

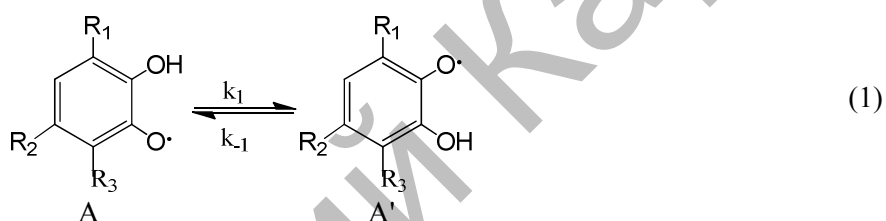
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(E-mail: masalimov-as@mail.ru)**Quantum-chemical investigations of the dual protolytic activity
of several semiquinone radicals**

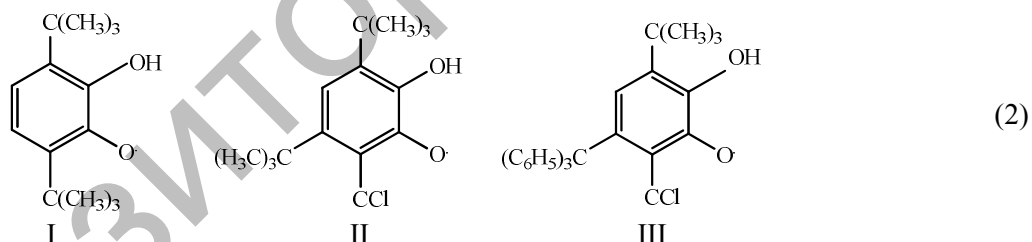
This investigation devoted for quantum chemical explanation of mechanism of intramolecular tautomerism in stable semiquinone radicals and dual protolytic reactivity of this paramagnetic H-acids, obtained formerly by dynamic EPR spectroscopy.

Key words: semiquinone radicals, EPR spectroscopy, protolytic reaction, proton transfer reaction, quantum chemical calculations, ab initio, molecular orbital.

The fast nanosecond radical tautomerism, due to by homolytic intramolecular migration of hydrogens atom, was discovered in the next stable screened orthoxy-phenoxyyls [1]:



Here: $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{H}$ is the simple orthoxyphenoxyyl (OP); $\text{R}_1 = \text{R}_3 = \text{C}(\text{CH}_3)_3$, $\text{R}_2 = \text{H}$ is 3,6-di-tert-butyl-2-oxyphenoxyyl (I); $\text{R}_1 = \text{R}_2 = (\text{CH}_3)_3$, $\text{R}_3 = \text{Cl}$ is 4,6-di-tert-butyl-3-chlorine-2-oxyphenoxyyl (II); $\text{R}_1 = (\text{CH}_3)_3$, $\text{R}_2 = \text{C}(\text{C}_6\text{H}_5)_3$, $\text{R}_3 = \text{Cl}$ is 4-threphenylmethyl-6-tert-butyl-3-chlorine-2-oxyphenoxyyl (III).



It should be noted that if the fast radical tautomerism in OP and I has degenerate character, because electronic structures of the reactionary isomers are identical, but this process in radicals II and III is nondegenerate, since tautomers of these compounds have different spatial molecular forms. The Table 1 illustrates values of kinetic and thermodynamic parameters of the fast homolytic intramolecular hydrogen transfer inside of stable semiquinone radicals, obtained by dynamic EPR-spectroscopy [2]. Physicochemical data for short-lived unsubstituted oxyphenoxyyl OP were studied by K.Lot in medium of mixture of dioxane and carbon tetra-chloride [3].

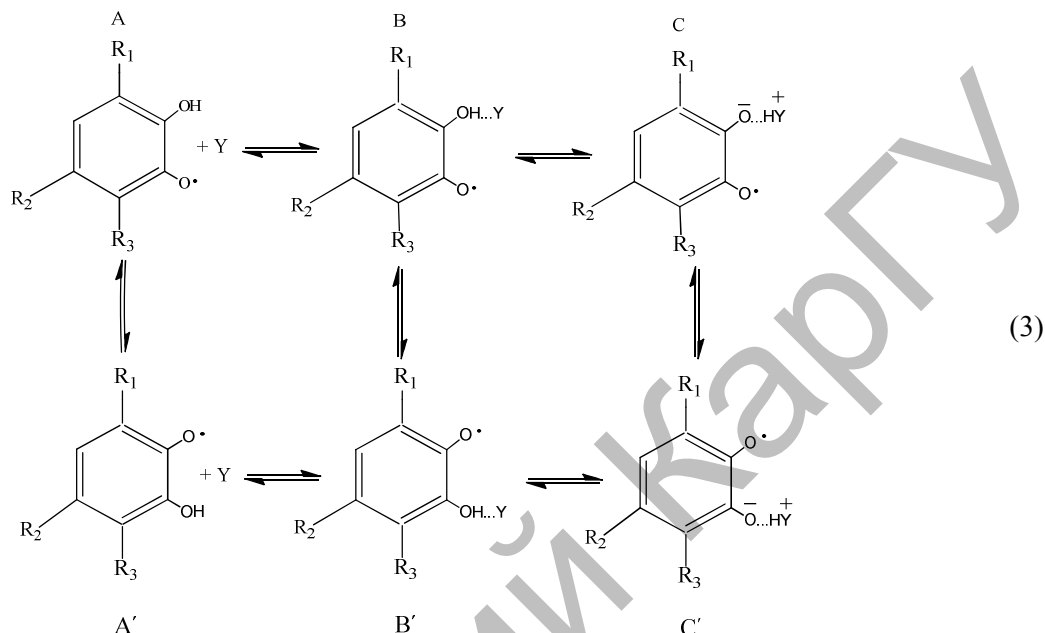
Table 1

**Kinetic and thermodynamic data of the intramolecular radical tautomerism in toluene solutions
of screened orthoxyphenoxyyls. Temperature 293 K**

Radicals	K_e	$\Delta H \pm 0,5$, kJ/mol	k_1 , c^{-1}	$E_1 \pm 1,0$, kJ/mol	k_{-1} , c^{-1}	$E_{-1} \pm 5,0$, kJ/mol
OP	1	0	$2,1 \cdot 10^7$	34,3	$2,1 \cdot 10^7$	34,4
I	1	0	$2,4 \cdot 10^9$	12,2	$2,4 \cdot 10^9$	12,2
II	1,2	1,38	$4,7 \cdot 10^8$	17,4	$3,1 \cdot 10^8$	15,9
III	5,5	-9,03	$3,8 \cdot 10^8$	8,4	$6,9 \cdot 10^7$	23,0

The data of table 1 show that the space tert-butyl substituents in radicals I, II and III increase values of monomolecular hydrogen transfer rate constants k_1 and k_{-1} in comparison with nonsubstituted oxyphenoxyl OP.

The fast intramolecular tautomerism in stable oxyphenoxyls I–III determines the phenomena of the dual protolytic reactivity of these paramagnetic OH-acids:



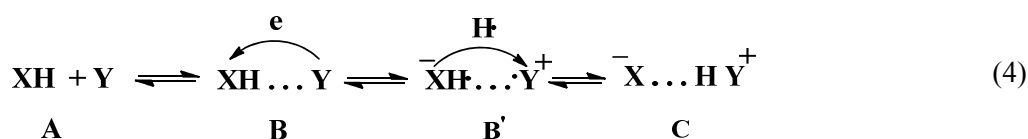
The Table 2 illustrates the values of physicochemical data of the fast protolytic reaction between stable radicals and alkaloid thebaine in toluenes medium, obtained by dynamic EPR spectroscopy.

Table 2

Kinetic and thermodynamic parameters of the fast reversible proton transfer reaction between semiquinone radicals I–III and thebaine in toluenes medium

Radicals	$K_e(293K)$, l/mol	$-\Delta H \pm 3,0$, kJ/mol	$k_1(293K)$, l/mol·c	$E_1 \pm 6,0$, kJ/mol	$k_{-1}(293K)$, c ⁻¹	$E_{-1} \pm 4,0$, kJ/mol
I	1,8	25,1	$5,4 \cdot 10^8$	17,2	$3,7 \cdot 10^7$	48,2
II	$8,5 \cdot 10^2$	47,3	$2,2 \cdot 10^8$	1,7	$2,6 \cdot 10^5$	49,0
III	$6,2 \cdot 10^3$	63,7	$3,0 \cdot 10^7$	1,0	$4,9 \cdot 10^3$	64,6

Here: k_1 is the value of summary rates constant of the direct protonation reactions $A \rightleftharpoons C$ and $A' \rightleftharpoons C'$, k_{-1} is the value of summary rates constant of the inverse protonation reactions $C \rightleftharpoons A$ and $C' \rightleftharpoons A'$. The equilibriums constant of the protonations reaction (3) is equal $K_e = k_1 / k_{-1}$. The experimental data of table 2 show that if the values of thermodynamic acidity (K_e) of oxyradicals increase in row I–II–III, but the values of kinetic acidity (k_1) of paramagnetic proton-donors decrease in this row. For explanation of this indicated experimental results was used the new model of acid-base protolytic reactions mechanism, which involves the process of one electron transfer as the primary elementary act of the fast reaction (3) [4, 5]:



The such mechanism of the fast protolytic reaction treats H-acids molecule XH as oxidant and bases molecule Y as reductant with correspondent values of ionization potentials (IP) required for the passing of intermolecular proton transfer reaction. It is possible to say for example, that the value of ionization potentials for alkaloid thebaine is equal $IP = 5,84$ eV and for atom of sodium $IP = 5,13$ eV. The certain typical

H-acids have values of ionization potentials $IP(H_2O) = 10,45$ eV, $IP(HCl) = 11,86$ eV, $IP(CH_3COOH) = 9,36$ eV.

It should be noted that the inverse proportional dependence between values of thermodynamic and kinetic acidity of radicals I–III presented on table 2, evidently, determines by steric effect in the protolytic reaction with molecule of natural alcaloid thebaine, having specific geometry and electronic structure.

Tautomerism is the equilibrium isomerism and the experimental determination a values of kinetic acidity for each individual isomer of radicals I, II and III represent the unsolved problem. But using of calculating methods of modern quantum chemistry allows to study the values of ionization potential for each isomers of paramagnetic acids — oxyphenoxyls I–III. One might suppose that the value of ionization potential of molecule maybe the better physical parameter for description of the oxidative properties of H-acids.

On Table 3 presented the calculated by nonempirical quantum chemical method values of ionization potential for different tautomeric structures of stable semiquinone radicals I–III and for comparison gives the analogues data of radical 4,6-di-tert-butyl-2-oxyphenoxyl (IV) and 4-triphenylmethyl-6-tert-butyl-2-oxyphenoxyl (V) [5–7].

Table 3

The values of total energy and ionization potentials for isomers of semiquinone radicals, obtained by UHF ab initio method with using 3–21G atomic basis

Isomer	Structure	E_{tot} , a.u.	IP , eV
IA		-688,28672500	-7,71315068
IIA		-1144,98141680	-7,94670227
IIA'		-1144,98057790	-7,75378609
IIIA		-1713,30380200	-7,91958206
IIIA'		-1713,30357220	-7,65534847

Table 3 continued

Isomer	Structure	E_{tot} , a.u.	IP , eV
IVA		-688,28334520	-7,70158915
IVA'		-688,28384350	-7,38364302
VA		-1256,60289980	-7,69344519
VA'		-1256,60367840	-7,19478113

It is interest to noted that the value of ionization potential for simple molecule of pyrocatechol is equal $IP = -7,18267540$ eV, while this value for corresponding paramagnetic acid or nonsubstituted 2-oxyphenoxy has more lower value $IP = -6,97378423$ eV. The calculated values of IP for isomers of radicals I–V presented on table 3 show that the one-electron ionization process of A-form are more difficult then for A'-form and they are more stronger oxydizers then A-tautomer or they have more acidity then A'-structures of semiquinone radicals. It is necessary to say that the calculated IP -data on table 3 have computer precision but no physical accuracy.

Table 4

The calculated values of enthalpy for $A \rightleftharpoons A'$ tautomeric transitions in several semiquinone radicals, obtained by UHF ab-initio method with using 3–21G atomic basis

Radicals	Calculated values of enthalpy ΔH , kJ/mol	Experimental values of $\Delta H \pm 0,5$, kJ/mol
I	0	0
II	2,20	1,38
III	0,60	-9,03
IV	-1,31	*
V	-2,04	*

Note. * — There are not tautomerism.

The calculated data presented on Table 4 show the values of energetic difference between tautomeric forms of stable radicals I–III or the enthalpies of intramolecular hydrogens atom transitions in oxyphenoxyls. It is necessary to remember that the analogous homolytic migration of hydrogens atom not observe in radicals IV and V by EPR spectroscopy. The calculated values of total energy for semiquinone radicals demonstrate that the introduce of chlorines atom to oxyphenoxyls IV and V increase the values of thermodynamic stability of the A-forms of corresponding radicals II and III.

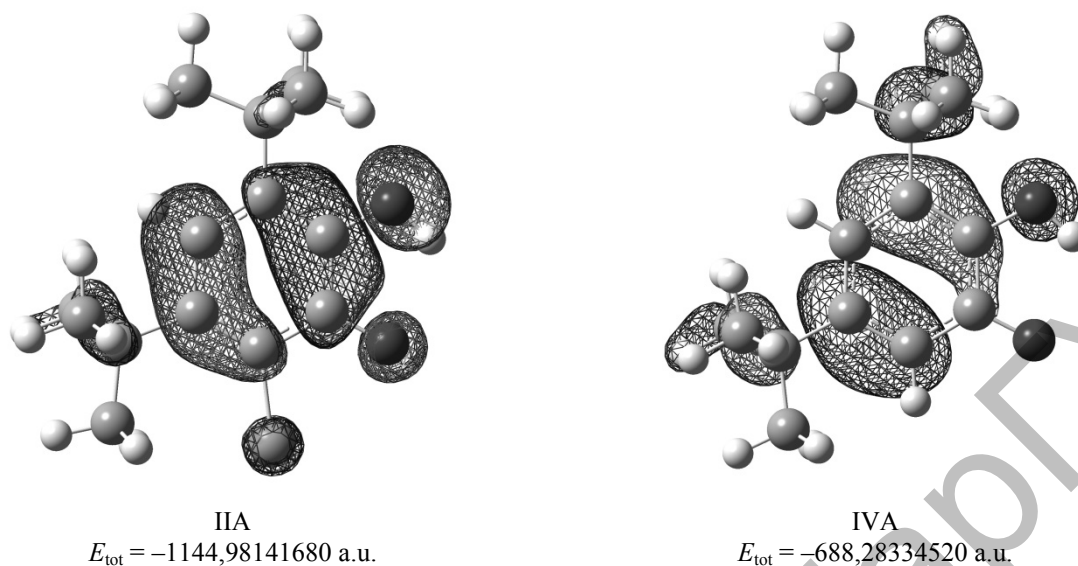


Figure 1. Electronic structures and HOMO for A-form of semiquinone radicals II and IV

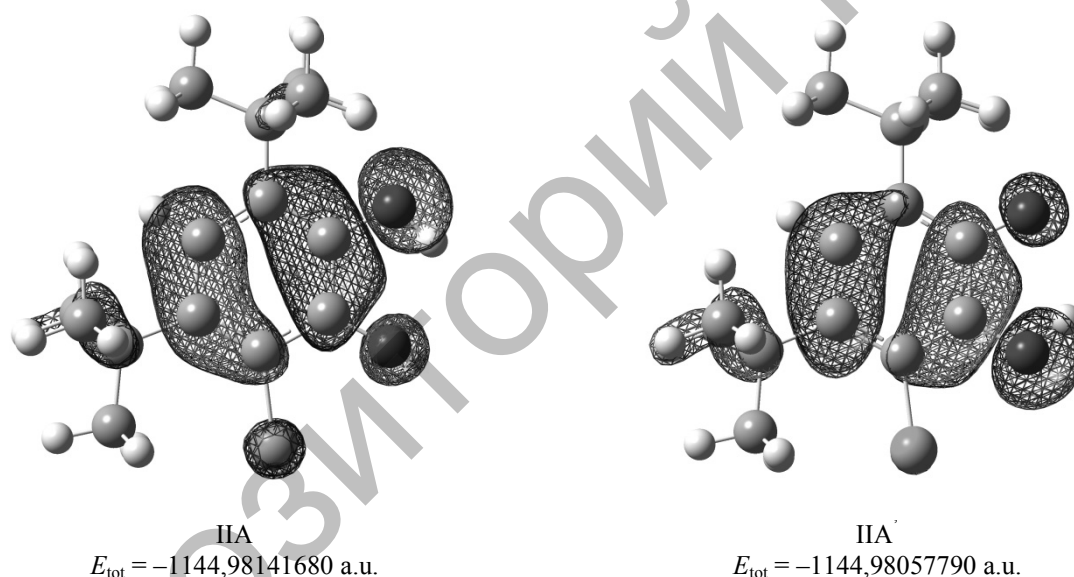


Figure 2. Electronic structures and HOMO for A and A' tautomer of radical II

The structures of higher occupied molecular orbitals (HOMO) presented on Pictures 1 and 2 show that the indicated phenomena connected with electronic conjugation of 3p-orbital of chlorines atom with π -electronic system of radicals formed by benzene ring and lone-electron pair of the oxygen atom.

References

- 1 Masalimov A.S., Nikolskiy S.N., Muldachmetov Z.M. Hydrogentropy and the fast proton transfer in semiquinone radicals // Chemical physics. — 1988. — Vol. 7, No. 8. — P. 1087–1091.
- 2 Weil J.A., Bolton J.R. Electron Paramagnetic Resonance. Elementary Theory and Applications. — New York: John Wiley&Sons, 2007. — P. 307.
- 3 Loth K., Graf F., Gunthard H. Chemical exchange dynamics and structure of intramolecular OHO bridges. An ESR and INDO study of 2-hydroxy- and 2,6-dihydroxyphenoxy1 // Chemical Physics. — North Holland Publishing Company, 1976. — № 13. — P. 95–118.
- 4 CRC Handbook of Chemistry and Physics. 86th Edition. — New York, 2006. — P. 8–42.

5 *Foresman J.B., Frish A.* Exploring Chemistry with Electronic Structures Methods. Second Edition. — Pittsburg: Gaussian Inc., 1996. — P. 302.

6 *Masalimov A.S.* The electron transfer in protolytic reactions // Book of abstracts of the 13th V.A.Fock Meeting on Quantum and Computational Chemistry. — Astana, 2012. — P. 59.

7 *Young D.C.* Computational Chemistry. — New York: Wiley&Sons, 2001. — P. 398.

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Семихинонды радикалдардың екі жақты протолиттік қабілеттілігін кванттық-химиялық зерттеу

Мақала динамикалық ЭПР-спектроскопия әдісімен зерттелген парамагнитті Н-қышқылдарының протолиттік реакциялық қабілеттілігіне және тұрақты семихинонды радикалдардың молекулалық таутомерия тетігінің кванттық-химиялық анықталуына арналған.

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Квантово-химические исследования двойственной протолитической способности семихинонных радикалов

Статья посвящена квантово-химической интерпретации механизма внутримолекулярной таутомерии в стабильных семихинонных радикалах и двойственной протолитической реакционной способности этих парамагнитных Н-кислот, изученных ранее методом динамической ЭПР-спектроскопии.