

References

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- Compound 1: Yield=78%; $^1\text{H-NMR}$ (acetone- d_6) δ 4.62-5.21 (m, 2H), 6.96-7.35 (q, 1H), 7.36-7.65 (m, 2H), 7.83-8.14 (m, 2H), 10.01 (s, 1H); IR (neat) 1766, 1698 (C=O), 1650 (C=C) cm^{-1} .
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- Compound 2: Yield=50%; mp. 114-116°C; $^1\text{H-NMR}$ (acetone- d_6) δ 3.86 (s, 3H), 4.65-5.20 (m, 2H), 6.95-7.32 (q, 1H), 7.35-7.65 (m, 2H), 7.93-8.36 (m, 3H); IR (KBr) 2218 (CN), 1765, 1737, 1725 (C=O), 1646, 1609, 1596 (C=C) cm^{-1} .
Compound 4: Yield=65%; mp. 120-122°C; $^1\text{H-NMR}$ (acetone- d_6) δ 4.63-5.21 (m, 2H), 6.95-7.33 (q, 1H), 7.37-7.68 (m, 2H), 7.89-8.35 (m, 3H); IR (KBr) 2232 (CN), 1677 (C=O), 1653, 1594 (C=C) cm^{-1} .
- Compound 3: Yield=90%; mp. 117-119°C; $^1\text{H-NMR}$ (acetone- d_6) δ 3.96 (s, 3H), 4.33 (s, 1H), 4.57-5.23 (m, 2H), 6.95-7.33 (q, 1H), 7.34-7.67 (m, 2H), 7.68-8.12 (m, 2H); IR (KBr) 2253 (CN), 1757 (C=O), 1648 (C=C) cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_5$: C, 60.54; H, 3.29; N, 12.46. Found: C, 60.62; H, 3.35; N, 12.54.
Compound 5: Yield=92%; mp. 169-171 (dec); $^1\text{H-NMR}$ (acetone- d_6) δ 4.60-5.17 (m, 3H), 6.89-7.32 (q, 1H), 7.32-7.64 (m, 2H), 7.70-8.06 (m, 2H); IR (KBr) 2262 (CN), 1764 (C=O), 1654 (C=C) cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_8\text{N}_4\text{O}_3$: C, 63.16; H, 2.65; N, 18.41. Found: C, 63.25; H, 2.61; N, 18.50.
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- Copolymer composition estimated from $^1\text{H-NMR}$ spectrum: 3/MMA=22/78 (mol/mol).
- Spectral data of copolymer containing approximately 22 mol% of 3 and 78 mol% of MMA: $^1\text{H-NMR}$ (acetone- d_6 , 60 MHz) δ 0.71-1.40 (m, 3H), 1.65-2.48 (m, 4H), 3.27-4.15 (m, 7H), 4.28-4.57 (s, 1H), 7.25-8.12 (m, 4H); IR (KBr) 2260 (CN), 1762, 1723 (C=O) cm^{-1} .

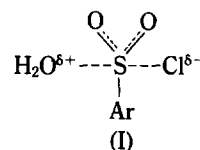
Theoretical Studies on the Substitution Reaction of Sulfonyl System: Hydrolysis of Methanesulfonyl Chloride in the Gas Phase

Kiyull Yang*, In Sun Koo, Dae Ho Kang, and Ikchoon Lee†

Department of Chemical Education,
Gyeongsang National University, Chinju 660-701†Department of Chemistry, Inha University,
Inchon 402-751

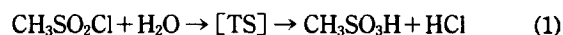
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Experimental studies on the hydrolysis or solvolysis of sulfonyl systems are numerous¹, but there seems to be no theoretical work reported on the intrinsic nucleophilic reactivity of sulfonyl system or tetracoordinate sulfur, except a few ground state analysis². From the experimental works of the hydrolysis of arylsulfonyl chloride, a trigonal bipyramidal structure was postulated for the $\text{S}_{\text{N}}2$ transition state, (I).



However, a four membered cyclic transition state, in which heavy atom reorganization(HAR) and proton transfer(PT) processes occur concertedly, should be considered in view of such transition state(TS) found for formaldehyde hydration in the gas phase³. In this transition state structure, an empty σ^* molecular orbital on sulfur-chlorine bond is available for the approaching nucleophile, and both entering and leaving groups will be in a plane perpendicular to the rest of the molecule, *i.e.*, a trigonal bipyramidal structure in addition to the four membered cyclic structure.

In this work, the hydrolysis reaction of methanesulfonyl chloride, eq. (1), was discussed theoretically by locating stationary points including transition state.



The Gaussian 92⁴ and MOPAC 6.0⁵ programmes were used throughout in this work for *ab initio* and semi-empirical molecular orbital calculations, respectively. The basis sets for the *ab initio* calculations were 3-21G* and 6-31G*, and hamiltonians for the semi-empirical calculations were AM1 and PM3⁶. It has been reported that the PM3 method successfully reproduces the heat of formation of hypervalent compounds without the use of *d* orbitals⁷, and parameters for the sulfur atom in the MOPAC program were revised⁵.

The transition state that corresponds to a saddle point on the 28-dimensional potential energy surface was characterized by confirming only one negative eigenvalue in the Hessian matrix.

Some optimized geometries of the system are summarized in Table 1, and a superimposed TS structure is shown in Figure 1 with the 6-31G* transition state structure and Pau-

*Author for correspondence.

Table 1. Optimized Geometries of Reactant(R) and Transition State(TS)

Geometry ^a	AM1	PM3	3-21G*	6-31G*
S-O ^b	1.392	1.423	1.423	1.420
S-Cl	2.109	2.104	2.022	2.031
R				
OSO	118.6	120.2	120.9	120.9
OSCl	108.5	106.7	109.6	107.0
CSCl	98.9	96.8	99.0	100.8
TS				
S-O _w	1.893	1.829	1.967	2.059
S-O	1.558	1.602	1.535	1.531
O _w -H	1.300	1.176	1.320	1.341
O-H	1.253	1.235	1.137	1.092
S-Cl	2.167	2.169	2.096	2.076
O _w SO	73.4	70.9	74.8	73.8
O _w HO	109.0	111.9	122.4	128.8
O _w SOH	1.5	3.2	3.6	6.9

^aBond lengths are in Å, bond angles and dihedral angles are in degree. ^bSee Figure 1.

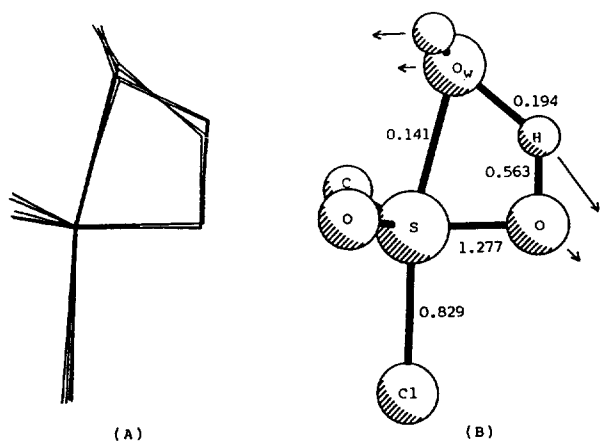


Figure 1. (A) Superposition of the transition states obtained by various methods and basis sets. (B) 6-31G* TS structure and Pauling bond order. For clarity methyl hydrogens are omitted.

ling bond orders^b: these are calculated according to $B = \exp \left[\frac{R(1) - R(B)}{a} \right]$ where R is the length of a bond order B and values of $R(1)$, for bonds with orders assumed to be unity, are taken from O-H in water and sulfonic acid, and from S-O in sulfonic acid. Constant a was adjusted to 0.25 in order that the sum of bond orders of all the bonds participated in rearrangement remains constant.

The rms deviations, *i.e.*, the root mean square fit in Å, compared between basis sets are 0.129(AM1-6-31G*), 0.125 (PM3-6-31G*) and 0.051(3-21G*-6-31G*) for all atoms except methyl hydrogens. The geometry obtained by semi-empirical method shows good agreement with that of *ab initio* method. The transition state structure of hydrolysis by one water molecule is quite similar to that of formaldehyde hydration which is first reported by Williams *et al.*³ The heavy atom reorganization, *i.e.*, S-O_w σ-bond making, S=O π-bond breaking, and S-Cl σ-bond breaking and proton transfer are occurring simultaneously. Moreover, the degree of proton transfer is larger than that in the carbonyl hydration reaction, *i.e.*, the O-H bond length in water (nucleophile) was longer than O-H bond length of sulfonate.

Inspection of bond orders reveals that the reaction proceeds *via* a concerted S_N2 mechanism; the degree of bond formation and bond breaking are the same along the O_w-S-Cl bonds at the transition state, and the degree of proton transfer is quite large. The arrows in Figure 1 indicate atomic displacements occurring in the normal vibrational mode corresponding to the 6-31G* reaction-coordinate frequency of 1367i cm⁻¹. From the dominant motion of an endocyclic hydrogen, it is natural to consider a primary kinetic isotope effect(KIE) for the reaction. The Hartree-Fock frequencies have been scaled by 0.9⁹, and the KIE was calculated based on the zero point energy differences(dZPE) and Bigeleisen equation(BIG)¹⁰. The calculated isotope effects are 1.582 (dZPE) and 3.565(BIG), which are smaller than the kinetic isotope effects of formaldehyde hydration, where the isotope effects are 1.708 and 3.749 for the dZPE and BIG, respectively. The possibility of tunneling in the TS will be small, since the TS is bent and O_w-H-O structure¹¹ is not symmetric.

Thermodynamic properties at 298 K are summarized in

Table 2. Calculated Energy Changes (kcal mol⁻¹) for hydrolysis of methanesulfonyl chloride at 298 K relative to separated reactants (SR)

Basis set	$\Delta E_a^{a,c}$	$\Delta E^{b,c}$	ΔH^*	$-T\Delta S^*$	ΔG^*	$\Delta G^* - \Delta E_a$
AM1	31.33	-20.91	31.33	11.63	42.96	11.63
PM3	27.64	-16.55	27.63	11.41	39.04	11.41
HF/3-21G*	32.98	-29.96	32.39	11.58	43.97	10.99
HF/6-31G*	56.19	-15.23	55.01	11.26	66.27	10.08
HF/3-21G*-SCRF	36.53					
HF/6-31G*-SCRF	57.72					
MP2/3-21G**/3-21G* ^d	24.63	-20.58				
MP4/3-21G**/3-21G* ^d	25.26	-20.33				
MP2/6-31G**/6-31G* ^d	39.27	-8.97				
MP4/6-31G**/6-31G* ^d	40.12	-9.10				

^aRefers to the energy differences between TS and SR. ^bRefers to the reaction energy. ^c0 K, except AM1 and PM3 energy. ^dSingle point MP2(MP4) calculation with the 3-21G*(6-31G*) optimized structure.

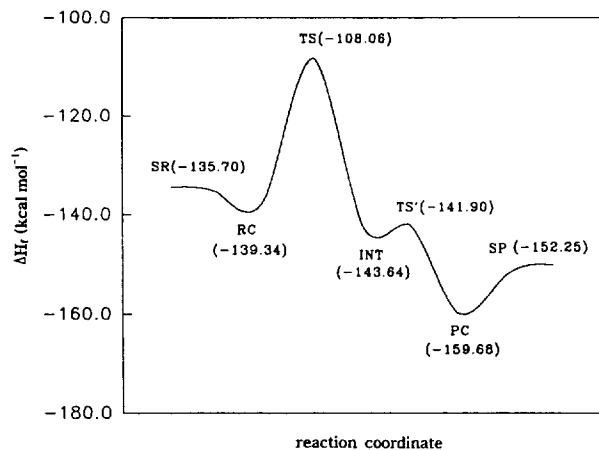


Figure 2. PM3 energy profile for the hydrolysis of methanesulfonyl chloride. SR and SP are the separated reactants and products, respectively. RC and PC are the reactant and product complex, respectively. INT is an intermediate.

Table 2. The energy barrier, $40.12 \text{ kcal mol}^{-1}$, which is obtained by the MP4/6-31G*, the highest level employed, of the reaction is higher than its experimental values for the hydrolysis reaction in solution¹. Since dipolar structure (I) is ruled out because it does not correspond to a stationary point on the potential energy surface in the gas phase, the reaction proceeds concertedly. According to Jencks¹², such reaction should be classified as the reaction with enforced concertedness. Though direct comparison of the absolute value of thermodynamic property in Table 2 is not significant, the activation energy is overestimated with the 6-31G* basis set. The reason is not clear at the moment but further investigations are in progress. However, activation entropies are comparable between the three basis sets within 2 entropy units(eu). The correlated activation energy shows the same trend, and energy differences among the basis set become small. From Table 2, it is clear that the second order perturbation energy is sufficient to represent Møller-Plesset correlation energy considering computational efforts. Also, trend of Gibbs free energy of activation is almost the same as that of activation energy at 0 K, and the activation barrier does not vary by including self consistent reaction field(SCRF) calculation.

For the substitution reaction of the second row element, one may consider retention of configuration at the center of reaction. We located transition state structure which accompany the retention of configuration. The activation barrier for the retention mechanism is higher by $10.61 \text{ kcal mol}^{-1}$ (3-21G*) or $9.09 \text{ kcal mol}^{-1}$ (6-31G*) compared to that of inversion.

The PM3 potential energy profile was generated beyond TS, and was shown in Figure 2. Though, there was slightly stable diol-type intermediate, it is decomposed readily to give final products, *i.e.*, hydrogen chloride and methanesulfonic acid, *via* second transition state(TS'). However, such a diol-type intermediate was not located by *ab initio* method. Two possibilities arise here; there is no genuine intermediate and TS' on the *ab initio* surface, or the second barrier is too

small to locate by default convergence criteria. Whatever the reason is for that, the barrier might be less than one kcal mol^{-1} , which could not affect the discussion of overall reaction mechanism. It should be noted, finally, that the semi-empirical and *ab initio* results of potential energy surface shows qualitatively good agreement, especially for the overall transition state structure. Some semi-empirical calculations for the larger sulfonyl systems are doing as well as *ab initio* calculations on the methanesulfonyl system for catalytic effect by adding a few water molecules or solvent molecules.

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