үшін иондану потенциалы, электронға жақындығы, протонға жағындығы және депротондану энергиясы тәрізді әр түрлі физико-химиялық қасиеттерінің мәндері алынды.

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ЭПР-спектроскопия быстрых реакций протонного обмена в растворах

Представлены кинетические параметры быстрых межмолекулярных реакций протонного обмена между радикалом 3,6-ди-трет. бутил-2-оксифеноксидом и различными Н-кислотами в растворе толуола, полученные методом ЭПР-спектроскопии. Показано, что NH-кислоты имеют большую протолитическую реакционную способность, чем карбоновые кислоты. В программе «Gaussian-2009» с помощью квантовохимических расчетов получены значения различных физико-химических свойств для некоторых Н-кислот, таких как потенциал ионизации, средство к электрону, средство к протону и энергия депротонирования.

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