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Proton exchange in ammonia, water and formic acid dimers: quantum-chemical calculation

Proton exchange in hydrogen-bounded complexes occupies an important place among dynamic processes taking place in molecular systems with hydrogen bond. However, despite numerous experimental and theoretical studies in this field, a single point of view on the mechanism of proton exchange has not yet been accepted by scientists. Ammonia, water and formic acid are small in size protolytes with widely differing acid-base properties. This makes them suitable and comfortable for theoretical modeling of proton exchange reaction. Quantum-chemical simulation of the proton exchange reaction in model dimers of ammonia, water and formic acid was carried out by AM1 and *ab initio* 6–31G, 6–31G++ methods of Gaussian-2009 program. The search of transition state structure was performed by using of QST2 procedure, the descent along the reaction coordinate was held by using of IRC procedure. The symmetrical structure of transition state in the case of formic acid dimer and the asymmetric structure of transition complex in the case of ammonia dimer were obtained for studied proton exchange reaction. A synchronous mechanism of proton exchange reaction is shown in the case of the formic acid dimer and a sequential mechanism is shown in the case of ammonia dimer. The dynamic shortening of the hydrogen bridge length was noted during proton exchange reaction in all model systems. It was suggested that the mechanism of proton exchange reaction is determined by the nature of the resulting transition state (symmetrical or asymmetrical). At the same time, the transition state structure is determined by the acid-base properties of reaction partners.

Keywords: proton exchange, dimer, sequential and synchronous reaction mechanism, hydrogen-bounded complex, AM1, *ab initio*, 6–31G, QST2, IRC.

Introduction

Proton exchange in hydrogen-bounded complexes occupies an important place among dynamic processes taking place in molecular systems with hydrogen bond [1]. Formation of the hydrogen bond can be considered as an intermediate stage of the proton exchange protolytic reaction in this case [2]. However, despite numerous experimental and theoretical studies in this field, a single point of view on the mechanism of proton exchange has notyetbeen accepted by scientists today [3]. Study of the proton exchange reaction mechanism by modern quantum chemistry methods can help us to clarify important aspects of the hydrogen bonding phenomenon, as well as specific features of a number of physical, chemical and biological phenomena.

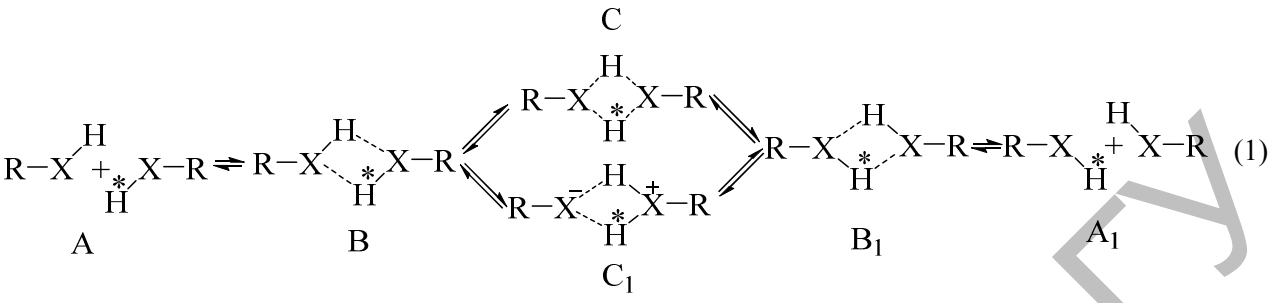
It is assumed that the proton exchange reaction proceeds through the formation of intermediate cyclic complexes with H-bonds [4]. As we know, many nitrogen- and oxygen-containing organic compounds tend to form cyclic dimers both in solutions and in the gas phase. Geometry of dimers is favorable for the proton exchange reaction [5]. For example, formic acid exists in dimer form both in liquid and gaseous state. Strong H-bonds between molecules can be found in water and liquid ammonia. At the same timeammonia, water and formic acid molecules have small size and very different acid-base properties. This makes them suitable and comfortable for theoretical modeling of proton exchange reaction.

Methods

The purpose of the investigation was to study the proton exchange reaction mechanism in water, ammonia and formic acid cyclic dimmers by quantum-chemical methods.Cyclic complexes of objects have been treated *ab initio* using the 6–31G and 6–31G++ basis sets as well as by the semiempirical AM1 method. The choice of methods was determined by the desire to compare the results of semiempirical and non-empirical modeling with each other, as well as the specification of methods.Thus, the semiempirical method AM1 is applicable for organic molecules calculation, especially those containing nitrogen and oxygen, as well as for hydrogen bonded systems. Simultaneously high-level *ab initio* methods can be used as a standard for interatomic interaction accurate description at the quantum-chemical level. The search of transition state structure was performed by using of QST2 procedure, the descent along the reaction coordinate was held by using of IRC procedure. Calculations were made using the Gaussian 2009 package [6, 7].

Results

Proton exchange in dimers of protoliths is an energy-degenerate process. New products are not formed as a result of this exchange reaction:

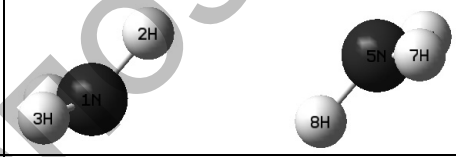
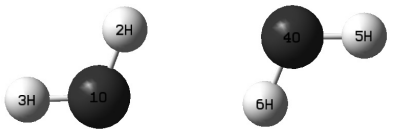
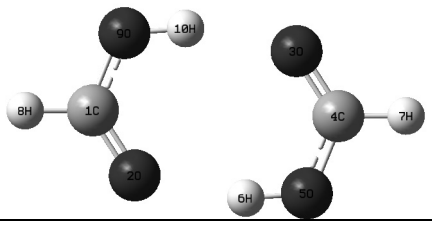


Scheme 1 shows that the initial A and final A_1 states are geometrically and energetically identical and correspond to two independent molecules of the protolith with intermolecular interaction. Hydrogen bonded cyclic complexes (dimers) B and B_1 were formed as a result of this type interaction. Synchronous double proton transfer can occur in the case of intermediate C formation -symmetric hydrogen bonded molecular complex (HBMC) and sequential proton transfer can occur in the case of intermediate C_1 formation — asymmetric hydrogen bonded ionic complex (HBIC). It was interesting to determine the proton exchange mechanism in ammonia, water and formic acid dimers by quantum chemical AM1 and *ab initio* methods and to perform their comparative analysis.

The calculation of ammonia, water and formic acidcyclic dimer structures was originally carried out (structures B and B_1 on Scheme 1). Regardless of the calculation method identical structure of the NH_3–NH_3, H_2O–H_2O, HCOOH–HCOOH cyclic complexes was obtained as a result of geometry optimization procedure. However, different length of hydrogen bridge in the same dimers were noted as a result of semiempirical or *ab initio* calculation method. Table 1 shows the structure and hydrogen bridge length R(X-X), Å, obtained as a result of quantum-chemical calculations for model associates. Table 1 also presents the literature experimental data of hydrogen bond lengths in studied cyclic associates. It can be seen from the experimental data that the hydrogen bridge length is maximal for ammonia dimer and minimal for formic acid dimer. The same relationship between the hydrogen bridge lengths was also obtained on the basis of quantum-chemical calculations.

Table 1

Structure and length of the hydrogen bridge for model dimers of ammonia, water and formic acid

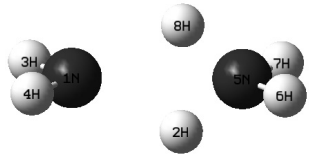
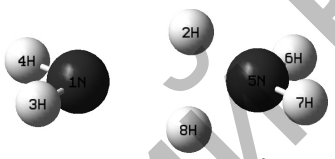
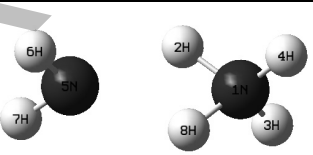
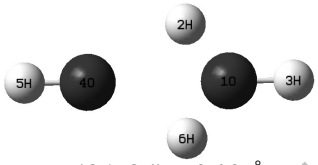
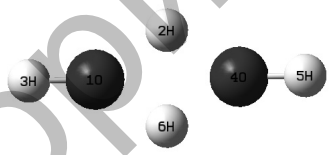
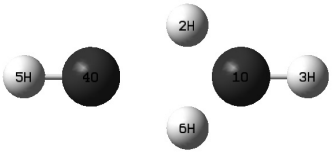
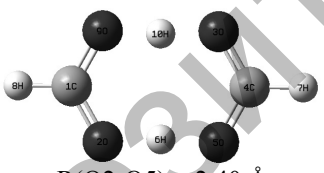
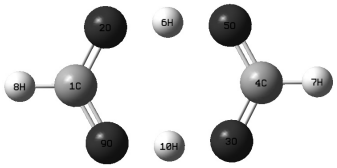
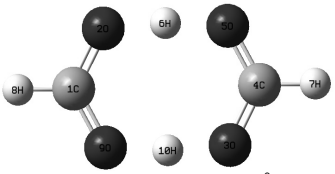
Dimer	Structure of dimer	R(X-X), Å	AM1	6–31G	6–31G++	Exp./gas.p.
NH_3-NH_3		R(N1-N5)	3.48	3.27	3.32	3.27 [8]
H_2O-H_2O		R(O1-O4)	2.68	2.67	2.68	2.76 [9]
HCOOH-HCOOH		R(O9-O3)	3.06	2.72	2.74	2.73 [10]
		R(O2-O5)	3.06	2.72	2.74	2.72 [10]

It can be seen from the data presented in Table 1 that the best agreement with the experimental data on the hydrogen bridge length was obtained by *ab initio* Hartree-Fock method for ammonia and formic acid dimers. The semiempirical AM1 method gives highly overestimated distances between heteroatoms in model dimers in the same time. There is however, a large difference in the calculated and experimental data of hydrogen bridge length for water dimer. This may be a consequence of the discrepancy between the theoretical model of the dimer and the practical one. This can be cause by difference between theoretical and practical model of water dimer. Data for linear structure water associates are given in literature generally. We did not succeed in obtaining accurate experimental data about water cyclic dimer structure.

Obtained structures of dimers have been used to simulate the proton exchange reaction. It was taken that initial and final states of the reaction system (scheme 1) are geometrically and energetically identical. The search of transition state structure was carried out by using of QST2 procedure (Quadratic Synchronous Transit Approach) [11]. Table 2 shows obtained geometric structures of the proton exchange reaction transition states. It is interesting to note that the hydrogen bridge length in transition state is smaller than in original dimer in all cases.

Table 2

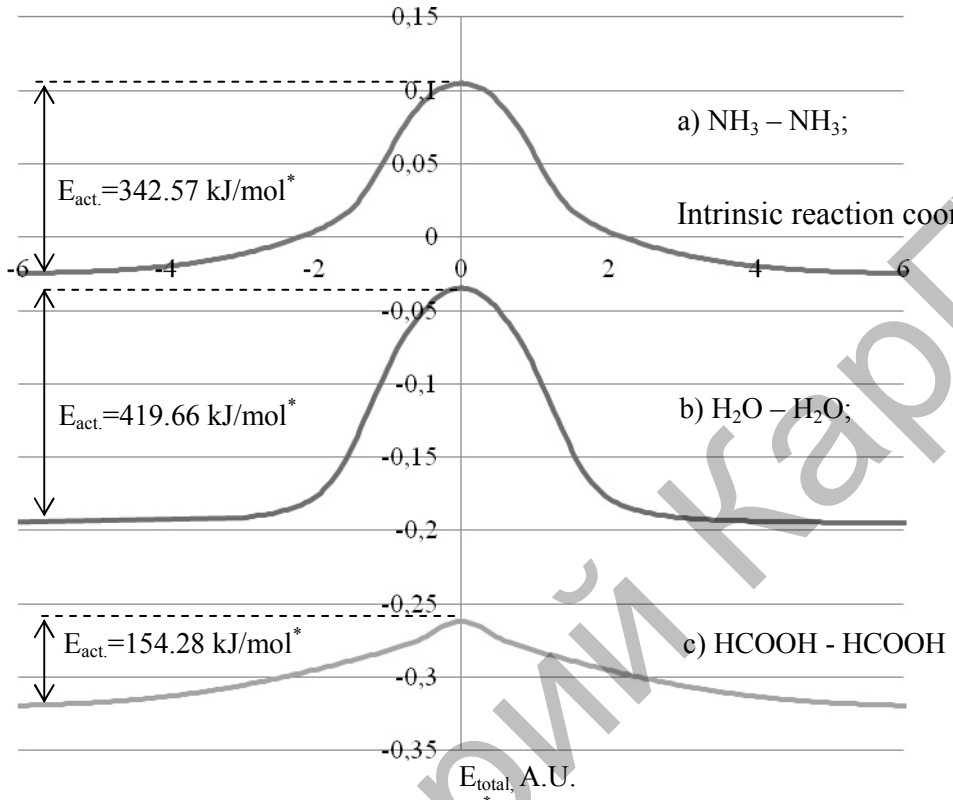
Geometric structures of transition states for proton exchange reaction in model dimers

Dimer	Structure of the transition state according to the method		
	AM1	6–31G	6–31G++
NH_3-NH_3	 R(N1-N5) = 2.34 Å	 R(N1-N5) = 2.36 Å	 R(N1-N5) = 2.44 Å
H_2O-H_2O	 R(O1-O4) = 2.08 Å	 R(O1-O4) = 2.05 Å symmetrical	 R(O1-O4) = 2.12 Å
HCOOH-HCOOH	 R(O2-O5) = 2.40 Å R(O3-O9) = 2.40 Å symmetrical	 R(O2-O5) = 2.39 Å R(O3-O9) = 2.39 Å symmetrical	 R(O2-O5) = 2.39 Å R(O3-O9) = 2.39 Å symmetrical

It can be seen from the data presented in Table 2, that there are two types of transition state: 1) symmetrical structure (structure C on scheme 1); 2) asymmetric structure (structure C_1 on scheme 1). Formation of an asymmetric structure of ion-type transition complex is observed for ammonia and water dimers (excepted for H_2O-H_2O complex calculated by 6–31G method). Formation of a symmetrical structure of molecular type transition complex is observed for dimers of formic acid. It can be assumed that symmetrical structure of transition state for proton exchange reaction is typical for dimers of acid type particles, and asymmetric structure of transition state is typical for basic type particles. Since water is ampholyte, it can form both types of transition state.

In the same time the mechanism of the proton exchange reaction will be determined by the molecular or ionic type of transition state. Synchronous double proton transfer should be expected in the case of symmetric type of transition state structure; sequential proton transfer should be expected in the case of asymmetric type of transition state structure.

The descent along the reaction coordinate was carried out by using of IRC procedure (Intrinsic Reaction Coordinate method) [11]. Figure 1 shows the reaction path diagram for proton exchange in model dimers, obtained by using of AM1 semiempirical calculation method.



Calculation method: AM1 (*1 A.U.=2625.5 kJ/mol)

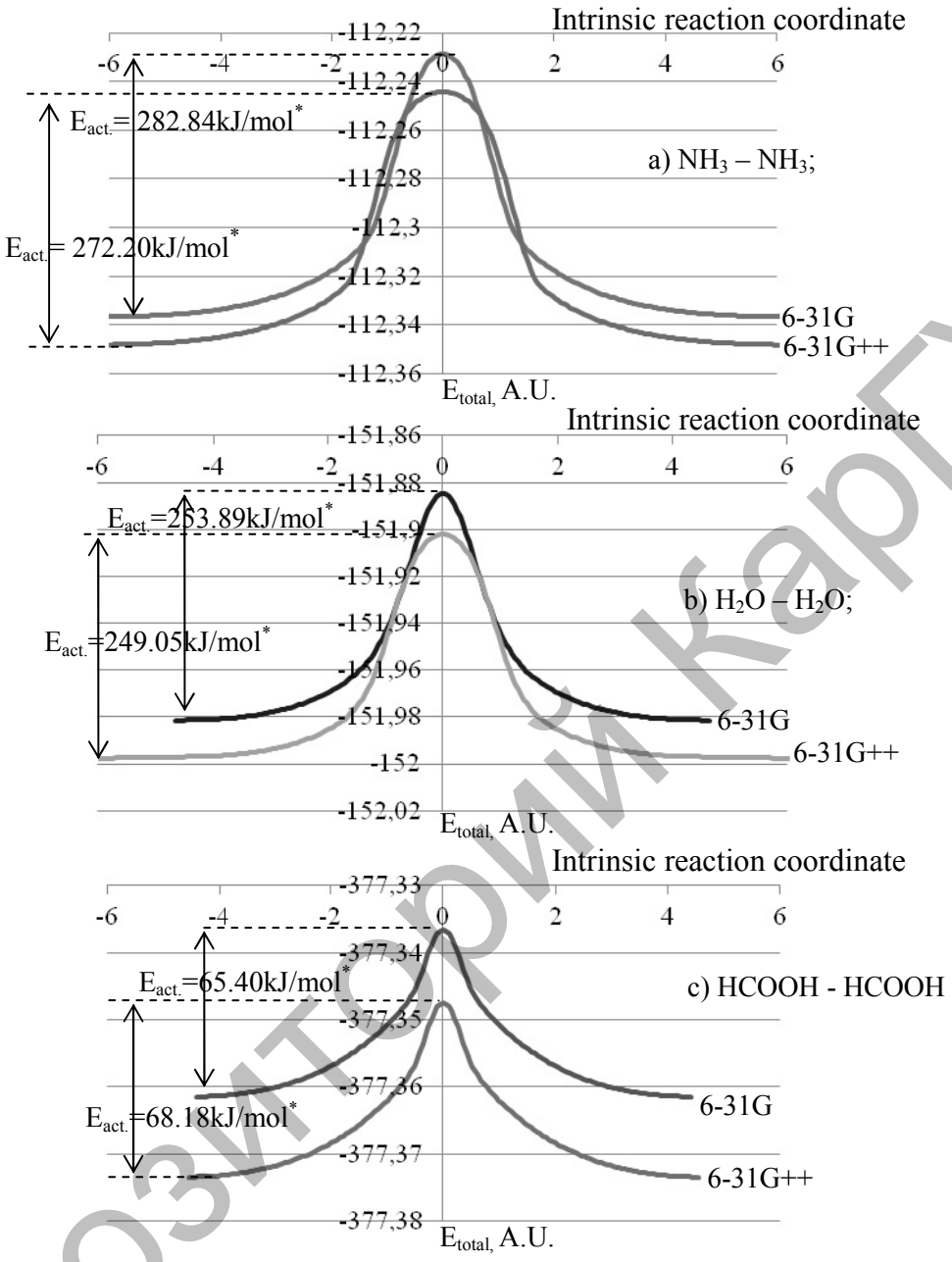
Figure 1. Reaction path diagram for proton exchange in model dimers

From graphs in Figure 1 we can see that the potential barrier height for proton exchange in water dimer is maximal, and in formic acid dimer is minimal. Activationenergyoftheproton exchange reaction was estimated as the difference in the total energies of the transition and initial states of the system. By AM1 activation energy calculations it was found 342.57 kJ/mol for ammonia dimer, 419.66 kJ/mol for water dimer and 154.28 kJ/mol for formic acid dimer. Calculated activation energy values are close to the covalent bond energy that indicates about overestimation of the hydrogen bond energy by the semiempirical AM1 method.

Reaction path diagrams for proton exchange in model dimers were obtained analogically by *ab initio* 6-31G, 6-31G++ calculations with the help of IRCprocedure. The results of calculations are shown in Figure 2.

Figure 2 shows that *ab initio* calculated curves have more acute energy peak in comparison with graphs obtained as a result of semiempirical AM1 calculation. The lower values of total energy were obtained as a result of 6–31G++ *ab initio* calculations. In the6–31G/ 6–31G++ basis set the barrier height of 282.84/272.20 kJ/mol for double proton transfer in ammonia dimer and 253.89/ 249.05 kJ/mol in water dimer and 65.40/68.18 kJ/mol in formic acid dimer was found. It should be noted that the barrier for the proton exchange in formic acid dimer obtained in the present investigation agree with the experimental results for the double proton transfer in DCOOH dimer (50.66 kJ/mol [12]). The difference in the values may be due to the difference in the phases: calculations were made for the gas phase, and the experiment was carried out for the liquid.

Thus, quantum-chemical simulation of the proton exchange reaction in model dimers of ammonia, water and formic acid was carried out by the AM1 and *ab initio* 6–31G, 6–31G++ methods. Activation energy, change of the reaction system geometry and of the hydrogen bridge length ΔR(X-X), Å were monitored during the calculations. Obtained characteristics are presented in Table 3.



Calculation method: 6–31G, 6–31G++ (*1 A.U.=2625.5 kJ/mol)

Figure 2. Reaction path diagram for proton exchange in model dimers

Table 3

Calculated characteristics of proton exchange in model dimers of water, ammonia and formic acid

Dimer	Method					
	AM1		6–31G		6–31G++	
	$E_{act.}$, kJ/mol	ΔR(X-X), Å	$E_{act.}$, kJ/mol	ΔR(X-X), Å	$E_{act.}$, kJ/mol	ΔR(X-X), Å
Ammonia	342.57	1.14	282.84	0.91	272.20	0.88
Water	419.66	0.6	253.89	0.62	249.05	0.56
Formic acid	154.28	0.66	65.40	0.33	68.18	0.35

It can be seen from the data presented in Table 3, that the shortening of the hydrogen bridge length during the proton exchange reaction was fixed both by the semiempirical AM1 method and *ab initio* calcula-

tions. The maximum shortening of the hydrogen bridge length was observed for proton exchange in ammonia dimer (ΔR(N-N) = 0.88–1.14 Å). There are asymmetric types of transition state structure and sequential proton exchange mechanism was fixed. The minimum shortening of the hydrogen bridge length was observed for proton exchange in formic acid dimer (ΔR(O-O)=0.33–0.65 Å). There are symmetrical types of transition state structure and synchronous proton exchange mechanism was fixed.

It should be noted that the barrier height for the proton exchange in formic acid dimer is minimal. In the case of water, which is the ampholyte, a synchronous mechanism of proton exchange was recorded by 6-31G *ab initio* calculations and a sequential mechanism was showed by AM1 and 6–31G++ calculations. It was suggested that the mechanism of proton exchange reaction is determined by the nature of the resulting transition state (symmetrical or asymmetrical). At the same time, the transition state structure is determined by the acid-base properties of reaction partners.

References

1 Бурейко С.Ф. Кинетическая спектроскопия процессов протонного обмена в системах с водородной связью: дис. … д-ра физ.-мат. наук: 01.04.07 / С.Ф. Бурейко. — СПб., 2003. — 309 с.

2 Chojnacki H. Correlation effects in the double proton transfer of the formic acid dimer / H. Chojnacki // Molecular Engineering. — 1997. — No. 7. — P. 161–167.

3 Танасюк Д.А. Водородные связи и протонный обмен в системе вода-этанол / Д.А. Танасюк, В.М. Бяков, В.И. Ермаков // Успехи в химии и химической технологии. — 2014. — Т. 28, № 6 (155). — С. 111–114.

4 Буренин А.В. Классификация энергетических уровней димера аммиака / А.В. Буренин // Оптика и спектроскопия. — 2014. — Т. 116, № 4. — С. 568–572.

5 Клишин Ю.А. Строение димеров аммиака, метана, ацетилена и фтороводорода / Наука, образование, общество: тенденции и перспективы: сб. науч. тр. — М.: ООО «АР-Консалт», 2014. — С. 26–30.

6 Frisch M.J. Gaussian 09, Revision C.01 / M.J. Frisch, G.W. Trucks, H.B. Schlegel. — Wallingford: Gaussian, Inc., 2009. — 245 p.

7 Dennington R. GaussView, version 5 / R. Dennington, T. Keith, J. Millam. — Semichem Inc., Shawnee Mission, KS, 2009. — Retrieved from http://www.gaussian.com/g_tech/gv5ref/gv5citation.htm

8 Лебедев Н.Г. Устойчивые геометрические конфигурации основного и возбужденных состояний димеров воды / Н.Г. Лебедев // Вестн. Волгоград. гос. ун-та. Сер. 1. Мат., физ. — 2011. — № 1 (14). — С. 113–120.

9 Гречухина О.Н. Моделирование молекулярной динамики в димерах карбоновых кислот: автореф. дис. … канд. физ.-мат. наук: 05.13.18 — «Математическое моделирование, численные методы и комплексы программ» / О.Н. Гречухина. — Астрахань, 2009. — 22 с.

10 Даринский Б.М. Изомеры димера из молекул воды / Б.М. Даринский, В.Ф. Селеменев, Е.М. Флягина // Сорбционные и хроматографические процессы. — 2013. — Т. 13, Вып. 6. — С. 902–911.

11 Cook D.B. Handbook of Computational Quantum Chemistry / D.B. Cook. — New York: Dover Publications, 2005. — 832 p.

12 Shettya S. A quantitative and a qualitative study of the resonance assisted double proton transfer in formic acid dimer / S. Shettya, S. Pal, D.G. Kanhere, A. Goursot // Indian Journal of Chemistry. — 2006. — Vol. 45A. — P. 202–212.

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Аммиак, су және құмырсқа қышқылы димерлеріндегі протон алмасу: квантты-химиялық есептеулер

Сутегі арқылы түзілген комплекстердегі протон алмасу сутегі байланысы бар молекулалық жүйелердегі динамикалық процестерде маңызды орын алады. Бірақ осы облыстағы көптеген тәжірибелік және теориялық берілгендерге қарамастан, протон алмасудың механизмі туралы ғалымдарда бірдей көзқарас қалыптаспаған. Аммиак, су және құмырсқа қышқылы күшті қышқылнегіздік қасиеттерімен ерекшеленетін, өлшемі жағынан кішкене, протон алмасу реакцияларын теориялық модельдеуге ыңғайлы протолиттер болып табылады. Аммиак, су және құмырсқа қышқылы модельді димерлерінде протон алмасу реакцияларының квантты химиялық модельдеуі Gaussian-2009 бағдарламасының *ab initio* 6–31G, 6–31G++ базистерінде және AM1 әдістері арқылы орындалды. Ауыспалы күйдің құрылысы QST2 процедурасының көмегімен анықталды, реакция координатасы бойынша түсу IRC процедурасының көмегімен жүргізілді. Зерттеліп отырған протон алмасу реакцияларында құмырсқа қышқылы димерінің ауыспалы күйінің симметриялы құрылысы және аммиак димерінің ауыспалы күйінің асимметриялы құрылысы алынды. Протон алмасу механизмі құмырсқа қышқылы димерінде бір уақытта, ал аммиакта сатылап жүретіндігі көрсетілді. Барлық модельді жүйелерде протон алмасу реакциясы кезінде сутектік байланыс ұзындығы қысқарады. Протон алмасу механизмі түзілетін ауыспалы күйдің табиғатына (симметриялы немесе

асимметриялы) негізделген, ал оның құрылысы реакцияға түсетін заттардың қышқыл-негіздік қасиеттерімен анықталады деген болжам жасалынды.

Кілт сөздер: протон алмасу, димер, реакцияның сатылап және бір уақыттағы механизмі, сутегі байланысы арқылы түзілетін комплекс, AM1, *ab initio*, 6–31G, QST2, IRC.

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Обмен протонами в димерах аммиака, воды и муравьиной кислоты: квантово-химический расчет

Протонный обмен в водородносвязанных комплексах занимает важное место среди динамических процессов, имеющих место в молекулярных системах с водородной связью. Однако, несмотря на многочисленные экспериментальные и теоретические изыскания в данной области, единой точки зрения на механизм протонного обмена учеными не выработано. Аммиак, вода и муравьиная кислота являются небольшими по размеру протолитами с сильно различающимися кислотно-основными свойствами, удобными для теоретического моделирования реакции обмена протона. Методами AM1 и *ab initio* в базисах 6–31G, 6–31G++программы Gaussian-2009 выполнено квантово-химическое моделирование реакции протонного обмена в модельных димерах аммиака, воды и муравьиной кислоты. Поиск структуры переходного состояния осуществлен с помощью процедуры QST2, спуск по координате реакции — с помощью процедуры IRC. Для исследуемой реакции обмена протонами получено симметричное строение переходного состояния в случае димера муравьиной кислоты и асимметричное строение переходного комплекса в случае димера аммиака. Показан синхронный механизм обмена протонами в димере муравьиной кислоты, последовательный механизм в димере аммиака. Во всех модельных системах отмечено динамическое сокращение длины водородного мостика в ходе реакции протонного обмена. Сделано предположение, что механизм обмена протонами обусловливается характером образующегося переходного состояния (симметричное или асимметричное), структура которого, в свою очередь, определяется кислотно-основными свойствами реакционных партнеров.

Ключевые слова: протонный обмен, димер, последовательный и синхронный механизмы реакции, комплекс за счет водородной связи, AM1, *ab initio*, 6–31G, QST2, IRC.

References

1 Bureyko, S.F. (2003). Kineticheskaia spektroskopiia protsessov protonnoho obmena v sistemakh s vodorodnoi sviaziu [Kinetic spectroscopy of proton exchange processes in systems with a hydrogen bond]. *Doctor's thesis*. Saint Petersburg [in Russian].

2 Chojnacki, H. (1997). Correlation effects in the double proton transfer of the formic acid dimer. *Molecular Engineering*, 7, 161–167.

3 Tanasyuk, D.A., Byakov, V.M., & Ermakov, V.I. (2014). Vodorodnye sviazi i protonnyi obmen v sisteme voda – etanol [Hydrogen bonds and proton exchange in water-ethanol system]. *Uspekhi v khimii i khimicheskoi tekhnolohii. — Advances in chemistry and chemical technology, 6,* 111–114 [in Russian].

4 Burenin, A.V. (2014). Klassifikatsiia enerheticheskikh urovnei dimera ammiaka [Classification of energy levels of ammonia dimer]. *Optika i spektroskopiia. — Optics and spectroscopy, 116, 4,* 568–572 [in Russian].

5 Klishin, Yu.A. (2014). Stroenie dimerov ammiaka, metana, atsetilena i ftorovodoroda [The structure of the dimers of ammonia, methane, acetylene and hydrogen fluoride]. *Nauka, obrazovanie, obshchestvo: tendentsii i perspektivy — Science, Education, Society: Trends and Perspectives.* Moscow: OOO «AR-Konsalt» [in Russian].

6 Frisch, M.J., Trucks, G.W., & Schlegel, H.B. (2009). *Gaussian 09, Revision C.01.* Wallingford: Gaussian Inc.

7 Dennington, R., Keith, T., & Millam, J. (2009). GaussView, version 5. Semichem Inc., Shawnee Mission, KS. Retrieved from http://www.gaussian.com/g_tech/gv5ref/gv5citation.htm

8 Lebedev, N.G. (2011). Ustoichivye heometricheskie konfihuratsii osnovnoho i vozbuzhdennykh sostoianii dimerov vody [Stable geometric configurations of ground and excited states of water dimmers]. *Vestnik Volhohradskoho hosudarstvennoho universiteta. Seriia 1, Fizika i Matematika. — Volhohrad state University Bulletin. Ser. 1, Mat. and Phys, 1(14),* 113–120 [in Russian].

9 Grechukhina, O.N. (2009). Modelirovaniie molekuliarnoi dinamiki v dimerakh karbonovykh kislot [Modeling of molecular dynamics in carboxylic acids dimmers]. *Extended abstract of candidate'sthesis.* Astrakhan [in Russian].

10 Darinsky, B.M., Selemenev, V.F., & Flyagina, E.M. (2013). Izomery dimera iz molekul vody [Isomers of dimer from water molecules]. *Sorbtsionnyie i khromatohraficheskie protsessy. — Sorption and chromatographic processes, 13, 6*, 902–911 [in Russian].

11 Cook, D.B. (2005). *Handbook of Computational Quantum Chemistry*. New York: Dover Publ.

12 Shettya, S., Pal, S., Kanhere, D.G., & Goursot, A. (2006). A quantitative and a qualitative study of the resonance assisted double proton transfer in formic acid dimer. *Indian Journal of Chemistry, 45A,* 202–212.