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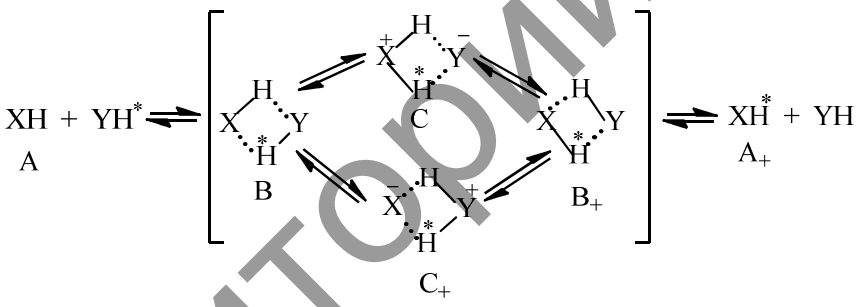
Quantum-chemical investigation of the fast intermolecular proton exchange reactions mechanism in paramagnetic systems

For a theoretical interpretation of the fast intermolecular proton exchange (IPE) reaction mechanism by ab initio methods of modern quantum chemistry potential energy surface in the oxymethyl – ammonia acid-base free-radical system was investigated. This system an experimental EPR spectroscopic kinetic data for such reactions in the real liquid phase systems was simulated. The role of short lived intermediates as molecular and ionic complex four-center hydrogen bond due to manage the flow of IPE-fast reactions in the acid-base paramagnetic compounds have been established.

Key words: semiquinone radicals, oxymetyl radical, EPR-spectroscopy, intermediate, hydrogen bridge, protolytic reaction, proton exchange reaction, proton transfer proton exchange, quantum chemical calculations, ab initio, potential energy surface.

The using of stable semiquinone radicals (XH) as spin probes for EPR-spectroscopic determination of rates constants of the fast intermolecular proton exchange (IPE) reactions allowed to study the protolytic activity of different organic acids and bases (YH) in solutions [1]. The systematic experimental investigations of kinetic of such acid-base reactions showed that they have the common mechanism described with next scheme:



(1)

Here: asterisk denotes the acids proton with another orientation of spin; B, B_+ and C, C_+ are the short-lived intermediates of IPE-reactions.

For example, as spin probes (XH) were used next stable semiquinone radicals: 3,6-di-tert.butyl-2-oxyphenoxyl (I), 4,6-di-tert.butyl-3-clorine-2-oxyphe-noxyl (II) and 4-triphenylmethyl-6-tert.butyl-3-clorine-2-oxyphenoxyl (III).

For theoretical calculations of mechanism of the fast IPE reaction illustrated by scheme (1) was used quantum chemical ab-initio method with UHF 3–21G orbital bases, contained in licensed program packet Gaussian-2009 (Pittsburgh, USA) [2–5]. For modeling of the fast IPE reactions between paramagnetic OH-acids I–III and NH-acids as primary and secondary amines, were taken simple smallish molecular system oxymethyl – ammonia. It should be noted that at the first time oxymetyl-radical was studied as OH-acid with dynamic EPR spectroscopy by H.Fischer in 1964 [6].

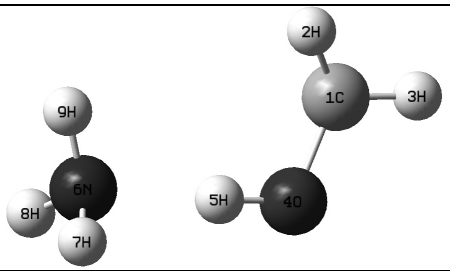
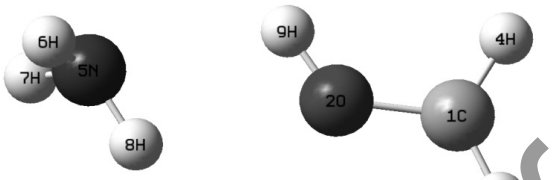
The quantum-chemical counts show that small molecule of paramagnetic OH-acid form with base molecule of ammonia two types of complexes with hydrogen bond CHB): linear and cyclic, presented on Table 1.

The computation estimates that value of thermodynamic stability of linear CHB more on ΔE = 10,3905 kcal/mol than total energy of cyclic complex with two hydrogen bridges. This effect may be explain by influence of the high values of ionization potentials: IP = 7.0663 eV for oxymethyl and IP = 8.0530 eV for ammonia [5].

For calculation of the potential energy surface (PES) of modeling protolytic system CH_2OH – NH_3 was used the specific bimolecular structure with three dummy atoms: 3X, 4X and 8X (see Fig. 1). Such approach allow to move two acid protons inside the cyclic CHB from initial to final reaction states with the value of rated step Δ = 0.01 Å.

Table 1

Electronic structures and the values of total energies for different CHB forming between oxymethyl and ammonia, obtained by ab-initio UHF 3- 21G method

CHB	Electronic structure	$-E_t$, a.u.
Linear complex		169.6672
Cyclic complex		169.6506

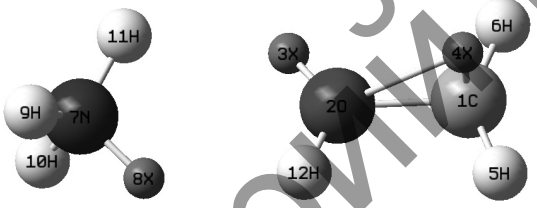


Figure 1. The structure of modeling IPE reaction system used for computation of PES

On the figure 2 presented the PES calculated by ab-initio method with using UHF 3–21G orbital bases and modeling illustrated by figure 1.

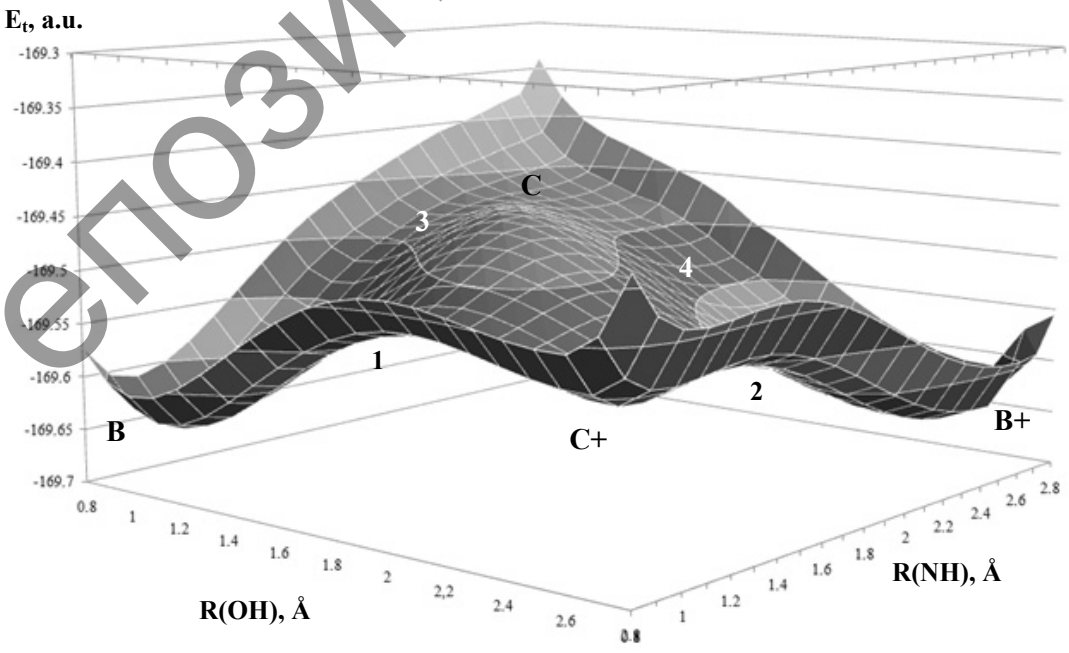


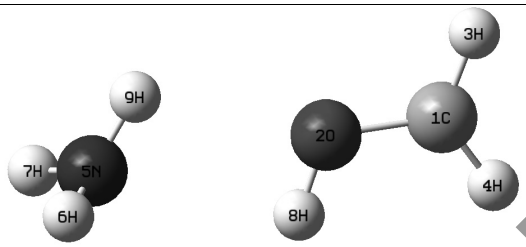
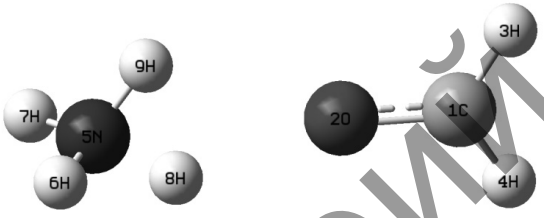
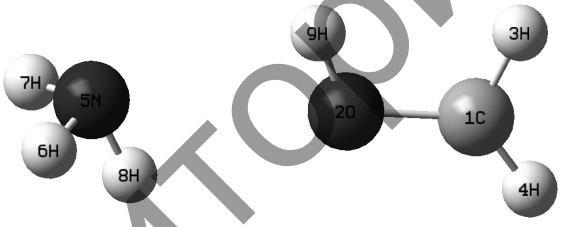
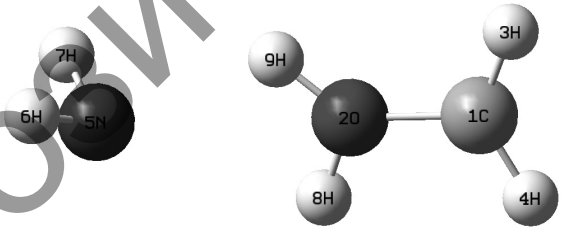
Figure 2. The three-dimensional potential energy surface for modeling protolytic reaction between oxymethyl and ammonia, obtained by ab-initio method with UHF 3–21G orbital bases

The potential energy surface on figure 2 illustrate electron-structural properties of the reversible two-channel fast IPE reaction going on ways: B ⇌ C^+ ⇌ B^+ and B ⇌ C ⇌ B^+. It should be noted that the rates of the initial step of IPE reaction (1) A ⇌ B controlled by diffusion in investigated liquid system.

The analyses of three-dimensional PES topology for the fast IPE reaction between modeling acid –base small molecules shows on formation of 2 short-lived intermediates C and C^+ that denote in scheme (1) and on existence of 4 saddle points corresponding to 2 channel for reactions: B ⇌ C^+ ⇌ B^+ and B ⇌ C ⇌ B^+. The values of total energies for this 4 intermediates presented on Table 2.

Table 2

Electronic structures and the values of total energies for intermediates of reaction between oxymethyl and ammonia, obtained by ab-initio UHF 3- 21G method

Intermediates	Electronic structure	$-E_t$, a.u.
B		169.6506
C^+		169.5611
B^+		169.6506
C		169.4625

The computed PES on figure 1 shows that the reaction channel B ⇌ C^+ ⇌ B^+ is the preferred for protolytic acid–base interaction between oxymethyl and ammonia. Thermodynamic stability of intermediate C^+ on the value ΔE = 70.8587 kcal/mol more than value of total energy for intermediate C.

The potential energy surface presented on Figure 2 give yet four saddle point of corresponding transition states which contained on Table 3. It is evidently that initial intermediate of reaction B has the value of total energy on ΔE = 56.1559 kcal/mol lower then ionic CHB C^+. It should be noted that initial B and final B^+ intermediates of the fast modeling IPE reaction have equal electronic structure and the values of total energy. The values of activation energy for direct B→C^+ transition received E_1 = 76.6735 kcal/mol and for reverse reaction C^+→B E_{-1} = 20.5163 kcal/mol. Analogous values for second channel of IPE reaction B⇌C are equal: E_1= 99.2680 kcal/mol and E_{-1} = 18.7480 kcal/mol.

Table 3

Electronic structures and the values of total energies for transition states of reaction between oxymethyl and ammonia, calculated by ab-initio UHF 3-21G method

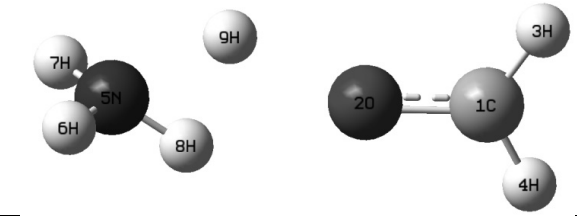
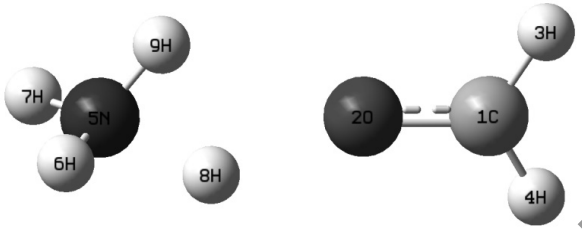
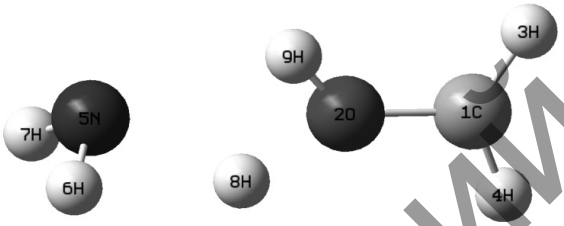
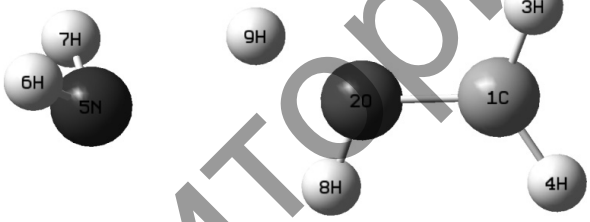
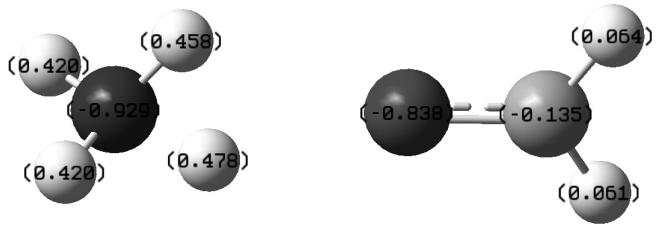
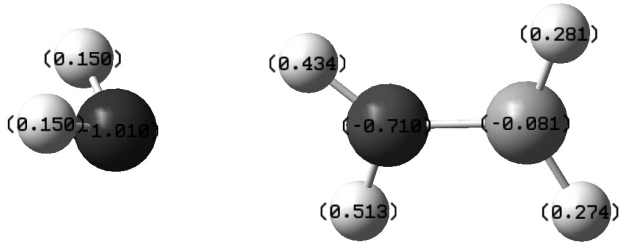
Transition states	Electronic structure	$-E_t$, a.u.
1		169.5284
2		169.5506
3		169.4924
4		169.4935

Table 4

Distribution of atomic charges in ionic intermediates of modeling IPE reaction between oxymethyl and ammonia

Intermediates	Distribution of atomic charges
Intermediate C_+	
Intermediate C	

It is necessary to say if the four-centered CHB B and B^+ are molecular intermediates of IPE reaction the another analogous CHB C and C^+ must be the ionic intermediates. The character of the atomic charges distribution presented on Table 4 confirms our assumption. For example: the value of common positive charge for ammonium cation in ionic CHB C^+ resulted as $q = +0.847$ and this value for protonated oxymethyl in ionic complex C is equal $q = +0.710$.

Figure 3 illustrates the experimental EPR spectra of the real short-lived particles C^+ and C registered in toluene mixtures of spin probe I with different acids and bases at low temperatures [6].

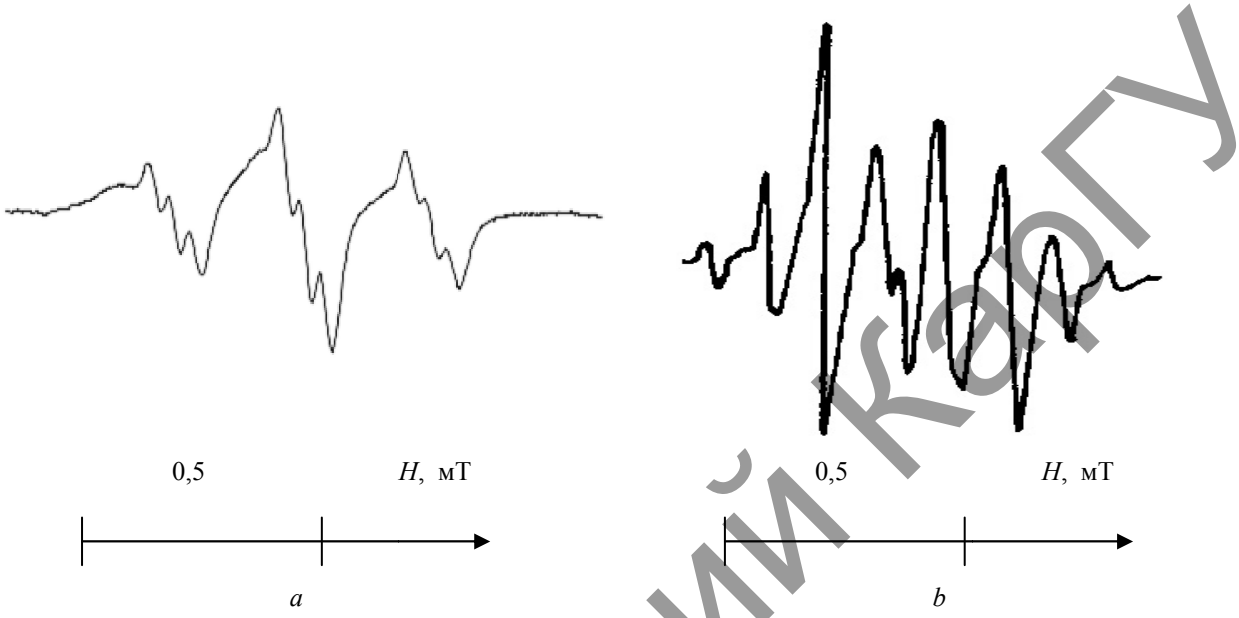


Figure 3. EPR spectra of ionic pair C^+ and C obtained in toluene solutions of stable radical I and tetrahydronicotine at 294 K (*a*) and hydrochloric acid at 185 K (*b*)

EPR spectra 3*a* present triplet of triplet and concern to contact ionic pair of anion-radical 3,6-di-tert.buthylortosemiquinone with cation of protonated molecule of tetrahydronicotine. The big triplet ($a_H = 0.335$ mT) formed by hyperfine interaction of unpaidred electron with 2 magnetic equivalent ring protons of anion-radical 3,6-di-tert.bu-thylortosemiquinone and small triplet ($a_N = 0.030$ mT) formed by splitting on nucleus of nitrogens atom of ammonium cation in contact ionic pair. The EPR spectra 3*b* concern to ionic pair of the protonated by hydrochloric acid semiquinone radical I.

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Парамагнитті жүйелерде жылдам молекулааралық протондық ауысу реакция механизмін кванттыхимиялық зерттеу

Мақалада қазіргі заманғы кванттыхимиялық эмпирикалық емес әдістермен молекулааралық протондық ауысудың жылдам реакциясы механизмінің теориялық интепретациялау үшін оксиметил-аммиак жүйесінде потенциалды энергияның беті зерттелді. Бұл жүйе нақты сұйықфазалы жүйелердегі осындай реакциялардың тәжірибелік ЭПР-спектроскопиялық кинетикалық мәліметтердің үлгісі болып табылады. Сутектік байланыс арқылы түзілген молекулалық және иондық төртцентрлі кешендердің аз өмір сүретін интермедиаттардың рөлдері анықталды.

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Квантовохимическое изучение механизма реакции быстрого межмолекулярного протонного обмена в парамагнитных системах

В статье для теоретической интерпретации механизма быстрой реакции межмолекулярного протонного обмена (IPE) неэмпирическими методами современной квантовой химии исследована поверхность потенциальной энергии в свободно-радикальной кислотно-основной системе оксиметил – аммиак, моделирующей экспериментальные ЭПР-спектроскопические кинетические данные для таковых реакций в реальных жидкофазных системах. Установлены роли короткоживущих интермедиатов молекулярных и ионных четырехцентровых комплексов за счет водородной связи в управлении протеканием быстрой IPE-реакции в парамагнитной кислотно-основной смеси.