Physical Chemistry

Ab initio calculations of activation energy of the reaction of hydrogen exchange on strongly acidic centers

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Ab initio calculations of fragments of the potential energy surfaces of hydrogen exchange reactions between H_2, CH_4, and alanine molecules and the H_3O^+ ion were performed by the restricted Hartree—Fock method, at the second-order Møller—Plesset level of perturbation theory, and by the method of coupled clusters using the 6-31G* and aug-cc-pVDZ basis sets. The one-center synchronous mechanism of hydrogen exchange reaction was studied and the activation energies and structures of transition states were determined. It was found that the geometric parameters of the H_2 and CH_4 molecules in the transition states are close to those of the H_3^+ and CH_5^+ ions. The higher the proton affinity of the reacting molecule in the reaction studied, the lower the activation energy of hydrogen exchange. The one-center mechanism studied can be used to describe the high-temperature solid-state catalytic isotope exchange (HSCIE) reaction. The results of *ab initio* calculations of synchronous hydrogen exchange between the H_3O^+ ion and hydrogen atoms in different positions of the alanine molecule are in good agreement with experimental data on the regioselectivity and stereoselectivity of the HSCIE reaction with spillover-tritium.

Key words: *ab initio* quantum-chemical calculations, activation energy, mechanism of substitution reaction, isotope exchange of hydrogen, hydrogen spillover.

Investigation of solid-state catalytic reactions on acidic centers of the surface of solid catalysts is of considerable interest. Acidic decationization of ammonium-exchanged forms of zeolites results in protonated H^+-forms containing stronger Brønsted acidic centers[1,2] compared to well-studied H-forms. It was established by IR spectroscopy that strongly acidic H^+-centers are H_3O^+ ions that interact with aliminum-oxygen nodes of the zeolite framework.[3] Recently,[4,5] it has been shown that the Brønsted centers also appear on the surface of zeolites under the action of spillover-hydrogen.[6] Small amounts of water molecules present on the surface of zeolites favor the appearance of these centers.

The synchronous mechanism of hydrogen transfer in organic compounds under the action of catalysts implies participation of two catalytic centers, one of which is a hydrogen donor while the other is a hydrogen acceptor. The two-center mechanism of catalysis is a generally

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recognized mechanism used for the description of reactions occurring both on oxide catalysts and in the presence of enzymes.[7] A two-center mechanism of the reaction of hydrogen exchange between methane and the H_3O^+ ion was proposed,[8] which also implies the involvement of H_2O as proton acceptor. In this case, hydrogen exchange in CH_4 occurs with inversion of the configuration. In our preceding study,[9] carried out in the framework of investigation of the solid-state isotope exchange of hydrogen in amino acids, we investigated a new one-center mechanism of hydrogen exchange at the saturated C atom with retention of the configuration. This mechanism implies a synchronous hydrogen exchange between an acidic center (the H_3O^+ ion) and a C—H group of the organic compound with the formation of a fragment with a pentacoordinated C atom in the transition state (TS). The activation energy of the reaction of hydrogen exchange between the CH_4 molecule and the H_3O^+ ion, calculated by the HF/6-311G* method and at the second-order Møller—Plesset level of perturbation theory (MP2/6-311G*//RHF/6-31G*) with inclusion of correlation corrections, is 27.2 and 21 kcal mol^{-1}, respectively. This work was carried out in a continuation of our studies of the one-center synchronous mechanism of hydrogen exchange. To this end, we performed *ab initio* calculations of the CH_4—H_3O^+ and H_2—H_3O^+ systems at higher levels of theory and studied the TS of the reaction between the alanine molecule and the H_3O^+ ion.

Calculation Procedure

Calculations of isolated molecular systems, fragments of the potential surfaces, and TS of the reaction of hydrogen exchange were performed using the Hartree—Fock (HF) method, at the second-order Møller—Plesset (MP2) level of perturbation theory,[10] and by the method of coupled clusters (CCSD(T))[11] with the 6-31G* and Dunning aug-cc-pVDZ [12] basis sets. The geometries of systems considered were optimized using analytical gradients without considering the point symmetry group. The quasi-Newtonian method of synchronous transition[13] was used in search for the transition states. The calculations were carried out using the GAUSSIAN-94 [14] and GAMESS [15] programs on a CRAY J-90 supercomputer (Berkeley, California, USA).

Ab initio calculations of geometric parameters of the TS of the hydrogen exchange reactions between amino acids and the H_3O^+ ion is a complex problem even for modern supercomputers. Because of this, we also developed a simplified procedure for calculations, which implies fixation of the geometry of the C—H_2—O fragment in the TS and optimization of all the remaining internal coordinates of the molecular system to search for a minimum of the total energy. In these calculations the geometric parameters of the C—H_2—O fragment were taken to be equal to those of the TS of the reaction of hydrogen exchange between methane and the H_3O^+ ion.

Results and Discussion

The results of *ab initio* calculations of H_2, H_2O, and CH_4 molecules and their complexes with a proton have been reported.[8,16] In these cases, the geometric parameters were optimized by the Hartree—Fock (HF/6-31G*) method and the energy parameters were calculated at the MP2 level of theory without geometry optimization. In this work, we studied a new route of the reaction of H_2 and CH_4 molecules with the acidic center (the H_3O^+ ion). The transition states of the reaction of hydrogen exchange following the one-center synchronous mechanism were determined. The geometry of the TS was optimized by the MP2/6-31G* method. The total energies of the molecular systems shown in Fig. 1 were calculated by the CCSD(T) and MP2 methods with the Dunning aug-cc-pVDZ basis set (Table 1).

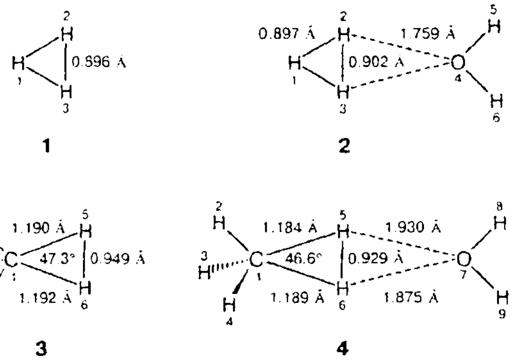


Fig. 1. Structures of complexes with a proton H_3^+ (**1**) and CH_5^+ (**3**) and transition states of the reaction of hydrogen exchange between the H_3O^+ ion and H_2 and CH_4 molecules (**2** and **4**, respectively). Complex **1** has D_{3h} symmetry; the H—H_2—O and C—H_2—O fragments in **2** and **4** are planar.

Table 1. Total energies (E_{tot}) of molecular systems and transition states of the hydrogen exchange reaction between the H_2 (**2**) and CH_4 (**4**) molecules and the H_3O^+ ion calculated in different approximations

System	E_{tot}/kcal mol^{-1}			
	RHF	MP2	MP2	CCSD
	6-31G*		aug-cc-pVDZ	
H_2	−1.1268	−1.1441	−1.1562	−1.1649
H_3^+	−1.2743	−1.2964	−1.3236	−1.3325
H_2O	−76.0107	−76.1968	−76.2609	−76.2739
H_3O^+	−76.2866	−76.4751	−76.5263	−76.5415
CH_4	−40.1952	−40.3370	−40.3676	−40.3954
CH_5^+	−40.3885	−40.5364	−40.5783	−40.6067
2	−77.3367	−77.5490	−77.6344	−77.6561
4	−116.4377	−116.7806	−116.8744	−116.9154

The activation energies (in kcal mol^{-1}) of the reactions of hydrogen exchange calculated by different methods are listed below:

Method	H_2 + H_3O^+	CH_4 + H_3O^+
HF/6-31G*	48.1	27.7
MP2/6-31G*	44.1	19.8
MP2/aug-cc-pVDZ	30.2	12.2
CCSD(T)/aug-cc-pVDZ	31.6	13.5

Increasing the level of calculations leads to some decrease in the activation energies. The results obtained by the MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ methods are close, *viz.*, 30—32 and 12—14 kcal mol^{-1} for hydrogen exchange in H_2 and CH_4, respectively.

The geometric parameters of the TS of the reactions of one-center isotope exchange in H_2 and CH_4 are listed in Table 2 and the effective charges on the atoms in the TS are listed in Table 3. When characterizing the structure of the TS of the hydrogen exchange reaction H_2 + H_3O^+, it should be noted that the H(1)—H(2) and H(1)—H(3) distances (see Fig. 1 and Table 2) virtually coincide with the H—H distance in the H_3^+ ion, equal to 0.896 Å (MP2/aug-cc-pVDZ). It is noteworthy that the effective charge of the H_3 fragment in the TS of the H_2 + H_3O^+ reaction (**2**) is +1.00 au (see Table 3).

Table 2. Results of calculations of bond lengths (*d*) and bond angles for structures of transition states of the hydrogen exchange reactions between H_2 (**2**) and CH_4 (**4**) molecules and the H_3O^+ ion

Transition state (method of calculations)	Bond	*d*/Å
2[a]	H(1)—H(2)	0.897
(MP2/aug-cc-pVDZ)	H(2)—H(3)	0.902
	H(2)—O(4)	1.759
	O(4)—H(5)	0.972
4[b]	C(1)—H(2)	1.088
(MP2/6-31G*)	C(1)—H(3)	1.102
	C(1)—H(4)	1.088
	C(1)—H(5)	1.184
	C(1)—H(6)	1.189
	H(5)—H(6)	0.929
	H(5)—O(7)	1.931
	H(6)—O(7)	1.875
	O(7)—H(8)	0.975
	O(7)—H(9)	0.975

[a] The H(5)—O(4)—H(6) angle is 105.81°.

[b] The H(8)—O(7)—H(9) angle is 105.27°.

Table 3. Effective charges (*q*/au) on the atoms of structures of transition states of the reactions of hydrogen exchange between the H_2 (**2**) or CH_4 (**4**) molecules and the H_3O^+ ion

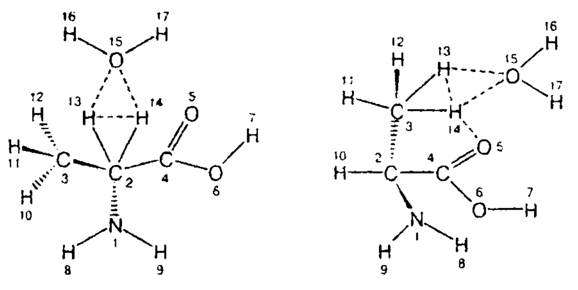
Transition state (method of calculations)	Atom	*q*
2	H(1)	0.14
(MP2/aug-cc-pVDZ)	H(2)	0.43
	O(4)	−0.53
	H(5)	0.26
4	C(1)	−0.91
(MP2/6-31G*)	H(2)	0.34
	H(3)	0.35
	H(4)	0.34
	H(5)	0.39
	H(6)	0.40
	O(7)	−0.87
	H(8)	0.48
	H(9)	0.48

For the CH_4 + H_3O^+ reaction, we found the transition complex (**4**), which is structurally close to the CH_5^+ cation (see Tables 2 and 3). The H(5)—H(6) distance in TS **4** and in the CH_5^+ cation, calculated at the same (MP2/6-31G*) level of theory, is 0.929 and 0.949 Å, respectively. The distances between the C atom and exchanging H atoms in TS **4** and in the CH_5^+ cation are respectively 1.184, 1.189 and 1.190, 1.192 Å. The effective total charge of the CH_5 fragment in complex **4** is +0.92 au. Thus, the structure of the transition states formed according to the one-center mechanism of the reaction of hydrogen exchange in H_2 and CH_4 on the H_3O^+ acidic center, as well as the charge distributions in these systems, are rather close to those characteristic of the H_3^+ and CH_5^+ ions. Because of this, the above transition states can be represented as cations bonded to a water molecule. On the contrary, *ab initio* calculations of the reactions between the H_2 and CH_4 molecules and bridging hydroxyl groups characteristic of H-forms of zeolites[8] showed that the TS are similar to the adsorbed H^- and CH_3^- anions, respectively. The activation energies of the reactions on this type of acidic centers (*i.e.*, bridging hydroxyl groups of zeolites) lie in the range 25—40 kcal mol^{-1}.

Based on the values of the total energies of neutral H_2, CH_4, and H_2O molecules and protonated forms (see Table 1), one can calculate the proton affinities of these molecules, which are equal to 105.2, 132.6, and 167.9 kcal mol^{-1}, respectively. The corresponding experimental values are 101.2,[17] 130.2,[18] and 165.0 kcal mol^{-1},[18] respectively. The enthalpies of the reactions of proton transfer from the H_3O^+ ion to the H_2 and methane molecule are respectively 63 and 35 kcal mol^{-1}. Thus, these reactions are extremely hampered, whereas the formation of TS with a close structure and charge distribution can occur with relative ease.

The studied one-center mechanism of hydrogen exchange can be used for description of the regioselectivity and stereoselectivity of the reaction of high-temperature solid-state catalytic isotope exchange (HSCIE) of hydrogen.[19] As has been shown previously, the basis for the HSCIE reaction is the phenomenon of hydrogen spillover.[20] It has been established experimentally that trace amounts of water favor hydrogen spillover over the surface of the inorganic support.[21] In this case the acidic centers formed (*e.g.*, of the H_3O^+ type) can participate in the reaction with a solid organic compound. Isotope exchange of hydrogen at the asymmetric C_α atom occurs with retention of the configuration, while the experimentally determined activation energy of the HSCIE reaction is 25.7 kcal mol^{-1} and 14 kcal mol^{-1} for hydrogen exchange in the α- and β-positions of the alanine molecule, respectively.[22]

Ab initio calculations of the alanine molecule and its possible conformations were reported.[23,24] We consid-



5 **6**

Fig. 2. Structures of transition states of the hydrogen exchange reactions between the H_3O^+ ion and alanine molecule for substitution in α- (**5**) and β-position (**6**).

Table 4. Results of calculations (variants *1—3*, see text) of bond lengths (*d*) and total energies (E_{tot}) of the structures of transition states of the hydrogen exchange reactions between H_3O^+ ion and alanine molecule in the case of substitution in α- (**5**) and β-position (**6**) and activation energies of the exchange (E_a)

Parameter (method of calculations)	**5**		**6**		
	1	*2*	*1*	*2*	*3*
Bond			d/Å		
N(1)—C(2)	1.410	1.408	1.452	1.450	1.447
C(2)—C(3)	1.574	1.573	1.536	1.538	1.525
C(2)—C(4)	1.541	1.544	1.521	1.521	1.522
C(4)—O(5)	1.179	1.172	1.175	1.176	1.189
C(4)—O(6)	1.304	1.314	1.335	1.334	1.307
C(2) (C(3))—H(13)	1.199	1.199	1.214	1.199	1.199
C(2) (C(3))—H(14)	1.204	1.204	1.221	1.204	1.204
H(13)—H(14)	0.876	0.876	0.864	0.876	0.876
O(15)—H(13)	2.004	2.004	2.077	2.004	2.004
O(15)—H(14)	1.957	1.957	1.985	1.957	1.957
O(5)—H(14)	2.330	2.958	3.861	3.855	2.164
O(6)—H(14)	3.045	2.321	2.925	2.332	3.775
N(1)—H(13)	2.022	2.042	2.719	2.460	2.512
N(1)—H(14)	2.199	2.172	2.404	2.692	2.884
Energy			$-E_{tot}$ (au)		
$-E_{tot}$ (RHF/6-31G*)	398.1084	398.1082	398.1151	398.1144	398.1250
$-E_{tot}$ (MP2/6-31G*)	399.2070	399.2075	399.2124	399.2126	399.2220
			E_a/kcal mol^{-1}		
E_a (RHF/6-31G*)	27.0	27.2	22.8	23.3	16.6
E_a (MP2/6-31G*)	20.0	19.6	16.6	16.4	10.5

ered the reaction of C—H bonds of an alanine molecule with the acidic center (the H_3O^+ ion, see Table 4 and Fig. 2). Transition state **6** is formed in the reaction of isotope exchange of the H atom at the C(3) atom of the alanine molecule. Geometric parameters of this TS were obtained from *ab initio* RHF/6-31G* calculations with full geometry optimization (see Table 4, variant *1*). The total energy and the activation energy of the reaction of hydrogen exchange were also calculated by the MP2/6-31G* method assuming a fixed geometry calculated by the RHF/6-31G* method. For TS **6**, we also calculated the same reaction provided that the parameters of the $C—H_2—O$ fragment are the same as in calculations of the TS of the hydrogen exchange reaction between methane and the hydroxonium ion (RHF/6-31G*) (variant *2*). From the data in Table 4 it can be seen that the total energies and geometric parameters of TS **6** in variants *1* and *2* are very close. Therefore, further calculations of the TS of the hydrogen exchange reaction between alanine and the hydroxonium ion were performed using this approach. The variant of calculations *3* corresponds to the case where TS **6** is formed in the reaction of the acidic center with such a conformation of the alanine molecule in which the O atom of the carbonyl group rather than the O atom of the hydroxyl group (constituting the carboxyl group) is the closest to the exchanging H atoms. In this case, the total energy of the alanine conformation corresponding to TS **6** is 0.9 kcal mol^{-1} higher than that calculated by the MP2/6-31G* method. Interconversion of the conformations occurs due to rotation of the carboxyl group of the amino acid molecule, with an activation barrier of 1.9 kcal mol^{-1} (calculations by the MP2/6-31G* method). Nearly free rotation of the carboxyl group becomes hindered in the course of the formation of the TS of the hydrogen exchange reaction and two types of TS **6** can be realized (variants *2* and *3*). In the latter case, the total energy of TS **6**, calculated by the MP2/6-31G* method, is 5.9 kcal mol^{-1} lower than in the former. From the analysis of the electron distribution for the TS of the exchange reaction for alanine (Table 5) it follows that the interaction between the O atom of the carboxyl group and the H_2 group is mainly of the Coulomb type. In fact, the charge of the H_2 group in the transition state is larger than +0.9 au. The effective charge on the O atom of the carboxyl group is about −0.5 au and that of the O atom of the hydroxyl group is −0.7 au. In the case where the exchanging H atom is at the C_α atom, the difference between the energies of TS **5** calculated using variants *1* and *2* is rather small and the structure in which the O atom of the hydroxyl group is closer to the exchanging H atoms is somewhat more favorable. The calculated values of the activation energy for different routes of the hydrogen exchange reaction are listed in Table 4. The activation energy of the hydrogen exchange reaction in the α-position of the alanine molecule is 19.6 kcal mol^{-1} (MP2/6-31G*), which is rather close to the corresponding value for the hydrogen exchange reaction in methane calculated using the same basis set (19.8 kcal mol^{-1}). According to the mechanism suggested, hydrogen exchange in the β-position occurs much easier than in the α-position (the calculated activation energy is 10.5 kcal mol^{-1} at the MP2/6-31G* level of theory). Most likely, the

Table 5. Calculated (variants *1—3*, see text) effective charges (*q*/au) on the atoms of the structures of transition states of the hydrogen exchange reaction between the H_3O^+ ion and the alanine molecule in α- (**5**) and β-positions (**6**)

Atom	*q*				
	5		**6**		
	1	*2*	*1*	*2*	*3*
N(1)	−0.79	−0.80	−0.88	−0.88	−0.86
C(2)	−0.37	−0.37	−0.07	−0.06	−0.08
C(3)	−0.54	−0.53	−0.71	−0.75	−0.75
C(4)	0.80	0.80	0.75	0.75	0.80
O(5)	−0.49	−0.47	−0.48	−0.48	−0.55
O(6)	−0.66	−0.69	−0.73	−0.73	−0.68
H(7)	0.51	0.51	0.50	0.50	0.50
H(8)	0.41	0.42	0.41	0.40	0.38
H(9)	0.41	0.41	0.39	0.39	0.41
H(10)	0.27	0.26	0.28	0.28	0.26
H(11)	0.27	0.26	0.34	0.35	0.34
H(12)	0.27	0.27	0.34	0.33	0.34
H(13)	0.45	0.45	0.40	0.41	0.43
H(14)	0.41	0.41	0.39	0.41	0.40
O(15)	−0.92	−0.92	−0.91	−0.92	−0.92
H(16)	0.49	0.49	0.49	0.49	0.48
H(17)	0.49	0.49	0.49	0.49	0.49

interaction between the O atom of the carbonyl group and exchanging H atoms in the TS can be responsible for enhancement of the reactivity of H atoms in this position.

The results of our *ab initio* calculations of the reaction of hydrogen exchange between alanine and a model acidic center (the H_3O^+ ion) are in good agreement with experimental data on regioselectivity and stereoselectivity of the reaction of solid-state isotope exchange of hydrogen by spillover-tritium. We hope that the one-center mechanism of the reaction of organic compounds with strongly acidic centers can be used in studies of the reactions occurring with participation of spillover-hydrogen and the reactions on the surface of H^+-forms of zeolites.

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