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ESR-Study of the Proton Exchange with Aliphatic Amino Acids in Toluene

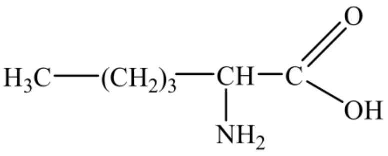
This paper presents the results of an ESR spectroscopic study of the intermolecular proton exchange kinetics with some isomers of aminocaproic acid, such as 2-aminohexanoic and 6-aminohexanoic acids in the toluene indifferent medium. A stable semiquinone radical, namely 3,6-di-*tert*-butyl-2-hydroxyphenoxyl, is used as a spin probe. The ESR spectra have been recorded on a RE-1306 spectrometer. The article provides the obtained dynamic spectra of the intermolecular proton exchange process. Modeling of the proton exchange ESR spectra has been carried out using a previously developed program, which is based on a four-jump model of this reaction and modified Bloch equations. The kinetic parameters of the process of acid-base interaction of the spin probe with amino acids and the activation barrier of the reaction have been estimated with a minimum error based on a comparison of the model spectra with the experimental ones. The obtained data have been analyzed and compared with previous studies. It has been found that the reaction rate of the intermolecular proton exchange between 3,6-di-tert-butyl-2-hydroxyphenoxy and studied aliphatic amino acids is comparable to the same with aliphatic carboxylic acids. Hoewever, in our case, there is an increase in the activation barrier, which apparently is associated with a negative effect on the intramolecular hydrogen bonding process between the amino and the carboxyl groups in the amino acid molecule.

Keywords: ESR-spectroscopy, proton exchange reactions, spin probe, semiquinone radical, Bloch equation, aminohexanoic acid, 3,6-di-*tert*-butyl-2-hydroxyphenoxyl, OH-acids.

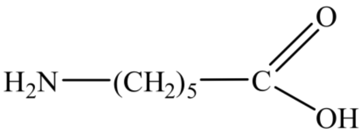
Introduction

The acid-base interactions are common phenomena in nature. They are widely used in scientific and practical activities. Theoretical ideas about acids and bases are often of primary importance in the formation of all conceptual systems of chemistry and have a versatile influence on the development of many theoretical concepts in all fundamental chemical disciplines. Typical acid-base interactions, according to the Bronsted–Lowry theory, include protolytic reactions involving proton. The proton exchange reaction is one of the varieties of such reactions. To date, plenty of papers are devoted to acid-base interactions. However, as can be seen from the literature analysis, most studies of protolytic reactions have been carried out in aqueous media, and there are data on such studies in non-aqueous media [1–6].

Previously, we have carried out ESR spectroscopic studies of proton exchange reactions between a stable semiquinone radical as a spin probe and various organic acids in non-aqueous media [7, 8]. It seems interesting to study the proton exchange reaction with aminohexanoic acids (1), namely 2-aminohexanoic (α-aminocaproic) and 6-aminohexanoic (ε-aminocaproic):



2-aminohexanoic acid



6-aminohexanoic acid

(1)

This study will make it possible to determine the protolytic ability of these acids and to evaluate the influence of their structure on the rate of the proton exchange reaction.

Amino acids play an important role in various biochemical processes. The scientists pay the attention to this class of compounds. This is confirmed by a large number of publications devoted to the study of their physicochemical properties [9–14].

Experimental

The method of recrystallization from tetrahydrofuran was used to purify 3,6-di-*tert*-butylcyclohexa-3,5-diene-1,2-dione (3,6-di-*tert*-butyl-*o*-benzoquinone) (N.D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, >98 % purity) and 3,6-di-*tert*-butylbenzene-1,2-diol (3,6-di-*tert*-butylcatechol) (N.D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, >98 % purity).

Toluene (CJSC "Ekos-1", >98 % purity) was purified by distillation under atmospheric pressure over sodium hydroxide.

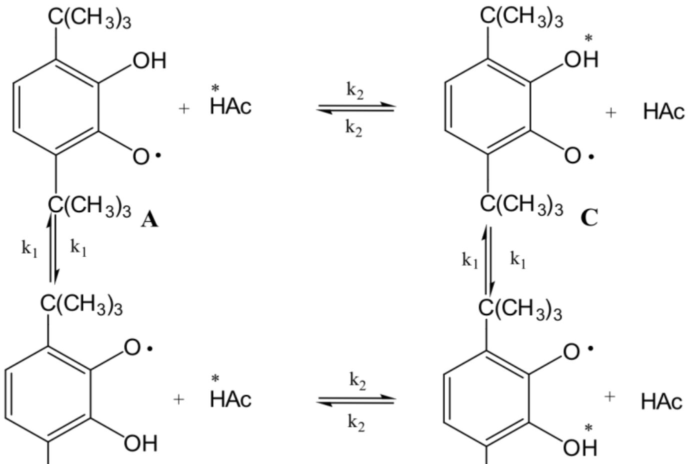
Amino acids, namely 2-aminohexanoic and 6-aminohexanoic (AppliChem GmbH), were used without additional purification since their purity exceeded 99 %. Amino acids were placed in the desiccator for 48 hours before use [15].

The studied system of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl — amino acids was obtained by direct mixing of 3,6-di-*tert*-butylcyclohexa-3,5-diene-1,2-dione with 3,6-di-*tert*-butylbenzene-1,2-diol in a glass ampoule followed by the addition of an amino acid solution in toluene of a given concentration. Then the ampoule was degassed and sealed. The spectra were recorded on a RE-1306 spectrometer (Russia) with a unit for temperature control in the range of 200–400K. The spectrometer was upgraded with a device that converts the analog signal to digital. The ESR EXCHANGE program was used to process the experimental data. Previously, we developed this program in the FORTRAN algorithmic language [16]. The ESR EXCHANGE program includes calculation of the theoretical spectrum, comparison of this spectrum with the experimental spectrum, calculation of the kinetic parameters of the intermolecular proton exchange reaction, Least-squares processing with determination of the standard error of measurement.

Results and Discussion

The ESR spectrum of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl is a triplet of doublets. It is formed by the interaction of an unpaired electron with ring protons (a_H= 0.392 mT) and with a proton of the hydroxyl group (a_{OH}= 0.162 mT). The advantage of the used spin probe is the hyperfine structure of the radical's ESR spectrum, which is sensitive to acid-base interactions [7, 8].

A four-jump model can describe the process of intermolecular proton exchange with H-acids:



(2)

Along with the above reaction (A↔C, B↔D), it includes tautomeric transformations of a semiquinone radical, i.e., intramolecular migration of the hydrogen atom of the hydroxyl group between oxygen atoms (A↔B, C↔D) [17].

This four-jump model (2) and the modified Bloch equation formed the basis of the previously developed program for modeling intermolecular proton exchange. In this program, the ESR spectra are calculated from the coupling constants, rate constants, and linewidths of all chemical configurations of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl. The rate constants of the reaction of intermolecular proton exchange, the activation energy of the process, and the measurement error can be found by comparing the model spectra with the experimental ones. It should be noted that the proton exchange process presumably has a “cooperative” mechanism, that is, a cyclic hydrogen-bonded complex is formed during the reaction. The lifetime of this complex directly affects the rate of the whole process [17].

The ESR spectra of the 3,6-di-*tert*-butyl-2-hydroxyphenoxyl — aminohexanoic acid system were obtained by the ESR method. The broadening of the hyperfine structure lines was noted with increasing temperature. This is characteristic of proton exchange and confirms that an intermolecular reaction of proton exchange is observed in the system under study.

Figure 1 shows experimental and simulated ESR spectra of the 3,6-di-*tert*-butyl-2-hydroxyphenoxyl — 6-aminohexanoic acid system in toluene.

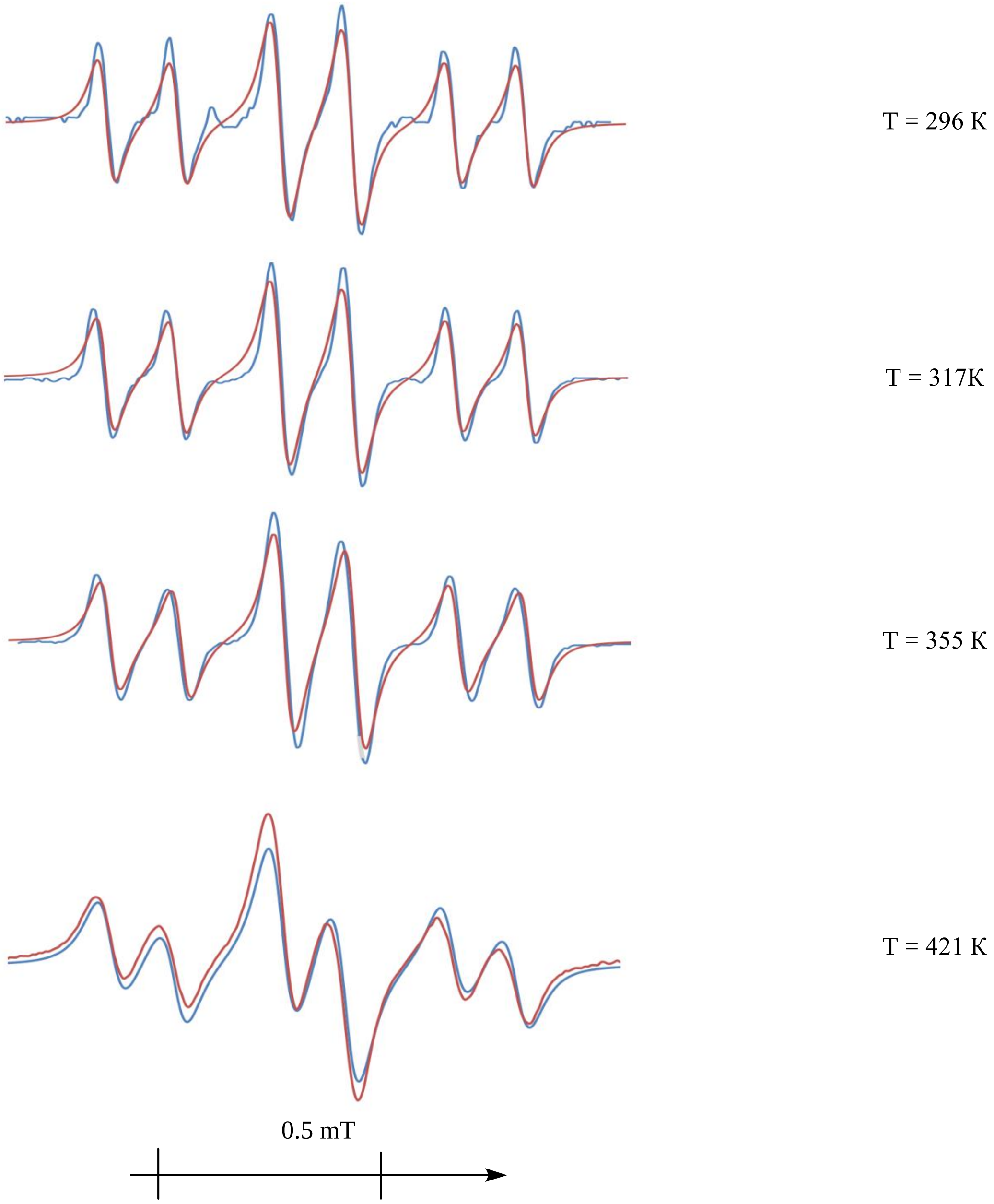


Figure 1. ESR spectra of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl — 6-aminohexanoic acid (0.05 mol/l) system in toluene at different temperatures. Blue line is an experimental spectrum; red line is a simulated spectrum

The decrease in the central components of the ESR spectrum triplet (Fig. 1) indicates a slowdown in proton migration between oxygen atoms in the radical. This means that the resulting intermediate of semiquinone radical with acid is sufficiently stable.

The Arrhenius plot showed a good linear relationship between $\lg k_{exch}$ and 1/T (Fig. 2). The plot in Figure 2 also demonstrates the values of the standard measurement error calculated by the ESR EXCHANGE program.

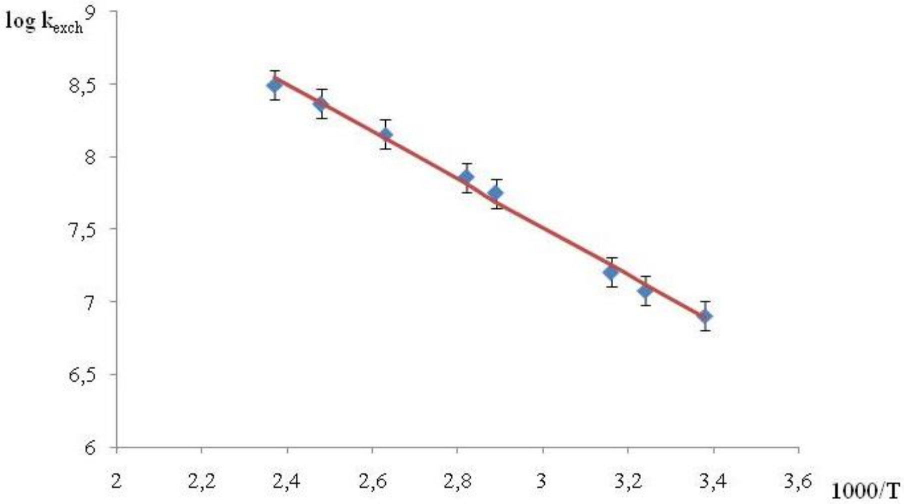


Figure 2. Arrhenius plot of the intermolecular rate constant (k_{exch}) for 3,6-di-*tert*-butyl-2-hydroxyphenoxyl — 6-aminohexanoic acid system in toluene obtained from the experimental and theoretical ESR spectra

Kinetic parameters of intermolecular proton exchange reaction between 3,6-di-*tert*-butyl-2-hydroxyphenoxyl and aminohexanoic acids were calculated using the ESR EXCHANGE program. Table 1 presents the obtained data and measurement error.

Table 1

Kinetic parameters of the intermolecular proton exchange reactions between 3,6-di-*tert*-butyl-2-hydroxyphenoxyl and H-acids in toluene solution

H-acid	k_{exch} (293K), l/mol·s	k^o_{exch}, l/mol·s	E_a, kJ/mol	pK_a
2-Aminohexanoic acid	$(3.58\pm0.44)\cdot10^7$	$1.96\cdot10^{10}$	15.4±0.7	2.34 9.83
6-Aminohexanoic acid	$(2.90\pm0.23)10^7$	5.9510^{10}	18.6±3.6	4.43
Hexanoic acid	$(8.01\pm0.24)\cdot10^7$	$2.78\cdot10^9$	8.7±0.5	4.88
Hexanedioic acid	$(7.22\pm0.70)\cdot10^8$	$5.09\cdot10^9$	4.8±0.8	4.43 5.28
2-Anilinobenzoic acid	$(3.15\pm0.20)\cdot10^7$	$9.25\cdot10^9$	13.8±1.1	5.28
Dodecan-1-amine	$(1.02\pm0.02)\cdot10^9$	$3.64\cdot10^9$	3.1±0.2	10.63

Table 1 shows similar parameters of hexanoic, hexanedioic, 2-anilinobenzoic acids and dodecan-1-amine for comparison [17, 18]. Analysis of available data suggests that despite their amphoteric nature 2- and 6-aminohexanoic acids in toluene react with the spin probe at a rate comparable to the rate of the proton exchange reaction with aliphatic monocarboxylic acids (hexanoic acid is given for an example). The value of this rate is far from the rates with aliphatic amines [18]. Therefore, a proton of the carboxyl group of aminohexanoic acid is involved in the proton exchange. It is assumed that the proton exchange will occur both in the amino group and in the carboxyl group simultaneously. At the same time, an increase in the rate should be recorded at least by an order of magnitude, as in the case of dicarboxylic hexanedioic acid, but we do not observe this. It should be noted that the high activation energy of the process is a feature of the proton exchange reaction with 2- and 6-aminohexanoic acids. There are competing reactions of the intra- and intermolecular interaction of the amino group with the carboxyl group of aminohexanoic acid. Also, this interaction is more pronounced in 6-aminohexanoic acid, where these functional groups occupy terminal positions, and the flexibility of the carbon skeleton of the molecule makes it possible to form fairly stable structures. All these processes have a negative effect on the resulting intermolecular complex with the spin probe and lead to an increase in the activation barrier. A similar situation is observed in the reaction of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl with 2-anilinobenzoic acid.

Conclusions

The intermolecular proton exchange reaction of the spin probe, namely 3,6-di-*tert*-butyl-2-hydroxyphenoxyl, with 2-aminohexanoic and 6-aminohexanoic acids, was carried out with the carboxyl group participation. The protolytic ability of aminohexanoic acid isomers in the toluene is comparable to that of aliphatic monocarboxylic acids and aromatic amino acids. The high activation barrier of the intermolecular proton exchange is due to the presence in the system of intramolecular and intermolecular interactions between the carboxyl and amino groups, which are typical of amino acids. This has a destructive effect on the intermediate reaction complex.

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И.Л. Стадник, Ф.Ж. Абилканова, Е.В. Кудрявцева, С.Н. Никольский, А.С. Масалимов

Толуол ортадағы кейбір алифаттық аминқышқылдарымен протон алмасу реакциясын ЭПР әдісімен зерттеу

Мақалада толуол сияқты индифферентті еріткіштегі 2-аминогексан қышқылы және 6-аминогексан қышқылы сияқты аминокапрон қышқылының кейбір изомерлерімен молекулааралық протон алмасу кинетикасын ЭПР-спектроскопиялық зерттеу нәтижелері келтірілген. Спиндік зонд ретінде 3,6-ди-трет-бутил-2-гидроксифеноксил тұрақты семихинон радикалы пайдаланылды. ЭПР спектрлері РЭ-1306 спектрометрінде тіркелінді. Молекулааралық протон алмасу процесінің алынған динамикалық спектрлері осы жұмыста келтірілген. Протон алмасуының ЭПР спектрлерін модельдеу осы реакцияның төрт секірмелі моделіне және модифицирленген Блох теңдеулеріне негізделген бұрын әзірленген бағдарлама арқылы жүзеге асырылды. Модель спектрлерін эксперимент нәтижесінде алынғандармен салыстыру спиндік зондтың аминқышқылдарымен қышқылдық-негіздік әрекеттесуінің кинетикалық параметрлерін ең аз қателікпен анықтауға және реакцияның активтену кедергісін бағалауға мүмкіндік берді. Осылайша алынған мәліметтер талданып, бұрын белгілі ақпаратпен салыстырылды. Зерттелетін алифатты амин қышқылдары спиндік зондпен 3,6-ди-трет-бутил-2-гидроксифеноксилдің алифаттық карбон қышқылдарымен молекулааралық протон алмасу реакциясының жылдамдығымен салыстырылатын жылдамдықпен әрекеттесетіні анықталды. Бірақ, біздің жағдайда, активтену тосқауылының жоғарылауы байқалады, бұл шамасы, амин қышқылы молекуласындағы амин тобы мен карбоксил тобы арасындағы молекулаішілік сутегі байланысы процесіне теріс әсер етумен байланысты.

Кілт сөздер: ЭПР спектроскопия, протон алмасу реакциялары, спиндік зонд, семихинонды радикал, Блох теңдеуі, аминогексан қышқылы, 3,6-ди-трет-бутил-2-гидроксифеноксил, ОН-қышқылдары.

И.Л. Стадник, Ф.Ж. Абилканова, Е.В. Кудрявцева, С.Н. Никольский, А.С. Масалимов

ЭПР-исследование реакции протонного обмена с некоторыми алифатическими аминокислотами в толуольной среде

В статье представлены результаты ЭПР-спектроскопического исследования кинетики межмолекулярного протонного обмена с некоторыми изомерами аминокапроновой кислоты, такими как 2-аминогексановая кислота и 6-аминогексановая кислота в среде индифферентного растворителя — толуола. В качестве спинового зонда был использован стабильный семихинонный радикал — 3,6-ди-трет-бутил-2-гидроксифеноксил. Спектры ЭПР регистрировали на спектрометре РЭ–1306. Полученные динамические спектры процесса межмолекулярного протонного обмена приведены в настоящей работе. Моделирование спектров ЭПР протонного обмена проводилось с помощью ранее разработанной программы, в основе которой лежит четырехпрыжковая модель данной реакции и модифицированные уравнения Блоха. Сопоставление модельных спектров с экспериментальными позволило нам с минимальной ошибкой определить кинетические параметры процесса кислотно-основного взаимодействия спинового зонда с аминокислотами и оценить активационный барьер реакции. Полученные таким образом данные были проанализированы и сопоставлены с ранее известными сведениями. Было обнаружено, что исследуемые алифатические аминокислоты реагируют со спиновым зондом со скоростями, сопоставимыми со скоростями реакции межмолекулярного протонного обмена 3,6-ди-трет-бутил-2-гидроксифеноксила с алифатическими карбоновыми кислотами. Но при этом в нашем случае наблюдается рост активационного барьера, который, видимо, связан с негативным влиянием на процесс внутримолекулярной водородной связи между амино- и карбоксильной группами в молекуле аминокислоты.

Ключевые слова: ЭПР-спектроскопия, реакции протонного обмена, спиновый зонд, семихинонный радикал, уравнение Блоха, аминогексановая кислота, 3,6-ди-трет-бутил-2-гидроксифеноксил, ОН-кислоты.

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