Brief Communications

New concepts of the mechanism of hydrogen exchange between organic molecules and strong acidic centers

Yu. A. Borisov,[a]* *Yu. A. Zolotarev,*[b] *E. V. Laskatelev,*[a] *and N. F. Myasoedov*[b]

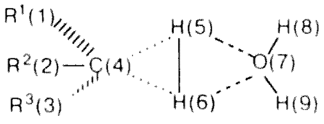
[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation
Fax: 007 (095) 135 5085
[b]*Institute of Molecular Genetics, Russian Academy of Sciences,*
26 pl. Kurchatova, 123182 Moscow, Russian Federation
Fax: 007 (095) 196 0221

Ab initio calculations of the activation energy of the reaction of hydrogen exchange between the methane molecule and the H_3O^+ ion in the gaseous phase have been carried out by using Hartree—Fock methods and Moeller—Plesset second order perturbation theory (MP2) methods. The structure of the transition state of this reaction has been found. The interaction of the H_3O^+ ion with molecules of aliphatic hydrocarbons and amino acids has been studied by the semiempirical AM1 method.

Key words: quantum-chemical calculations, isotope exchange, activation energy.

In this work, we have carried out a theoretical study of the mechanism of hydrogen exchange of organic molecules (methane, propane, alanine, glycine, methionine) with a model acidic center. For the latter, we used the gaseous positive ion H_3O^+. For the $CH_4-H_3O^+$ pair, *ab initio* calculations by methods of Hartree-Fock[1] and the second order perturbation theory method[2] by Moeller—Plesset (MP2) in various basis sets (3-21 G, 6-31 G*, 6-311 G*) with the use of the GAMESS program[3] were performed. For more complicated interactions between "H_3O^+ and the organic molecule," the semi-empirical calculations used the AM1 method.[4]

It was shown for the $CH_4-H_3O^+$ pair that as the interacting reagents approach one another the following configuration of the transition state can occur:



1

This structure is unusual in that, due to the formation of an H—H bond (atoms 5 and 6 of the above structure), there is a decrease in the activation energy of the hydrogen exchange reaction. It should also be mentioned that the bond angles and lengths of C—H bonds at the C(4) carbon atom almost completely coincide with the corresponding parameters of the CH_5^+ ion.[5] Table 1 presents the calculated total energies of the initial compounds and of the transition state for hydrogen exchange between methane and H_3O^+ in three basis

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1852—1854, July, 1996.

Table 1. Total energies of the initial compounds and the transition states (T.S.) in the exchange of hydrogen between methane and H_3O, calculated for various bases, a.u.

System	HF/3-21G	HF/6-31G*	HF/6-311G*	MP2/6-311G*
H_3O^+	−75.8912	−76.2866	−76.3151	−76.5204
CH_4	−39.9769	−40.1952	−40.2034	−40.3514
T.S.	−115.8049	−116.4377	−116.4752	−116.8384

Table 2. Geometric parameters of the transition state of hydrogen exchange between CH_4 and H_3O calculated by Hartree—Fock and AM1 methods

Parameter	3-21G	6-31G	6-311G*	AM1
Bond			R/Å	
1—4	1.081	1.080	1.078	1.12
2—4	1.092	1.089	1.089	1.12
3—4	1.078	1.079	1.077	1.12
4—5	1.200	1.199	1.199	1.34
4—6	1.201	1.204	1.204	1.35
4—7	2.856	3.049	3.031	2.87
5—6	0.896	0.876	0.889	0.86
5—7	1.805	2.004	1.994	2.11
6—7	1.793	1.957	1.939	2.08
7—8	0.970	0.953	0.943	0.96
7—9	0.970	0.953	0.943	0.96
Bond angle		α/deg		
1—4—2	106.8	108.9	109.3	110.7
1—4—3	114.2	116.3	116.9	113.1
2—4—3	108.5	110.2	110.0	108.6
1—4—5	119.9	117.7	117.0	113.9
2—4—5	85.8	82.9	81.8	90.0
3—4—5	116.5	115.4	115.8	117.9
4—5—6	68.2	68.9	68.6	71.1
4—6—5	68.0	68.3	68.0	71.5
4—5—7	143.0	143.1	142.1	110.3
4—6—7	144.3	148.6	148.4	111.8
4—7—8	125.3	127.0	126.2	132.5
4—7—9	125.3	127.1	126.2	121.3
Torsion angle		β/deg		
5—6—7—8	100.4	99.6	99.6	157.3
5—6—7—9	−100.5	−100.6	−100.1	−13.5
1—4—5—6	66.6	67.3	69.9	76.9
2—4—5—6	173.6	175.0	177.5	−170.3
3—4—5—6	−77.8	−76.0	−74.3	−59.2

sets (3-21G, 6-31G* and 6-311 G*) for the Hartree—Fock approximation and in the 6-311 G* basis set within the MP2 method. In Table 2 the geometric parameters values of the transition state are found. The geometry optimized in the HF/6-311 G* approximation was used for MP2 calculations. On the basis of these calculations, the activation energies of hydrogen exchange between methane and the H_3O^+ ion were determined as shown below for various approximations:

Approximation	Energy activation /kcal mol^{-1}
HF/3-21G	39.6
HF/6-31G*	27.7
HF/6-311G*	27.2
MP2/6-311G*	21.0

It is of interest to compare the established activation energies of the synchronous transfer of two protons between the hydroxonium ion and the methane molecule with the *ab initio* calculation results[6] for the potential surface of the reaction of hydrogen exchange in the $H_3O^+—CH_4—H_2O$ system. In this study, a mechanism involving synchronous transfer of two protons and the participation of two water molecules was examined. The activation energy for this system was found to be equal to 30 kcal mol^{-1} (MP2/6-311G*), which exceeds the energy determined in our work for the mechanism involving one water molecule.

It has been hitherto accepted as conventional that the synchronous transfer of a proton takes place with the participation of two catalytic centers.[7,8] It follows from our calculations that a path of hydrogen exchange between CH_4 and H_3O^+ exists, in which the transition state has structure **1**. As far as we know, this is the first time when a one-center mechanism of hydrogen exchange has been observed.

In a recent work,[9] the nature of highly acidic centers of zeolites was investigated using molecular spectroscopy methods. It follows from this work that the most acidic protons are localized on water molecules adsorbed on zeolite surfaces. These adsorbed water molecules are bound to the surface by hydrogen bonds. Consequently, the model suggested in our work can be applied to the analysis of reactions proceeding on highly acidic catalytic centers of zeolites. Hydrogen exchange in the methane molecule on zeolite has been experimentally studied (*cf.* Ref. 10). The activation energy of this reaction was determined to be equal to 29 kcal mol^{-1}, correlating well with the value of the activation energy that we found for the one-center synchronous transfer of a proton.

The geometric structure of the transition state in both the *ab initio* calculations and in the semi-empirical calculations by the AM1 method are very similar (Table 2), and the activation energy calculated by the AM1 method, is equal to 18 kcal mol^{-1}, which is close to the value of 21.0 kcal mol^{-1} obtained *ab initio*.

Based on the similar agreement between the *ab initio* and AM1 calculations, we have carried out AM1 calculations of some systems that require long computation time even on CRAY type computers.

For instance, for propane structure **1** of the transition state is occurs in the exchange of both the primary (R^1 = C_2H_5, R^2 = H, R^3 = H) and the secondary (R^1 = CH_3, R^2 = CH_3, R^3 = H) hydrogen atoms. The activation energy calculated by the AM1 method is about 15 kcal mol^{-1} in both cases. *Ab initio* calculations with respect to propane were also made. The activation energy was 12.8 kcal mol^{-1} for the exchange of the primary hydrogen atom and 11.2 kcal mol^{-1} for the exchange of the secondary atom (MP2/6-31G*) with analogous transition state structures.

For the hydrogen exchange reaction at the alanine β-atom the activation energy was found to be 11 kcal mol^{-1} by the AM1 method with the same transition state structure (R^1 = CH(NH_2)COOH, R^2 = H, R^3 = H); for the α-atom it was 21 kcal mol^{-1} (R^1 = COOH, R^2 = NH_2, R^3 = CH_3). The calculation results obtained allow us to offer a new interpretation of the hydrogen isotope exchange reaction conducted under conditions of high-temperature solid-state catalytic isotopic exchange (HSCIE)[11] of organic compounds with activated tritium. In this reaction, methyl groups are the most reactive groups in aliphatic amino acids. Isotope exchange at the asymmetric carbon atoms proceeds with retention of the configuration. These particular features of the HSCIE reaction can be accounted for by the suggested mechanism of synchronous transfer at one catalytic center. Later we intend to undertake a theoretical study of isotope exchange for aromatic and heteroaromatic molecules.

References

1. C. C. J. Roothaan, *Rev. Mod. Phys*, 1951, **23**, 69.
2. M. J. Frisch, M. Head-Gordon, and J. A. Pople, *Chem. Phys. Lett.*, 1990, **166**, 275.
3. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
4. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
5. S. Yamabe, Yo. Osamura, and T. Minato, *J. Am. Chem. Soc.*, 1980, **102**, 2268.
6. E. M. Evleth, E. Kassab, and L. R. Sierra, *J. Phys. Chem.*, 1994, 98, 1421.
7. K. I. Zamaraev, *Russ. Chem. Rev.*, 1993, **62**, 1051.
8. R. M. Minyaev and V. I. Minkin, *Dokl. Akad. Nauk*, 1995, **340**, 634 [*Dokl. Chem.*, 1995, **340** (Engl. Transl.)].
9. L. S. Kosheleva, *Russ. Chem. Bull.*, 1995, No. 2, 236.
10. G. J. Kramer, R. A. Van Senten, and C. A. Nowak, *Nature*, 1993, **363**, 529.
11. Yu. A. Zolotarev, E. M. Dorokhova, V. N. Nezavibatko, Yu. A. Borisov, S. G. Rosenberg, G. A. Velikodvorskaia, L. V. Neumivakin, V. V. Zverlov, and N. F. Myasoedov, *Amino Acids*, 1995, **8**, 353.

Received November 21, 1995;
in revised form February 26, 1996

Ions with a strong symmetric H-bond in solutions of sodium acetate in acetic acid

V. D. Maiorov,* V. V. Burdin, G. I. Voloshenko, and N. B. Librovich

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: 007 (095) 938 2156. E-mail: elorma@glas.apc.org. subject: Maiorov

The multiple attenuated total reflection IR spectra of solutions of sodium acetate in acetic acid have been recorded in the range from 900 to 4000 cm^{-1}. The CH_3COO^- anion and an acid molecule form the complex $(CH_3COO...H...OOCCH_3)^-$ with a strong symmetric H-bond.

Key words: IR spectra; hydrogen bond; solutions, acetic acid.

Nonaqueous solutions of strong acids are efficient catalytic systems, whose activity is determined in many cases by proton solvates formed due to symmetric H-bonds.[1,2] When a salt of one of these acids is dissolved in a strong oxygen-containing acid, negatively charged complexes with a strong symmetric H-bond are formed, for example, $(HO_3SO...H...OSO_3H)^-$.[3,4] In aqueous solutions of acetic acid, the concentration of dissociated protons is low, and the acid molecules form strong hydrates.[5–7] In this work, solutions of CH_3COONa in CH_3COOH have been studied by multiple attenuated total reflection (MATR) IR spectroscopy[8] with the purpose of elucidating the ability of acetic acid to form ions with strong symmetric H-bonds in nonaqueous solutions.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1854—1857, July, 1996.