Transition-State Structures for Solvolysis of Methanesulfonyl Chloride

Kiyull Yang*, Keumduck Kang, In Sun Koo, and Ikchoon Lee[†]

Department of Chemical Education, Gyeongsang National University, Chinju 660-701, Korea
[†]Department of Chemistry, Inha University, Inchon 402-751, Korea
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Solvolyses of methanesulfonyl chloride (CH_3SO_2Cl) in water and methanol have been studied theoretically using *ab initio* self-consistent reaction field (SCRF) molecular orbital method. All stationary structures including transition state on the potential energy surface in solution have been found and compared with the gas phase structures. The overall reaction occurs *via* a concerted S_N2 mechanism with a non-cyclic trigonal bipyramidal transition state, and the activation barrier is lowered significantly in solution. The transition state for the hydrolysis reaction is looser than that for the methanolysis reaction, and this is in accord with the experimental findings that an S_N2 type mechanism, which is shifted toward an S_N1 process or an S_AN process in the hydrolysis and alcoholysis reaction, respectively, takes place. The catalytic role of additional solvent molecules appears to be a purely general-base catalysis based on the linear transition structures. Experimental barrier can be estimated by taking into account the desolvation energy of nucleophile in the reaction of methanesulfonyl chloride with bulk solvent cluster as a nucleophile.

Introduction

Although nucleophilic substitution at sulfur center is an important reaction in chemistry and biochemistry,[1] there have been only a few theoretical studies of this reaction. These studies have tended to focus on di- or tricoordinate sulfur system,[2] using molecular orbital methods with relatively lower level of basis sets, but there seems to be no high-level theoretical work reported on substitution at tetracoordinate sulfur.

It is recognized that nucleophile substitution at tetracoordinate sulfur can proceed *via* a trigonal-bipyramidal intermediate (addition-elimination) or by a concerted S_N2 mechanism.[3] A particularly important and simple system which contains tetracoordinate sulfur is CH_3SO_2Cl. Methanesulfonyl chloride (MSC) is important reagent in organic synthesis, and substitution reactions of these compounds bridge inorganic and organic chemistry.[4]

Solvent effects and linear free energy relationships in the solvolyses of sulfonyl chlorides, especially substituted benzenesulfonyl chlorides, have received much experimental attention,[5,6] but little work has been done on the intrinsic nucleophilic reactivities in the gas phase or in the solution.[7] Robertson and co-workers found[8] that the kinetic solvent isotope effects for benzenesulfonyl chloride and methanesulfonyl chloride are almost the same. These results are interesting since they suggest that phenyl and methyl groups have similar electronic effects in this reaction. In previous works,[9] we reported *ab initio* calculations on the solvolysis of methanesulfonyl chloride in the gas phase. In those works cyclic transition states (I), in which heavy atom reorganization and proton transfer processes occur in concert, was suggested.

As a continuation of these works, this study examines the transition state structure of the solvolysis reaction of methanesulfonyl chlorides in solution using Onsager's self-consistence reaction field (SCRF) method.[10] In the Onsagar treatment the system is placed in a spherical cavity imm-

Ia   Ib
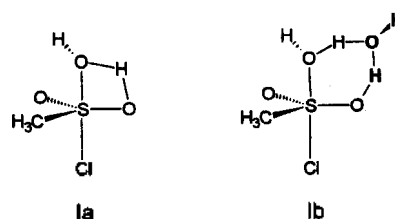
ersed in a continuous medium of dielectric constant ε. If the structure possesses a permanent dipole moment, a dipole moment is induced in the solvent, and the interaction between the two stabilizes the system. In view of the well-known transition state model for the hydration of carbonyl groups in solution,[11] transition states representing general acid (II), general base (III), bifunctional catalyst (Ib), and hydration of leaving group (IV) will be considered. According to the calculations for the gas phase solvolysis reaction of MSC,[9b] II, III, and IV are ineffective, with an absence of bound states on the potential energy surface. We have therefore examined the role of additional solvent molecules in the reaction field in solution.

II   III   IV
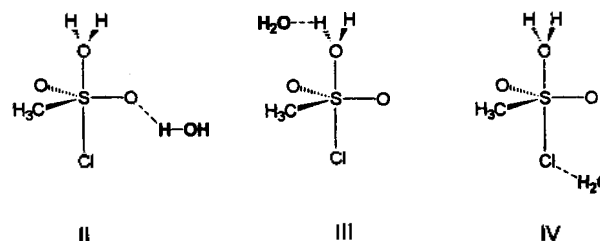
Computations

All calculations were performed using the Gaussian 94[12] on the Sun Sparc workstation and Intel Pentium Pro processors (200 MHz) under the Linux operation system.[13] Computational performance of the Pentium Pro processor is quite encouraging and comparable with that of high-end

workstation. Structures were fully optimized at the 3-21G* level and then refined at the HF/6-31G* level. In addition to the Hartree-Fock energies, single-point calculations were performed with the frozen-core approximation at the second-order Møller-Plesset perturbation (MP2) theory with the 6-31G* basis set on the HF/6-31G*-optimized geometries, since geometry optimization at the MP2 level in the reaction field is not eligible with current version of Gaussian package. Trial transition state structures were located by the reaction coordinate method, and a final refinement was achieved using OPT=CALCALL option, in which force constants are calculated in every iteration. All transition structures exhibited one imaginary frequency. For the SCRF calculation, the previously optimized gas-phase structures were used to estimate the radius of the cavity using Wong, Wiberg, and Frisch treatment[10] incorporated in Gaussian. However, refined structures were generally quite different from the gas phase structures in this work. Therefore additional optimization was performed using the cavity size which was estimated from the previous optimization for consistency. Dielectric constants of 78.5 and 32.6 were used to describe water and methanol solvents, respectively.

Results and Discussion

Table 1 collects the Hartree-Fock and MP2 electronic energies and some properties of the species computed in this work for the solvolysis of MSC in water and methanol using SCRF treatment. S, H, and M refer to MSC, water, and methanol, respectively, and rc and ts refer to reactant complex and transition state, respectively. Table 2 summarizes the HF and MP2 activation energies relative to the reactant complexes (RC) at 0 K.

Uncatalyzed Solvolysis of MSC. The geometries of

Table 1. Electronic energies (hartrees), dipole moments μ (D) and cavity radii a_0 (Å) of the optimized structures for the hydrolysis and methanolysis of methanesulfonyl chloride in solution

Molecules	HF/6-31G*	MP2/6-31G*	μ	a_0
CH_3SO_2Cl	- 1046.24803	- 1047.01096	4.43(4.29)	3.75
$CH_3SO_2Cl^a$	- 1046.24789	- 1047.01085	4.89(4.29)	3.75
SHrc	- 1122.26713	- 1123.21921	3.67(2.42)	3.98
SHts(linear)	- 1122.23031	- 1123.18055	18.33	3.90
SHts(cycle)	- 1122.16685	- 1123.14322	3.74(3.02)	3.98
SMrc	- 1161.29077	- 1162.36818	2.90(2.50)	4.15
SMts	- 1161.25266	- 1162.33175	17.50(3.41)	4.16
SHHrc	- 1198.29657	- 1199.43469	11.14(1.51)	4.18
SHHts	- 1198.26993	- 1199.41266	19.48(15.51)	4.19
SHHts^b	- 1198.25716	- 1199.39605	20.55	4.30
SMMrc	- 1276.34093	- 1277.72936	10.43(1.29)	4.53
SMMts	- 1276.30919	- 1277.70651	19.42(17.46)	4.53
SHHHrc	- 1274.32690	- 1275.65355	14.45	4.35
SHHHts	- 1274.30765	- 1275.64131	21.76(11.88)	4.33
SMMMrc	- 1391.39213	- 1393.09454	13.51	4.79
SMMMts	- 1391.36020	- 1393.07327	22.54	4.89

a In methanol. *b* Transition state for the hydration of leaving group. *c* Gas phase values are in parentheses.

Table 2. Activation energies (kcal/mol) for the hydrolysis and methanolysis. Values refer to the energy differences between transition state (TS) and reactant complex (RC)

TS	Gas	SCRF		
	HF/6-31G*	HF/3-21G*	HF/6-31G*	MP2/6-31G*
SHts(linear)	--	10.16	23.11	24.26
SHts(cyclic)	63.35	45.49	62.93	47.68
SMts	62.98	9.84	23.91	22.86
SHHts	60.13	2.06	16.72	13.82
SHHts^a	–	–	24.73	24.08
SMMts	53.69	4.28	19.92	14.38
SHHHts	17.15	–	11.85	7.68
SMMMts	–	–	20.04	13.35

a Transition state for the hydration of leaving group.

the structure calculated for uncatalyzed hydrolysis and methanolysis in the reaction field at level of the HF/6-31G* are given in Figure 1 as well as those in the gas phase.[4b]

Apparent structures of the reactant complexes (SHrc and SMrc) in solution are the same as in the gas-phase. The complexes exhibit O^1H^1-O hydrogen bonding and HO^1-HCH_2 hydrogen bonding rather than S-O^1 interaction because of the steric effects of the substituents on sulfur. This differs from the interaction in the SO_3-H_2O complex,[14] in which an S-O interaction is preferred. Charge density of one of the methyl hydrogens (+0.2852 e at the HF/6-31G* level) is sufficient to accept hydrogen bond from oxygen atom (O^1) of the nucleophile.

In general the introduction of a dielectric medium seems to have a little effect on the calculated geometries of MSC and reactant complexes. The largest change is found with the hydrogen bond length between sulfonyl oxygen (O) and proton (H^1) of the entering nucleophiles. This bond length is decreased by about 0.2 Å due to the introduction of polar
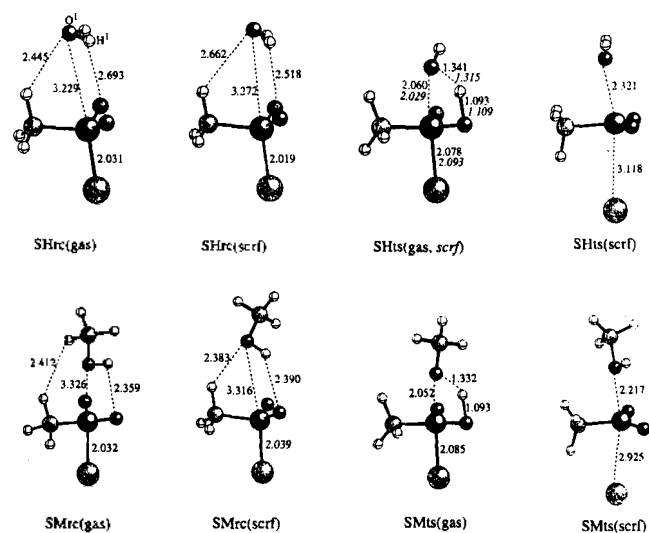

Figure 1. HF/6-31G* (SCRF) structures of reactant complexes (rc) and transition state (ts) for the uncatalyzed solvolysis reaction. S, H, and M refer to methanesulfonyl chloride (MSC), H_2O, and MeOH, respectively. Black atoms are oxygen, small white atoms are hydrogen, and largest grey atom is chlorine. Carbon and sulfur atom are located at the center of tetrahedron in rc.

media. Dipole moment μ of the reactant complex is smaller than that of free MSC because of the cancelation of dipole moment of entering nucleophiles. For both nucleophiles dipole moment of the reactant complex was increased on going from the gas phase to polar solution due to the polarization of the RC in the media.

As shown in Figure 1, there are two types of transition structures SHts(gas, *scrf*) and SHts(scrf), for the hydrolysis of MSC whereas there is only one type of transition structure for the methanolysis of MSC in solution. Though the introduction of a dielectric medium seems to have little effect on the geometries of reactant complexes, the solvent reaction field has a strong influence on the shape and molecular geometry of the transition structures.[10d,e]

One of the transition state structures in the hydrolysis reaction is four-membered cyclic transition structure SHts (gas, *scrf*), in which heavy atom reorganization (HAR) and proton transfer (PT) processes occur concerted, and it was also found in the gas phase reaction. However, the other transition structure, SHts(scrf) is an acyclic trigonal bipyramidal structure termed linear transition structure hereafter, in which no proton transfer process occurs, and is postulated for the S_N2 transition state for many years.[5] In this structure an empty d_z orbital on sulfur is available for the approaching nucleophile, and both entering and leaving groups will be in a plane perpendicular to the rest of the molecule as suggested by experimentally.[5d] In fact, in the activation process the sulfonyl chloride passes from a distorted tetrahedral structure in the ground state to the structure, in which remarkable relief of strain is expected. Although geometrical parameters for the cyclic transition structure in water are not very different from those in the gas phase, more bond forming, more leaving, and less proton transfer occurred in water. In the linear transition structure, SHts (scrf), degree of bond breaking is quite impressive, *i.e.*, S-Cl bond length (3.12 Å) shows that the bond is cleaved completely in the reaction field. In addition bond length between nucleophile (H_2O) and substrate (MSC) at TS is quite long comparing to those for the gas phase structure. The simplest definition of transition state looseness[15] is using the forming/breaking bond length directly, that is

$$R^{\neq}=R^{\neq}{}_{SNu}+R^{\neq}{}_{SL} \qquad (1)$$

where the nucleophile and the leaving group are labeled Nu and L, respectively, and the symbol $\neq$ refers to the transition structure. Though this measure does not distinguish between different nucleophiles and leaving groups, it might be able to use this equation in analysing the looseness of the reaction since leaving group is the same, and the only difference is the methyl group in methanol nucleophile. In solution distance between nucleophile and leaving group in RC is 5.29 Å, and $R^{\neq}$ in linear TS is 5.42 Å, and this corresponds to a purely concerted S_N2 process. Such a loose TS, where μ is 18.33 D, is stabilized by a strong dipole-dipole interaction in the reaction field. In contrary to the hydrolysis reaction, the only one type of transition state structure, SMts(scrf) which is linear, was located for the methanolysis reaction in solution, and the structure is an acyclic trigonal bipyramidal structure which was mentioned above for the hydrolysis reaction. In the linear transition structure, less bond formation occurs whereas bond break-

ing occurs almost completely comparing with those of the cyclic transition structure of the methanolysis reaction in the gas phase. The overall bond distances between nucleophile and leaving group are 5.35 Å and 5.12 Å (R^+) in SMrc(scrf) and SMts(scrf), respectively. This reveals that the TS in the hydrolysis is looser than in methanolysis reaction as expected from the experiment.[5d] If we take into account the size of the methyl group in methanol, the relative looseness is even larger in the hydrolysis reaction. This also leads to the findings that an S_N2 type mechanism, which is shifted toward an S_N1 process (looser TS) or an S_AN process (tighter TS) in the hydrolysis and methanolysis reaction, respectively, takes places, and $-T\Delta S^{\neq}$ of the methanolysis is greater than $-T\Delta S^{\neq}$ of the hydrolysis reaction.[16] Another index to support this is to estimate force constant for the S-Cl bond stretching vibration in MSC and TSs. The S-Cl vibrational force constants at the MSC are 0.1811 and 0.1813 hartree/bohr^2 in water and in methanol, respectively. However, the force constants at the TS are 0.4197×10^{-2} and 0.1029×10^{-1} hartree/bohr^2 for the hydrolysis and methanolysis, respectively. Force constants for the O^1-S stretching vibration are 0.2378×10^{-1} and 0.2497×10^{-1} hartree/bohr^2 for the hydrolysis and methanolysis, respectively. Based on the force constants it shows that bond formation between nucleophile and substrate is less sensitive to the media while bond breaking is more sensitive to the media, and it also verifies the partial conclusion that S_N2 type mechanism, which is shifted toward an S_N1 process (looser TS) in the hydrolysis reaction, takes place.

The HF/3-21G* activation energies summarized in Table 2 are considerably lower than those obtained at the HF/6-31G*. The lower activation energies at the HF/3-21G* level are somewhat unrealistic comparing the experimental activation energy of the hydrolysis (20.18 kcal/mol) and methanolysis (18.28 kcal/mol).[5,16] In addition, correlation energies for the activation energy computed by the second-order Møller-Plesset (MP2) perturbation method are smaller than those for the gas phase. This can be attributed to the less bond reorganization in the TS in solution. Therefore subsequent energetics will be discussed using HF/6-31G* or MP2/6-31G* level of theory. High activation energies in the gas phase reaction were lowered significantly in the reaction field even in uncatalyzed reaction, where the TS is highly polar. For the cyclic TS in the hydrolysis reaction the barrier is still higher, and is almost the same as in the gas phase even though the TS is immersed in the reaction field. The lowering of the activation barrier on going from the gas phase to the solution is attributed to the fact that RO-H bond in nucleophile is not cleaved at all at the linear TS, whereas the bond is cleaved significantly at the cyclic TS in solution. The cost for the proton transfer from nucleophile to the substrate can be estimated as 23 kcal/mol at the MP2 level. Attempt to compare relative activation energy between the hydrolysis and methanolysis with experimental energy is well reproduced at the MP2 level.

Solvent-Catalyzed Hydrolysis and Methanolysis of MSC. The geometric parameters are shown in Figure 2 for the reactant complexes and transition states for the reactions catalyzed by one solvent molecule.

All structures are acyclic in the reaction field whereas all structures are cyclic in the gas phase. Acyclic structures are
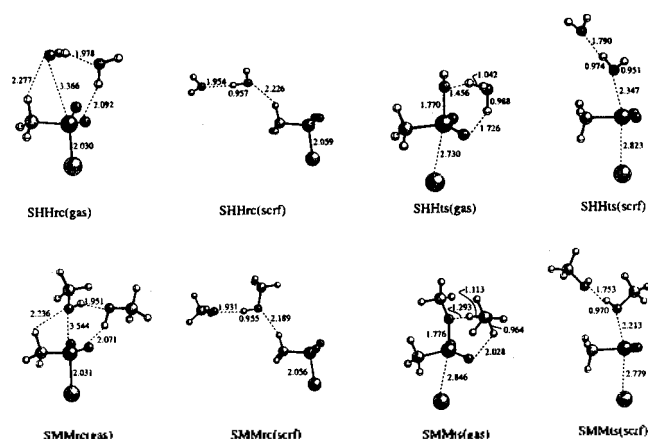
Figure 2. HF/6-31G* (SCRF) structures of reactant complexes and transition state for the catalyzed solvolysis reaction with one solvent molecule. See Figure 1 and text for abbreviation.

able to maximize their dipole moments so as to maximize favourable dipole-dipole interaction between the supermolecule and the polar media, and this offsets the favorable S=O--H hydrogen bonding interaction which is the dominant interaction in the gas phase cyclic structure. Dipole moment of the RC for hydrolysis reaction, SHHrc(scrf) in the reaction field is 11.14 D, and it can be compared with the dipole moment of the gas phase 1.51 D. However, dipole moment difference between the transition states in polar media and in gas phase is not large; dipole moment μ in gas phase is 15.62 D, and μ in SCRF is 19.48 D for the hydrolysis transition state. The large dipole moment in the gas phase is attributed to the highly positive hydronium ion-like structure of nucleophile in the gas phase TS SHHts(gas). The same trend is found in the methanolysis reaction. Catalytic role of additional solvent was bifunctional in the gas phase as reported in the earlier work,[9b] but the structures shown in figures reveal that the role of additional solvent molecule is purely general base catalyst (II) for both the hydrolysis and methanolysis reactions in solution. In the work for the hydration of formaldehyde in the reaction field reported by Wolfe et al.,[11] apparent SCRF and gas phase structures are the same which is bifunctional (Ib), and the catalytic role of additional solvent molecule is not changed on going from the gas phase to the solution phase.

The O^1H^1 bond length in nucleophilic solvent molecule (RO^1H^1) is increased by about 0.02 Å on going from RC (0.957 Å) to TS (0.974 Å), and O--H hydrogen bond length in solvent cluster is decreased by 0.16-0.18 Å at TS for the one solvent-catalyzed solvolysis reaction. This is another evidence for the general base catalyst in solution.

Large medium effects on geometry was also reported by Schelyer et al.[17] for the donor-acceptor complexes, and the effects seem to be found only for complexes in which the donor molecule has a permanent dipole moment. All reactants, water or methanol and MSC have permanent dipole moment, and dipole moment of MSC is quite large.

Transition state looseness R^+ are 5.17 Å and 4.99 Å for hydrolysis and methanolysis, respectively, and it shows that the reaction is shifted toward an S_N1 process with looser transition states in the hydrolysis reaction. The looseness is

slightly smaller than uncatalyzed solvolysis reaction.

Another interesting pictures for the structures of RC and TS in both solvolyses reaction is a linearity of the supermolecule. This is favoured entropically since quite a few vibrational modes can be assigned as internal rotations which have very low frequencies. We did not discuss the entropy changes here since a precise estimation of statistical entropy of the system having many low vibrational frequencies in condensed media is not feasible within the Gaussian package at the moment, because the low vibration frequencies can overestimate the vibrational contribution of statistical entropy as well as the difficulties arised in treatment of translational and rotational contribution of entropy in condensed media.[18]

We could find transition structure (IV) corresponding to hydration of the leaving group, which was not a stationary structure in the gas phase. As seen in Table 2 activation energy along the path containing the SHHts' is about 10 kcal/mol higher than that of the general-base model, SHHts at the SCRF MP2 level.

Geometry of the RC and TS of the reaction catalyzed by two solvent molecules are shown in Figure 3. Transition state looseness R^+ are 5.09 Å and 4.99 Å for the hydrolysis and methanolysis, respectively. The looseness difference is reduced continuously on going from uncatalyzed reaction to solvent catalyzed reaction. As seen in one solvent molecule catalyzed reaction, O-H bond length of attacking nucleophile at TS is increasing on going from the catalytic solvent molecules to nucleophilic solvent by about 0.01 Å for both the reactions.

As can be seen from Table 2, activation energies are lowered by 10.44 and 8.48 kcal/mol at the MP2/6-31G* level for one solvent-catalyzed hydrolysis and methanolysis, respectively. Degree of the lowering of the activation energy is larger in hydrolysis than in methanolysis. Such effects will be seen at two solvents-catalyzed solvolysis reaction; 6.14 and 1.03 kcal/mol at the MP2 level for hydrolysis and methanolysis, respectively. This lowering of the ac-
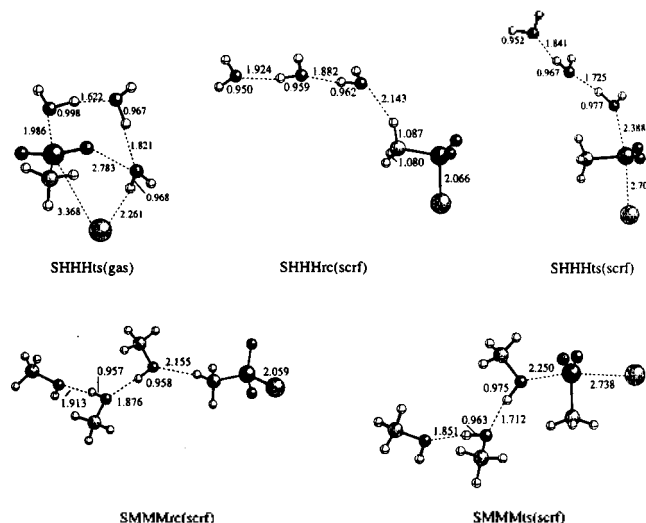

Figure 3. HF/6-31G* (SCRF) structures of reactant complexes (rc) and transition state (ts) for the catalyzed solvolysis reaction with two solvent molecules. See Figure 1 and text for abbreviation.

tivation energies can be attributed to the linear structure of the transition state, *i.e.*, a large dipole moment in the linear TS has quite favorable interaction in the polar media as discussed above. However, this lowering seems not to be converged readily, and the activation barriers are too smaller than experimental values.[5,16] Moreover, calculated barrier for the hydrolysis is smaller than that for the methanolysis, which is in reverse of the experimental order. To overcome this problem and to be parallel to the experimental activation energy of the solvolysis reaction, we considered a reaction of MSC with bulk solvent clusters such as solvent dimer to octamer or to tetramer for water and methanol, respectively;

$$(\text{Solvent})_n + \text{MSC} \rightarrow \text{TS}_m + (\text{Solvent})_{n-m} \qquad (2)$$
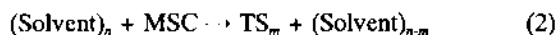
where n and m are the number of solvent molecules in solvent cluster and transition structure, respectively. The structures of water clusters have been the subject of numerous experimental and theoretical studies.[11a,19] The lowest energy structures of the water dimer and trimer are well established from experiment, but larger clusters have so far resisted structural characterization. There is now general agreement from calculations that global minima of the water trimer and tetramer are simple ring structures and that the octamer and larger clusters prefer three-dimensional structures. Though the hexamer has a large number of low-energy structures, energy difference between the comformers is not larger than 1 kcal/mol.[19] We adopt a hexamer structure in which two cyclic trimers are fused by hydrogen bonds so as to have nine hydrogen bonds, and adopt the pentamer and heptamer as cyclic and three-dimensional structure. We also arrive at cubelike structure composed of eight water molecules[20] by fusing two cyclic tetramers together as shown in Figure 4. Alcohols have been known for a long time to form clusters of 2, 3, or 4 molecules, presumably cyclic or linear. Based on very recent study of Benson[21] for the structures of liquid alcohols, cyclic tetramer is a major component in most liquid alcohols. We optimized the geometry of methanol clusters at the HF/6-31G* (SCRF), and MP2 single point calculation in the reaction field was performed. The cyclic methanol tetramer is shown in Figure 4, and it shows alternate *cis-trans* conformation which is slightly
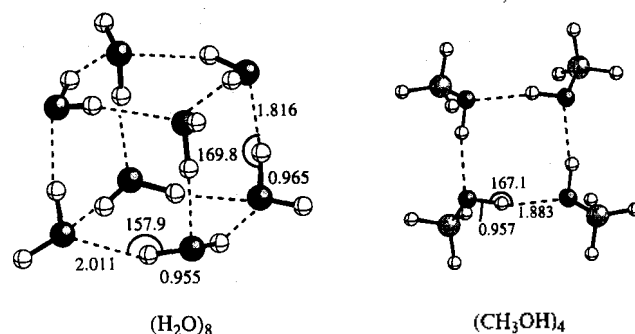

(H₂O)₈   (CH₃OH)₄

Figure 4. HF/6-31G* (SCRF) structures of water octamer and methanol tetramer.

more stable than all-*cis* isomer. Hartree-Fock and MP2 electronic energies of water and methanol clusters are summarized in Table 3.

In fact, two hydrogens in a water molecule are able to participate in hydrogen bond in water clusters, but there are twelve hydrogen bonds in water octamer, and four hydrogen atoms are not participated in hydrogen bond at water octamer as shown in Figure 4. However, there is only one hydrogen bond per methanol in methanol clusters, *i.e.*, four hydrogen bonds in methanol tetramer. In methanol clusters all alcoholic hydrogen atoms participate in hydrogen bond.

We did not calculate methanol clusters containing more than four methanol molecules because the main purpose of this treatment was to see that the activation energy is raised when bulk solvent is treated as a nucleophile, and desolvation energy of the nucleophile can be taken into account in the estimation of overall activation energy of solvolysis reaction which mimics the real system.

The activation energy of the reaction with solvent cluster are raised somewhat as can be seen in Table 4. Since the most dominant composition of the liquid water and methanol are octamer[20] and tetramer,[21] respectively, and in order to represent the solvent as crowded cluster with hydrogen bonds, the results obtained in columns c and b in the table for hydrolysis and methanolysis, respectively, are used in the discussion. The lowest barrier is 24.24 kcal/mol at the MP2 level for the reaction with two waters-catalyzed hydrolysis (TS₃) when solvent was treated as an octamer. However, if some water tetramers participate in the reaction, the barrier will be reduced. Since the Arrhenius activation

Table 3. Electronic energies (hartrees) and cavity radii a_0 (Å) of solvent clusters in solution (SCRF)

Molecules\Method	HF/6-31G*	MP2/6-31G*	a_0
H₂O	−76.01429	−76.19952	2.53
(H₂O)₂	−152.03494	−152.40739	3.61
(H₂O)₃	−228.06319	−228.62762	3.45
(H₂O)₄	−304.09019	−304.84480	3.60
(H₂O)₅	−380.11685	−381.06223	3.94
(H₂O)₆	−456.14480	−457.28230	4.06
(H₂O)₇	−532.17225	−533.49995	4.23
(H₂O)₈	−608.20945	−609.73102	4.39
MeOH	−115.03690	−115.34636	3.05
(MeOH)₂	−230.08341	−230.70550	3.67
(MeOH)₃	−345.13325	−346.07252	4.23
(MeOH)₄	−460.18697	−461.44206	4.32

Table 4. Activation energies (kcal/mol) for the solvolysis reaction of methanesulfonyl chloride

solvent\method		HF/6-31G*			MP2/6-31G*		
		a	b	c	a	b	c
	TS₁	23.11	28.00	34.47	24.26	29.87	38.58
water	TS₂	16.72	20.93	27.07	13.82	22.41	29.51
	TS₃	11.85	10.21	20.73	7.68	9.37	24.12
	TS₁	23.91	30.72	–	22.86	30.52	–
methanol	TS₂	19.92	26.52	–	14.34	25.66	–
	TS₃	20.04	23.69	–	13.35	20.88	–

[a] reactant complex (rc) → transition state (ts). [b] solvent₄ + MSC → TS_n + solvent₍₄₋ₙ₎. [c] solvent₈ + MSC → TS_n + solvent₍₈₋ₙ₎.

energy at the experiment consists quite a few factors where some of the factors are not feasible to evaluate at the theoretical basis we employed in this work, it was not possible to reproduce exact experimental barrier with energetics concerning the transition states. Knowing the exact composition of water clusters, which is possible through the exact estimation of entropies of solvent clusters at the condensed media as well as electronic energies of the clusters, may allow to estimate Arrhenius activation energy of the reaction more precisely. In spite of these difficulties, the activation energy difference between hydrolysis and methanols is comparable to the experiment.

References

1. (a) Block, E. In *Reactions of Organosulfur Compounds*; Academic Press: New York, 1981. (b) Allison, W. S. *Acc. Chem. Res.* **1976**, *9*, 293. (c) Zefirov, N. S.; Makhonkov, D. I. *Chem. Rev.* **1983**, *82*, 615.

2. (a) Minkin, V. I.; Simkin, B. Ya.; Minyaev, R. M. In *Quantum Chemistry of Organic Compounds*; Springer-Veralg: New York, 1990; p 154, and references therein. (b) Volatron, F.; Demolliens, A.; Lefour, J.-M.; Eisenstein, O. *Chem. Phys. Lett.* **1986**, *130*, 419. (c) Lyons, J. E.; Schiesser, C. H. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1655. (d) Ferris, K. F.; Franz, J. A. *J. Org. Chem.* **1992**, *57*, 777. (e) Markham, G. D.; Bock, C. W. *J. Phys. Chem.* **1993**, *97*, 5663. (f) Okuyama, T.; Nagase, S. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1011.

3. Okuyama, T. In *The Chemistry of Sulphinic Acids, Esters and Their Derivatives*; Pata, S.; Rappoport, Z., Eds.; Wiley: Chichester, U. K., 1990; Chapter 21.

4. (a) Bentley, T. W. In *The Chemistry of Sulphinic Acids, Esters and Their Derivatives*; Pata, S.; Rappoport, Z., Eds.; Wiley: Chichester, U. K., 1990; Chapter 16. (b) Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, *17*, 65. (c) Gordon, I. M.; Kaskill, H.; Ruasse, M. F. *Chem. Soc. Rev.* **1989**, *18*, 123. (d) Stedman, G. In *Mechanisms of Inorganic and Organometallic Reactions*; Twigg, M. V., Ed.; Plenum: New York, 1992; Vol. 8, Chapter 4.

5. (a) Hall, H. K. Jr. *J. Am. Chem. Soc.* **1956**, *78*, 1450. (b) Robertson, R. E.; Laughton, P. M. *Can. J. Chem.* **1957**, *35*, 1319. (c) Rossall, B.; Robertson, R. E. *Can. J. Chem.* **1971**, *49*, 1451. (d) Ballistreri, F. P.; Cantone, A.; Maccarone, E.; Tomaselli, G. A.; Tripolone, M. *J. Chem. Soc., Perkin II* **1981**, 438. (e) Foon, R.; Hambly, A. N. *Austral. J. Chem.* **1962**, *15*, 668, 685. (f) Foon, R.; Hambly, A. N. *Austral. J. Chem.* **1971**, *24*, 713.

6. (a) Kim, W. K.; Lee, I. *J. Korean Chem. Soc.* **1973**, *3*, 163. (b) Koo, I. S.; Bentley, T. W.; Kang, D. H.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1991**, 175. (c) Koo, I. S.; Bentley, T. W.; Llewellyn, G.; Yang, K. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1175. (d) Koo, I. S.; Lee, I.; Oh, J.; Yang, K. *J. Phys. Org. Chem.* **1993**, *6*, 223.

7. (a) Lee, I.; Kim, U. R.; Bai, S. H. *J. Korean Chem. Soc.* **1973**, *17*, 171. (b) Kim, U. R.; Lee, K. Y.; Bai, S. H.;

8. Lee, I. *J. Korean Chem. Soc.* **1974**, *18*, 3.

8. Robertson, R. E.; Rossall, B.; Sugamori, S. E.; Treindl, L. *Can. J. Chem.* **1969**, *47*, 4199.

9. (a) Yang, K.; Koo, I. S.; Kang, D. H.; Lee, I. *Bull. Korean Chem. Soc.* **1994**, *15*, 4199. (b) Yang, K.; Koo, I. S.; Lee, I. *J. Phys. Chem.* **1995**, *99*, 15035.

10. (a) Onsagar, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486. (b) Miertus, S.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1981**, *55*, 117. (c) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Chem. Phys.* **1991**, *95*, 8991. (d) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4776. (e) Kim, K. S.; Cho, S. J.; O, K. S.; Son, J. S.; Kim, J.; Lee, J. Y.; Lee, S. J.; Lee, S.; Chang, Y.-T.; Chung, S. K.; Ha, T.-K.; Lee, B.-S.; Lee, I. *J. Phys. Chem. A,* **1997**, *101*, 3776.

11. (a) Wolfe, S.; Kim, C.-K.; Yang, K.; Weinberg, N.; Shi, Z. *J. Am. Chem. Soc.* **1995**, *117*, 4240, and references cited therein. (b) Wolfe, S.; Shi, Z.; Yang, K.; Ro, S.; Weinberg, N.; Kim, C.-K., Submitted for publication.

12. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian, Inc., Pittsburgh PA, 1995.

13. Barnes, D.; Ewing, M.; Fulbright, M.; Johnson, M. K.; Knobe, J.; Maher, M.; Matthews, H.; Smith, C. Jr.; Troan, E.; Red-Hat Linux 4.2, See Web site at http://www.redhat.com.

14. Hofmann, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1994**, *116*, 4947. (b) Chen, T. S.; Moore Plummer, P. L. *J. Phys. Chem.* **1985**, *89*, 3689.

15. Schrøder, S.; Jensen, F. *J. Am. Chem. Soc.* **1997**, *119*, 227.

16. Koo, I. S.; Yang, K. Unpublished results. The Arrhenius activation energy and $-T\Delta S^+$ are 20.18 and 3.58 kcal/mol, respectively, for the hydrolysis of methanesulfonyl chloride. The Arrhenius activation energy and $-T\Delta S^+$ are 18.28 and 6.56 kcal/mol, respectively, for the methanolysis of methanesulfonyl chloride.

17. Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1994**, *116*, 7429.

18. Amzel, L. M. *Proteins* **1997**, *28*, 144.

19. (a) Mhin, B. J.; Kim, H. S.; Kim, H. S.; Yoon, C. W.; Kim, K. S. *Chem. Phys. Lett.* **1991**, *176*, 41. (b) Mhin, B. J.; Kim, J.; Lee, S.; Lee, J. Y.; Kim, K. S. *J. Chem. Phys.* **1994**, *100*, 4484. (c) Kim, K.; Jordan, K. D.; Zwier, T. S. *J. Am. Chem. Soc.* **1994**, *116*, 11568.

20. (a) Benson, S. W.; Siebert, E. D. *J. Am. Chem. Soc.* **1992**, *114*, 4269. (b) Kim, J.; Mhin, B. J.; Lee, S. J.; Kim, K. S. *Chem. Phys. Lett.* **1994**, *219*, 243 and references cited therein.

21. Benson, S. W. *J. Am. Chem. Soc.* **1996**, *118*, 10645.