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Theoretical study of the medium polarity influence on the OH-acids strength

Deprotonation energy for a number of OH-acids theoretically estimated by UHF 6–31G *ab initio* CPCM methods using Gaussian-2009. Reducing of acids deprotonation energy with increasing of the medium polarity is shown by quantum chemical methods. Theoretical justification of EPR spectroscopic data on decrease of rate of the proton exchange reaction between semiquinone radical 3,6-di-tert-butyl-2-oxyphenoxyl and some carboxylic acids in polar media is given.

Key words: OH-acids, semiquinone radicals, protolytic reaction, proton exchange reaction, deprotonation energy, solvation, acidity and basicity, quantum chemical calculations, *ab initio*, Gaussian-2009.

According to the Brønsted-Lowry acid–base theory, acid is a hydrogenous particle of the substance, capable to be the donor of a proton, and the basis is a particle of the substance, capable to be an acceptor of a proton [1]. Acid-base reactions — is a reaction in which a proton is transferred from the acid to the base. Such reactions are called protolytic reactions. In general protolytic reaction can be described by the following equation:

$$HA + B \leftrightarrow A^- + HB^+. \quad (1)$$

Proton-donor and proton-acceptor ability of substances (their acidity and basicity) is determined by the proton affinity. Free proton does not exist in solution. Therefore equation (1) characterizing balance between acid and base, doesn't represent real system Actually all acid-base equilibrium proceed with sH solvent participation:

$$HA + sH \leftrightarrow A^- + sH_2^+, \quad (2)$$

where sH_2^+ — lyonium ion which is resulting from the process of a proton addition, i.e. a solvated proton;

$$B + sH \leftrightarrow s^- + HB^+, \quad (3)$$

where s^- — lyate ion.

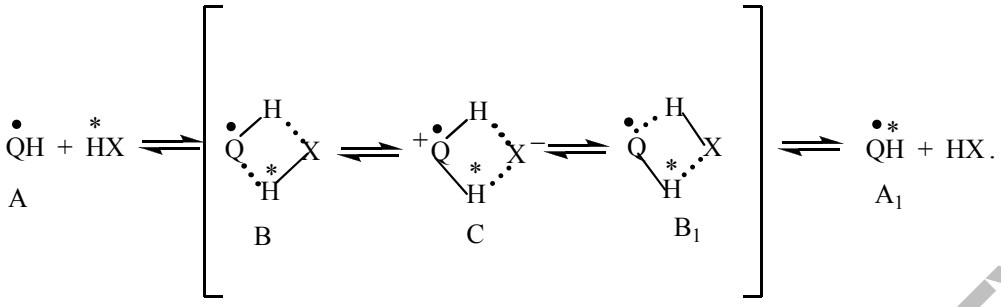
Thus, the nature of the solvent has a significant effect on the protolytic equilibrium. Change of solvent can change the direction of the acid-base reaction.

According to its acid-base properties solvents separated on aprotic and protic [2]. Aprotic solvents don't show the acid-base properties. Molecules of such substances don't give and don't attach protons. Benzene, toluene belongs to their number, hexane, carbon tetrachloride, chloroform and some other. Aprotic solvents influence to the acid-base properties of the substances dissolved in them a little.

Protic solvents have strong acid-base properties. Molecules of similar solvents are capable to give or attach protons. In protic solvent the relative strength of acids depends by nature solvent and is determined by the energy necessary for transfer of a proton from a molecule or an ion on infinitely long distance. Influence of solvent is defined by its dielectric permeability and prototropic properties. Thereof the relative strength of acids can change depending on the solvent nature.

The influence of solvated effects on kinetics of an intermolecular proton exchange reaction between semiquinone radical 3,6-di-tert-butyl-2-oxyphenoxyl (radical I) and some mono-carboxylic fatty acids was previously studied by EPR spectroscopy in KSU [3]. The following general mechanism of intermolecular

proton exchange between radical I and OH-acids was proposed on the basis of earlier conducted systematic radio-spectral studies:



(4)

As solvents were used toluene (ε=2,4), 1,4-dioxane (ε=3,0) and nitrobenzene (ε=35,5). All used solvents have the aprotic nature, i.e. their influence on photolytic equilibrium can be characterized by the dielectric constant of the medium.

Using EPR spectroscopy it was found [3] that specific rate of bimolecular reaction is ten times lower in the dioxane medium, than in indifferent solvent toluene, and also that proton exchange rate is slightly decreased with increasing dielectric constant of the medium.

It was interesting to study influence of solvent on the OH-acids strength by quantum chemistry methods. Earlier it was shown [4] that deprotonation energy can serve for the quantum-chemical characteristic of acids strength. Deprotonation energy of acid can be quantum chemical estimated as a difference between the total energy values acid and its anion:

$$HA \rightarrow A^- + H^+. \quad (5)$$

The total energy of a proton is equal to zero, therefore:

$$\Delta E_{\text{deprot.}} = E_{\text{total.}}(HA) - E_{\text{total.}}(A^-). \quad (6)$$

As the required differential size ΔE_{deprot} is some orders less than each of counted energy separately, calculations must be carried out as accurately as possible. That's why quantum-chemical evaluation of the deprotonation energy we carried out *ab initio*-UHF method in an extended basis 6–31G. Calculations were carried out by means of Gaussian-2009 software package [5].

The solvent influence at the deprotonation process was taken into account within by the Conducting Polarisable Continuum Model (CPCM). In this model, the solvent is presented as a polarizable continuum and the solute is placed in a cavity within the solvent [6, 7]. The cavity in the classical model PCM defined as a set of overlapping areas, the size of which is proportional to the van der Waals radius the corresponding atoms.

Quantum chemical calculations were performed for a homologous series of mono-carboxylic acids investigated earlier by EPR spectroscopy [3] and also for the semiquinone radical 3,6-di-tert-butyl-2-oxyphenoxyl — radical I — used as a spin probe. Calculations were carried out with full optimization of geometry by UHF 6–31G *ab initio*-method taking into account solvent within macroscopic model of CPCM. Water (ε=80) and aprotic benzene (ε=2,3), toluene (ε=2,4), chlorobenzene (ε=5,7) were taken as the solvent. Selection of solvents is caused by their different nature, range of dielectric permeability of the medium, and the parameterization of macroscopic polarized continuum model CPCM for a limited number of solvents.

Table 1

Results of quantum chemical UHF 6–31G *ab initio* CPCM calculations for a number of the studied OH-acids. Solvent — water

Acid	Acid Formula	Total energy HA, A.U.	Total energy A^-, A.U.	$\Delta E_{\text{deprot.}}$, A.U.	pK_a
Formic	HCOOH	–188,6767	–188,2053	0,4713	3,75
Acetic	CH_3COOH	–227,7119	–227,2336	0,4782	4,76
Butyric	$CH_3(CH_2)_2COOH$	–305,7487	–305,2707	0,4779	4,82
Valeric	$CH_3(CH_2)_3COOH$	–344,7672	–344,2891	0,4780	4,86
Caproic	$CH_3(CH_2)_4COOH$	–383,7857	–383,3077	0,4780	4,88
Caprylic	$CH_3(CH_2)_6COOH$	–461,8227	–461,3446	0,4781	4,89
Tridecanoic	$CH_3(CH_2)_{11}COOH$	–656,9150	–656,4369	0,4781	–
Palmitic	$CH_3(CH_2)_{14}COOH$	–773,9456	–773,4922	0,4533	–
Stearic	$CH_3(CH_2)_{16}COOH$	–852,0034	–851,5292	0,4742	–
Radical I	$C_6H_2(C(CH_3)_2)OOH$	–691,8277	–691,3333	0,4943	–

Results of quantum chemical UHF 6–31G *ab initio* CPCM calculations are presented in table 1 (solvent — water). Handbook [8] values of the p*Ka* for a number of the studied OH-acids are also given in the table 1.

Data presented in table 1 show that with growth of a carbon chain in a homological row OH-acids, acidity is decrease (p*Ka* is increase), deprotonation energy is increase from 0,47 to 0,49 A.U. This is logical, since strong acid easily gives a proton and has a lower deprotonation energy. It should be noted the big size of deprotonation energy for the radical I compared to all investigated carboxylic acids. Therefore, the radical I is the weakest acid in a studied range of OH-acids. It will play a base role in photolytic reactions with carboxylic acids.

It was interesting to present in graphical form relationship between deprotonation energy and handbook value p*Ka* for a studied range of OH-acids (solvent — water; fig. 1).

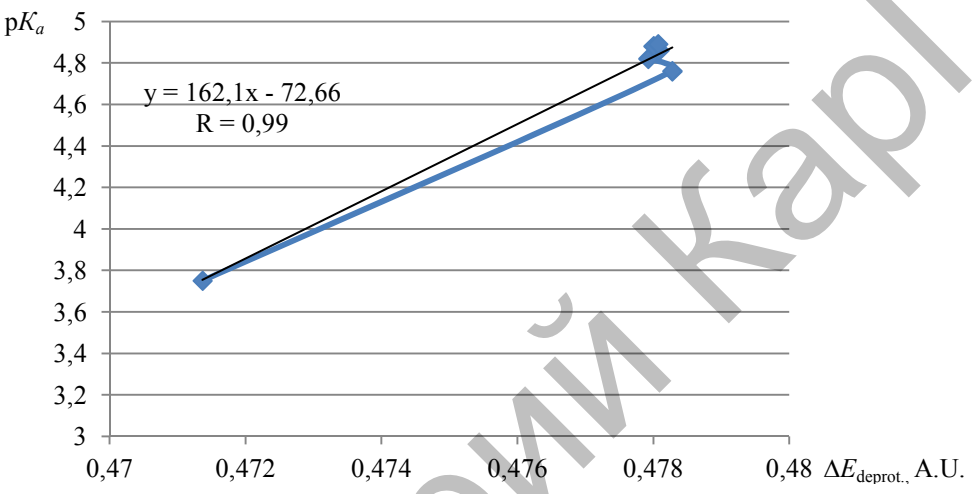


Figure 1. Relationship between deprotonation energy and handbook p*Ka* value for a studied range OH-acids. Solvent — water

The analysis of the graphic dependence presented in figure 1, showed existence of direct proportional dependence between an indicator of acidity and deprotonation energy of acid in a case when as solvent water was considered. Pearson correlation coefficient for the given relation is large enough (R=0,99), suggesting that there is a high correlation between the deprotonation energy of acid and its acidity.

Results of quantum chemical UHF 6–31G *ab initio* CPCM calculations are presented in table 2 (solvent — chlorobenzene). Handbook [8] values of the p*Ka* for a number of the studied OH-acids are also given in the table 2.

Table 2

Results of quantum chemical UHF 6–31G *ab initio* CPCM calculations for a number of the studied OH-acids. Solvent — chlorobenzene

Acid HA	Acid Formula	Total energy HA, A.U.	Total energy A^-, A.U.	$\Delta E_{deprot.}$, A.U.	pK_a
Formic	HCOOH	–188,6699	–188,1869	0,4830	3,75
Acetic	CH_3COOH	–227,7032	–227,2149	0,4883	4,76
Butyric	$CH_3(CH_2)_2COOH$	–305,7414	–305,2522	0,4891	4,82
Valeric	$CH_3(CH_2)_3COOH$	–344,7667	–344,2706	0,4961	4,86
Caproic	$CH_3(CH_2)_4COOH$	–383,7852	–383,2892	0,4960	4,88
Caprylic	$CH_3(CH_2)_6COOH$	–461,8222	–461,3260	0,4961	4,89
Tridecanoic	$CH_3(CH_2)_{11}COOH$	–656,9144	–656,4183	0,4962	–
Palmitic	$CH_3(CH_2)_{14}COOH$	–773,9698	–773,4736	0,4962	–
Stearic	$CH_3(CH_2)_{16}COOH$	–851,9999	–851,5105	0,4893	–
Radical I	$C_6H_2(C(CH_3)_2)OOH$	–691,8254	–691,3178	0,5076	–

Data presented in table 2 show that with growth of a carbon chain in a homological row OH-acids, deprotonation energy is increase from 0,48 to 0,51 A.U. This seems to be correct because the stronger the acid, the easier it gives a proton, the less deprotonation energy. A large amount of deprotonation energy for radical I compared to all investigated carboxylic acids should also be noted. Consequently, the radical I in protolytic reactions with carboxylic acids will act as a base. That's why radical I will play the role of a base in protolytic reactions with carboxylic acids.

It was interesting to present in graphical form relationship between deprotonation energy and handbook value p*Ka* for a studied range of OH-acids (solvent — chlorobenzene; fig. 2).

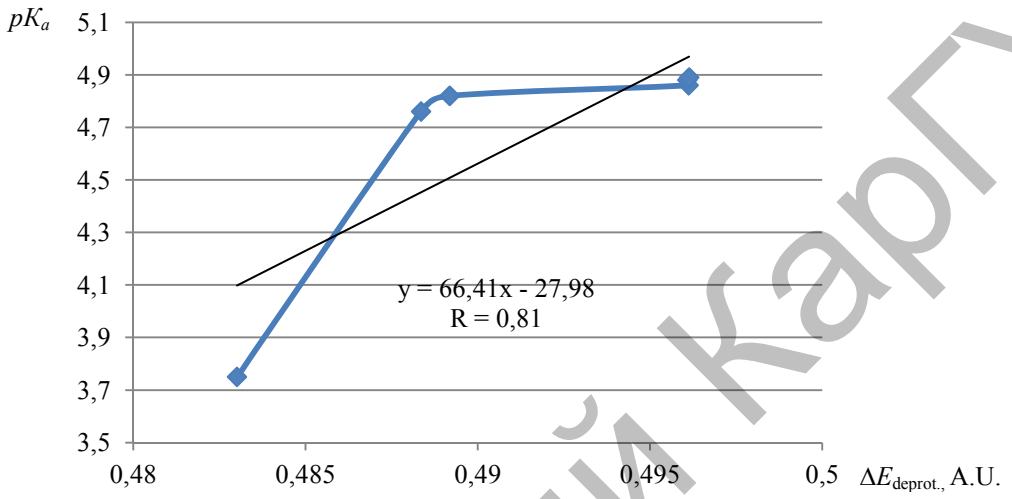


Figure 2. Relationship between deprotonation energy and handbook p*Ka* value for a studied range OH-acids. Solvent — chlorobenzene

The analysis of the graphic dependence presented in figure 2, showed existence of direct proportional dependence between an indicator of acidity and deprotonation energy of acid in a case when as solvent chlorobenzene was considered. Note the smaller value of the Pearson correlation coefficient (R=0,81) compared with the case when the water solvent is taken into account (R=0,99). Limited application of the reference p*Ka* value for the acid strength characteristic in non-aqueous solutions it shows.

Similar quantum chemical UHF 6–31G *ab initio* CPCM calculations for a number of investigated OH-acids (solvents — toluene (ε=2,4) and benzene (ε=2,3)) were performed. Growth of the deprotonation energy from 0.50 to 0,52 A.U. with increasing of the carbon chain in the homologous series of carboxylic acids was also noted in the calculations with toluene and benzene solvents. The fact of reducing the difference between the deprotonation energies of carboxylic acid and radical I in these calculations (≈0,01 A.U.) compared to the previous one when water as the solvent was taken into account (≈0,02 A.U.) has attracted attention. It allows to assume that the difference in strength of carboxylic acids and the radical I is reduced, the acidity of the proton exchange reaction participants becomes comparable in non-polar media. Increasing the speed of the proton exchange in indifferent mediums, fixed by EPR spectroscopy, is the result of it. The difference in the acidity of the proton exchange reaction participants is increased in the polar medium due to the polarizing effect of the solvent. Delay of speed proton exchange reaction in polar media is the result of it.

It was interesting to analyze the obtained settlement quantum chemical data of the deprotonation energy for a studied range OH-acids in the medium of water, chlorobenzene, benzene and toluene (Table 3). Value averages were calculated by us for the comparative analysis:

$$(\Delta E_{deprot.})_{middle} = \Sigma(\Delta E_{deprot.}); \quad (7)$$

$$\Delta_{middle} = \Delta E_{deprot.}(\text{radical I}) - (\Delta E_{deprot.})_{middle}. \quad (8)$$

The average value $(\Delta E_{deprot.})_{middle}$ will allow us to characterize the dependence of the OH-acids deprotonation energy from the medium. The value of Δ_{middle} will allow us to characterize the average difference between the deprotonation energies of carboxylic acids and radical I.

Table 3

Deprotonation energies for a studied range OH-acids. Calculation method — UHF 6–31G *ab initio* CPCM

Acid	Acid Formula	pK_a	$\Delta E_{deprot.}$, A.U. Solvent:			
			water (ε=80)	chlorobenzene (ε=5,7)	toluene (ε=2,4)	benzene (ε=2,3)
Formic	HCOOH	3,75	0,4713	0,4830	0,5056	0,5073
Acetic	CH_3COOH	4,76	0,4782	0,4883	0,5112	0,5130
Butyric	$CH_3(CH_2)_2COOH$	4,82	0,4779	0,4891	0,5117	0,5134
Valeric	$CH_3(CH_2)_3COOH$	4,86	0,4780	0,4961	0,5207	0,5226
Caproic	$CH_3(CH_2)_4COOH$	4,88	0,4780	0,4960	0,5207	0,5226
Caprylic	$CH_3(CH_2)_6COOH$	4,89	0,4781	0,4961	0,5208	0,5227
Tridecanoic	$CH_3(CH_2)_{11}COOH$	–	0,4781	0,4962	0,5208	0,5227
Palmitic	$CH_3(CH_2)_{14}COOH$	–	0,4533	0,4962	0,5216	0,5227
Stearic	$CH_3(CH_2)_{16}COOH$	–	0,4742	0,4893	0,5118	0,5135
Radical I	$C_6H_2(C(CH_3)_2)OOH$	–	0,4943	0,5076	0,5267	0,5282
$(\Delta E_{deprot.})_{middle}$, A.U.			0,4762	0,4938	0,5172	0,5189
Δ_{middle}, A.U.			0,0181	0,0138	0,0095	0,0093

Data presented in table 3 show that the deprotonation energy of acid increases, the difference in energies of deprotonation of carboxylic acids and radical I decreases with decreasing of the solvent polarity.

It was interesting to analyze by graph the relationship between the average of deprotonation energy $(\Delta E_{deprot.})_{middle}$ and dielectric permeability ε of the medium. The obtained graph is shown in figure 3.

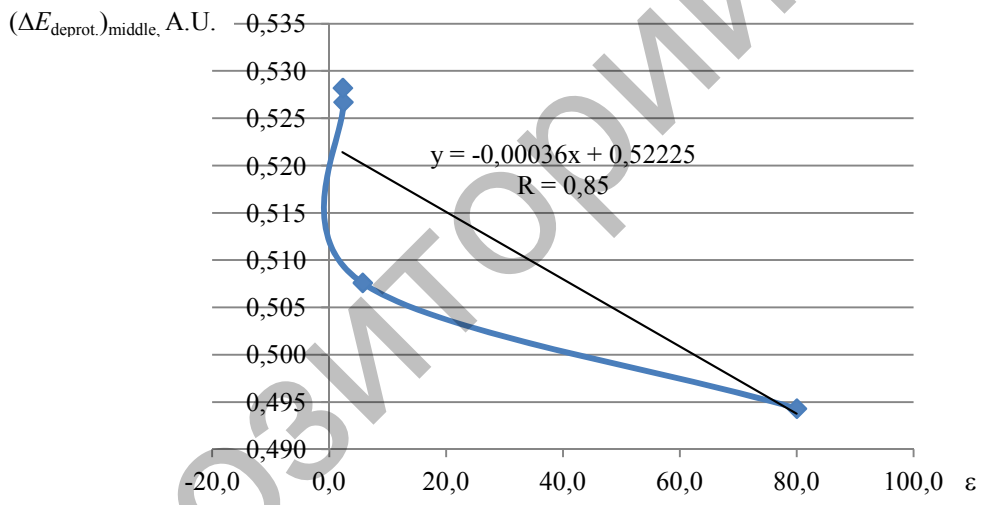


Figure 3. Relationship between the average of deprotonation energy $(\Delta E_{deprot.})_{middle}$ and dielectric permeability ε of the medium

Data presented in figure 3 show that between dielectric permeability of solvent and acid deprotonation energy there is the inverse proportional relationship. Deprotonation energy of acid decreases with increasing of the medium polarity. This indicates an increase of the substances acidity in a polar solvent.

The following conclusions were formulated based on the obtained data:

– Deprotonation energy of acids decreases with increasing of the medium polarity. This suggests that the acidity of substances is higher in polar solvents than in indifferent mediums;

– The difference in acidity of the radical I and carboxylic acids is less in non-polar media. This leads to increased speed of the proton exchange between its in indifferent mediums;

– Radical I is demonstrated more basicity in polar solvents. This causes a slight decrease the rate of the proton exchange reaction in polar media.

The results obtained are in good agreement with the EPR spectroscopic data of proton exchange reactions between carboxylic acids and semiquinone radical I. The results suggest a theoretical justification for

the fact a slight decrease the rate of the proton exchange reaction in polar media. Further it would be interesting to continue quantum chemical researches of the OH-acids behavior in other solvents.

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ОН-қышқылдарының күшіне орта полярлығының әсерін теориялық зерттеу

Ab initio UHF әдісінің 6–31G базисінде Gaussian-2009 бағдармалық пакетінің CPCM полярлаушы континуум макроскопиялық моделінің шегіндегі еріткіштің әсерін ескере отырып, ОН-қышқылдар қатарының депротондану энергиясы теориялық бағаланды. Ортаның полярлануының өсуімен қышқылдардың депротондану энергиясының төмендеуі квантықхимиялық көрсетілді. Полярлы ортадағы семихинонды радикал 3,6-ди-үш.бутил-2-оксифеноксилдің карбон қышқылдарымен протон алмасу жылдамдығының ЭПР-спектроскопиялық берілгендерінің төмендеуіне теориялық негіздеме берілді.

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Теоретическое изучение влияния полярности среды на силу ОН-кислот

Методом *ab initio* UHF в базисе 6–31G с учетом влияния растворителя в рамках макроскопической модели поляризуемого континуума CPCM программного пакета Gaussian-2009 теоретически оценены энергии депротонирования ряда ОН-кислот. Квантовохимически показано снижение энергии депротонирования кислот с ростом полярности среды. Дано теоретическое обоснование ЭПР-спектроскопических данных о снижении скорости протонного обмена карбоновых кислот с семихинонным радикалом 3,6-ди-трет.бутил-2-оксифеноксилом в полярных средах.

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