

Ab Initio GB Study of Chemical Intermediates in Solution; Ethylenesulfonium Ion in Hydrolysis of 2-Chloroethyl Methyl Sulfide

Osamu Kikuchi, Naoyuki Tomisawa, Ohgi Takahashi,
and Kenji Morihashi

Department of Chemistry, University of Tsukuba, Tsukuba 305, Japan

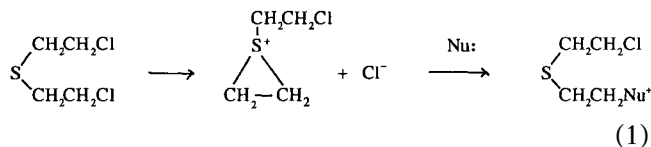
Received 1 September 1997; revised 3 December 1997

ABSTRACT: *Ab initio MO theory including solvent effects has been applied to the structure and reactivity of methyl ethylenesulfonium ion, 1, in aqueous solution as a model of the three-membered cyclic sulfonium intermediate expected in the toxic action of sulfur mustard. The 6-31 + G* geometry optimization of the cyclic sulfonium ion 1 suggested that the ring size of 1 is expanded slightly by solvation. The contour lines map of the interaction energy between 1 and Cl⁻ has a very shallow and wide well at 5–6 Å distance from 1. This is the solvent-separated ion pair, and the contact ion pair was not found between 1 and Cl⁻. The calculated energy diagrams for the S_N2-type reactions of 1 with Cl⁻, H₂O, and OH⁻ that give ring-opened compounds indicated the following: (1) The energy of the 1 + Cl⁻ system is similar to that of chloroethyl methyl sulfide (CEMS, 2), and the interconversion between 1 + Cl⁻ and 2 occurs easily in aqueous solution. The 3-21 + G(*) and 6-31 + G* activation energies for the 2 → 1 + Cl⁻ reaction, 20–22 kcal/mol, agree well with the experimental enthalpy of activation for the hydrolysis of 2. (2) The reaction of 1 with OH⁻ gives a very stable hydroxyl compound, 4, and no transition state was found. (3) The reaction of 1 with H₂O gives an unstable addition product that is expected to be converted to 4 with the assistance of another H₂O molecule. This mechanism is consistent with that proposed by Bartlett and Swain in their pioneering work*

on the hydrolysis of sulfur mustard. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:503–510, 1998

INTRODUCTION

2,2'-Dichlorodiethyl sulfide [sulfur mustard, S(CH₂CH₂Cl)₂] is a highly toxic compound, and its reactivity with nucleophiles has been a subject of interest [1]. The reaction of sulfur mustard with nucleophiles is believed to involve an initial loss of Cl⁻ and the formation of a cyclic sulfonium ion, which is then attacked by an external nucleophile, with the opening of the ring; in the case of hydrolysis, the three-membered ring is attacked by water and a thio-diglycol is eventually obtained.



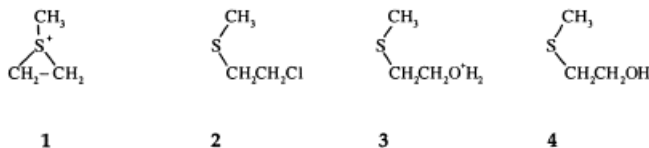
The kinetics and mechanism of the hydrolysis of sulfur mustard and its monochloro derivatives (RSCH₂CH₂Cl) have been studied extensively [1–8]. The enthalpy of activation for the conversion of mustard to chlorohydrin is 18.5 kcal/mol [7], while that for 2-chloroethyl methyl sulfide (CEMS) is 19.3–19.7 kcal/mol [2,6]. These studies have confirmed the above-mentioned steps; the first step is the formation of a cyclic sulfonium cation intermediate that is produced by intramolecular assistance of the neighbor-

ing sulfur atom, and this reacts quickly with a water molecule to form the 2-hydroxyethyl sulfide.

Recent theoretical studies [9–14] have examined the structure and reactivity of sulfur mustard and CEMS. Politzer and Habibollahzadeh [11] calculated the bonding properties of sulfur mustard in solution using ab initio SCRf theory with Onsager's reaction field model. Donovan analyzed the mechanism of isotopic scrambling in CEMS (2) in the gas phase and in aqueous solution, and the stepwise mechanism, in which the cyclic sulfonium cation 1 is involved, was proposed [13]. In these studies, however, the structure of the cyclic sulfonium cation was not calculated in solution. It is expected that the SCRf calculations with a fixed cavity cannot describe correctly the reaction in which bond dissociation occurs.

Donovan and White [14] applied the semiempirical SM3-PM3 method to Reaction 1 in aqueous solution and showed that the two processes in Reaction 1 proceed faster in solution than in the gas phase. Although this study describes well the overall feature of the hydrolysis processes of sulfur mustard, the calculated energy barrier for the first step seems to be too high (39.4 kcal/mol) to produce the cyclic sulfonium ion. Furthermore, the structure of the corresponding transition state in aqueous solution was not determined.

The cyclic sulfonium ion is a key species in the toxic action of sulfur mustard, and its reactivity with nucleophiles plays a significant role in biological systems. Most theoretical studies on the cyclic sulfonium ion are concerned with the gas-phase structure [11,15]. Although the structure in solution has been determined by the semiempirical level of calculations [14], its optimized structure was not given. In the present study, we employed the ab initio generalized Born (GB) method to calculate the molecular structure and reactivity of the cyclic sulfonium ion 1 in aqueous solution. The S_N2 -type reactions of 1 with Cl^- , H_2O , and OH^- to form 2, 3, and 4, respectively, were examined, and the hydrolysis reaction of CEMS (2) was considered as the model of the sulfur mustard hydrolysis.



METHOD

In the continuum model using the generalized Born formula, the solvation free energy of a molecule is expressed as [16–18]

$$\Delta G_{\text{sol}} = -\frac{1}{2} \left(1 - \frac{1}{\epsilon}\right) \sum_A \sum_B Q_A Q_B \Gamma_{AB} \quad (2)$$

where ϵ is the dielectric constant of the solvent, A and B are atoms in the solute molecule, and Q_A and Q_B are fractional charges. Γ_{AB} represents the interaction between A and B atoms. The energy of a molecule in solution is expressed by the sum of the energy in its isolated state and the solvation energy:

$$E_{\text{sol}} = E_0 + \Delta G_{\text{sol}} \quad (3)$$

By applying the variational theorem to this energy functional, Tapia derived correct Fock matrix elements including the solvent effect for semiempirical MO calculations [19]. Kozaki et al. combined this model with MNDO theory and applied it to several chemical reactions [20,21]. Cramer and Truhlar extended it to the AM1 and PM3 versions including the cavitation energy [22,23]. We have incorporated the GB model into the ab initio SCF method; the ab initio GB method has been described in previous articles [24–26]. In the ab initio GB model, the Fock matrix elements including the solvent effect for a closed-shell molecule are

$$F_{\mu\nu} = F_{\mu\nu}^0 + F_{\mu\nu}^{\text{sol}} \quad (4)$$

$$F_{\mu\nu}^{\text{sol}} = -\sum_{\lambda} \frac{\partial \Delta G_{\text{sol}}}{\partial Q_A} (S^{1/2})_{\mu\lambda} (S^{1/2})_{\nu\lambda} \quad (5)$$

where $F_{\mu\nu}^0$ is the Fock matrix element for an isolated molecule and $F_{\mu\nu}^{\text{sol}}$ describes the contribution of solvent. In Equation 5, A is the atom to which λ belongs. The partial derivative in Equation 5 is expressed as

$$\frac{\partial \Delta G_{\text{sol}}}{\partial Q_A} = -\left(1 - \frac{1}{\epsilon}\right) \left\{ Q_A \Gamma_{AA} + \frac{1}{2} Q_A^2 \frac{\partial \Gamma_{AA}}{\partial Q_A} + \sum_{B \neq A} \left(Q_B \Gamma_{AB} + Q_A Q_B \frac{\partial \Gamma_{AB}}{\partial Q_A} \right) \right\} \quad (6)$$

The calculation of the terms in Equation 6 have been shown in earlier articles [24–26].

Because the chemical reactions considered here involve anionic species, the inclusion of diffuse functions is indispensable in ab initio calculations of the energetic properties for chemical reactions. In the present study, the RHF method with the 3-21+G(*) [27] and 6-31+G* [28] basis sets were used to calculate the structures and energies of 1–4 and the related species in aqueous solution ($\epsilon = 79$).

All MO calculations were carried out using our ABINIT program on the HP-J210 workstations and GAIA-300 personal supercomputers.

RESULTS AND DISCUSSION

Molecular Structures

The molecular structures of 1–4 and the transition states for the $1 + Cl^- \rightarrow 2$ and $1 + H_2O \rightarrow 3$ reactions

were determined in aqueous solution ($\epsilon = 79$). In the calculations of molecular structures, the C_3 local symmetry was assumed for the CH_3 group, and other geometrical parameters were optimized. Some of the molecular parameters determined are listed in Table 1. In Figure 1, three-dimensional shapes of the optimized structures are shown by ball-stick model representations.

The cyclic sulfonium cation is the key species in the toxic action of mustard gas. Politzer and Habibollahzadeh failed to determine the molecular structure of the cyclic sulfonium ion in reaction 1 in aqueous solution by the SCRF method [11]. Donovan calculated the parameters of the isotope scrambling mechanism in 2-chloroethyl methyl sulfide via the cyclic sulfonium ion **1**. However, the molecular structure of the sulfonium cation **1** in aqueous solution was not calculated [13]. The SCRF solvation model provided in the MO package they used may be unfavorable for the calculation of ionic species such as the sulfonium cation. The present ab initio GB model can determine the molecular structure of **1** in solution without any difficulty. Although the present study focuses on the structure and reactivity in solution, the molecular structure of **1** in the gas phase was also optimized and compared with that in aqueous solution. The solvent polarity affects the structure, although the effect is small; the C–C and C–S bond lengths are slightly longer in solution. The calculated hydration energy of **1** is 72.0 kcal/mol (6–31 + G*), which is compared with the experimental values of 61–87 kcal/mol for alkylsulfonium ions [29]. The conformations of **2** and **3** in Figure 1 are consistent with the most stable conformation calculated for sulfur mustard [12].

Interaction of **1** with Chloride Ion

The interaction of **1** with Cl^- in aqueous solution was calculated. The optimized molecular structure of **1** was fixed so that the SC_1C_2 frame is on the xy plane (Figure 2). The chloride anion was moved on the xy or yz plane, and the interaction energies were calculated using the 3-21 + G(*) basis set. The calculated interaction energies are represented as contour lines in Figures 3 and 4. These maps indicate that a potential energy well exists at 5–6 Å distance from the sulfonium ion. The molecular structure corresponding to the energy minimum was calculated by geometry optimization for the interacting system; the location of Cl^- determined by the 3-21 + G(*) and 6-31 + G* calculations are $(x, y, z) = (0.0, -3.8, 4.7)$ and $(x, y, z) = (0.0, -5.5, 2.1)$, respectively. This potential energy well is very shallow, and the minimum area is very flat. Thus the minimum point is very sensitive to the method of calculation, and it is not important to locate the minimum point closely. It should be noted that the distance between the chloride ion and the C and H atoms in the CH_2 groups is long (about 6 Å) and the energy minimum appearing in Figures 3 and 4 does not correspond to the contact ion pair (CIP) but rather to the solvent-separated ion pair (SSIP). Our GB model does not consider the specific solute–solvent interaction in an SSIP but mimics the SSIP through the steric factor that is involved in Γ_{AB} and accounts for the exclusion of the solvent shell volume of two species when they approach each other and enter each other's solvent shell. The nonexistence of a CIP for the interaction between **1** and Cl^- has also been suggested by SCRF calculations [13].

TABLE 1 Geometrical Parameters^a of the Cyclic Sulfonium Ion (**1**), CEMS (**2**), and Related Species in Aqueous Solution ($\epsilon = 79$) Optimized by Ab Initio GB Calculations^b

Species	Basis Set	C_1-C_2	$S-C_1$	$S-C_2$	$S-C [Me]$	C_1-X	C_2-X	C_1-C_2-S	$S-C_2-C_1-X$
1	3-21G(*)	1.484	1.814	1.814	1.801	—	—	65.9	—
	3-21+G(*)	1.487	1.811	1.811	1.798	—	—	65.8	—
	6-31+G*	1.477	1.790	1.790	1.787	—	—	65.6	—
		(1.461)	(1.688)	(1.688)	(1.821)	—	—	(66.6)	—
2	3-21+G(*)	1.526	2.774	1.815	1.815	1.826	2.755	112.0	180.0
	6-31+G*	1.519	2.772	1.808	1.810	1.804	2.740	112.5	179.9
3	3-21+G(*)	1.518	2.733	1.817	1.815	1.546	2.495	109.7	181.6
	6-31+G*	1.513	2.742	1.812	1.807	1.503	2.445	110.7	179.9
4	3-21+G(*)	1.528	2.788	1.815	1.815	1.468	2.455	112.7	178.5
	6-31+G*	1.523	2.794	1.807	1.809	1.422	2.427	113.8	179.1
5	3-21+G(*)	1.452	2.302	1.849	1.813	2.601	3.308	87.5	179.8
	6-31+G*	1.452	2.325	1.824	1.808	2.467	3.190	89.7	179.5
6	3-21+G(*)	1.453	2.290	1.847	1.812	2.124	2.863	87.0	180.2
	6-31+G*	1.461	2.390	1.826	1.805	1.976	2.762	92.6	179.4

^aAtomic distance in Å and bond angle in degrees. X is Cl or O.

^bThe values in parentheses for **1** are those in the gas phase.

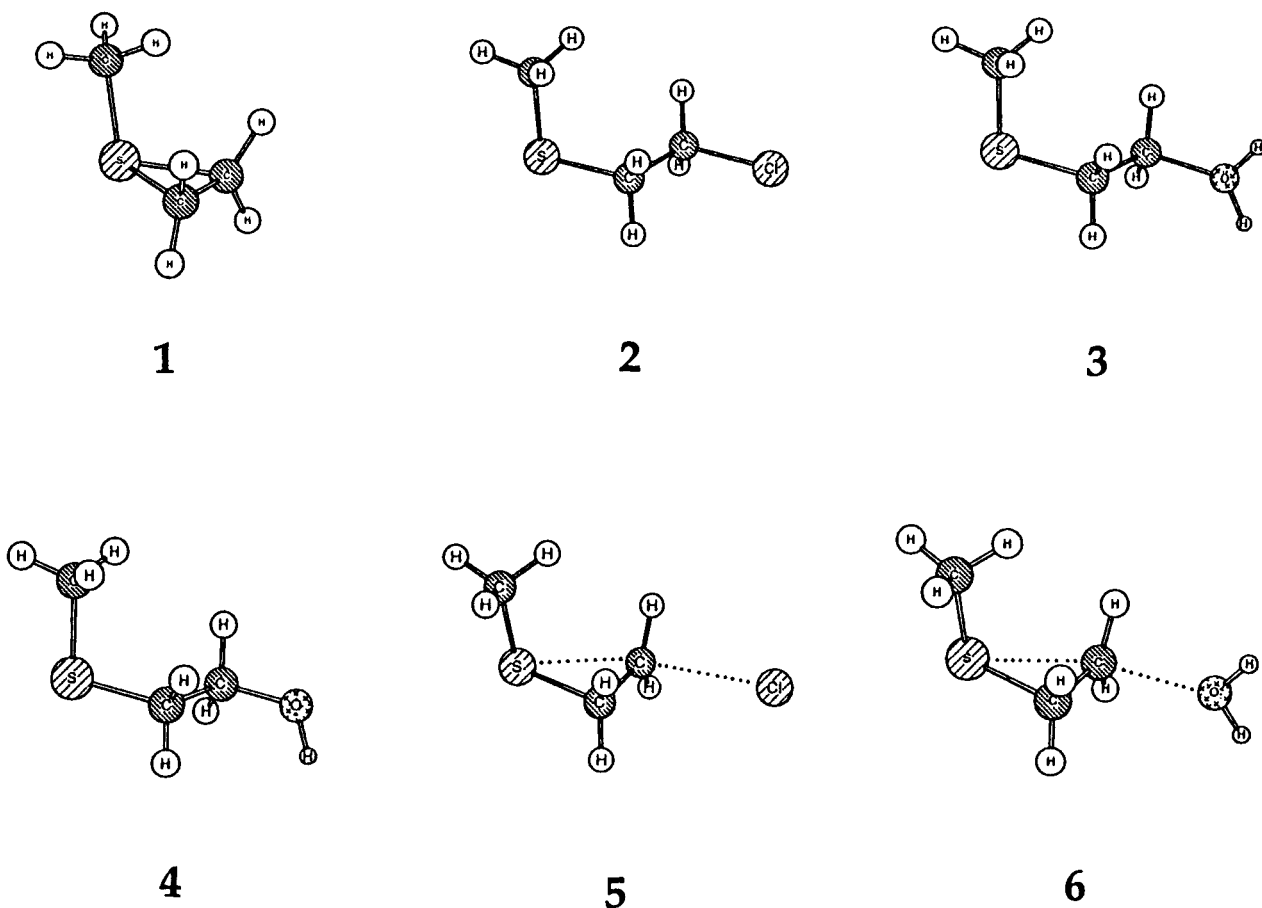
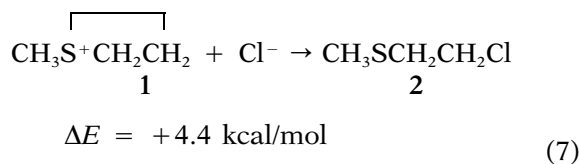


FIGURE 1 Ball and stick representations of 6-31+G* optimized structures in aqueous solution. **5** and **6** are transition states for the $1 + \text{Cl}^- \rightleftharpoons 2$ and $1 + \text{H}_2\text{O} \rightleftharpoons 3$ reactions, respectively.

Reaction of 1 with Chloride Ion

The cyclic sulfonium ion **1** can be attacked by nucleophiles such as water, alcohols, or halide ions to give the ring-opened products. The reaction of **1** with Cl^- gives **2**.



The energy change of this reaction in aqueous solution was estimated by the energy difference between the reactant and product. In Table 2, the calculated energies are listed for **1**–**4** and the related species. As was discussed earlier, there is no CIP between **1** and Cl^- , and the potential energy well corresponding to SSIP is very wide and shallow (Figs. 2 and 3). Also, the vibrational mode at the transition state **5** has indicated that the Cl atom moves on the SC_2C_1 plane (xy plane in Fig. 2) in the $1 + \text{Cl}^- \rightleftharpoons 2$ reaction. The

transition state structure **5** has a high energy, and the association state will not be formed in the $1 + \text{Cl}^- \rightleftharpoons 2$ reaction. Thus we adopted the separated reactant molecules, $1 + \text{Cl}^-$, as the energy standard, and the energy of **2** relative to the reactant, 4.4 kcal/mol (6-31+G*), is assigned to **2**. Thus the relative energies of **2**, **3**, and **4**, which are shown in parentheses, are the energies relative to $1 + \text{X}$, where X is Cl^- , H_2O , or OH^- , respectively. The relative energies of the transition states **5** and **6** are relative ones with respect to $1 + \text{Cl}^-$ and $1 + \text{H}_2\text{O}$, respectively.

The transition state structure **5** was determined by minimization of the norm of the energy gradient and confirmed by diagonalization of the force constant matrix; the SC_2C_1 angle is 89.7° , and the $\text{C}_1\text{--Cl}$ distance is 2.467 Å (Table 2). The energy diagram for the $1 + \text{Cl}^- \rightleftharpoons 2$ reaction is shown in Figure 5. The energy difference between the reactant and the reaction product depends largely on the basis set, because **1** is a strained compound. The 6-31+G* basis set includes the polarization functions for all heavy

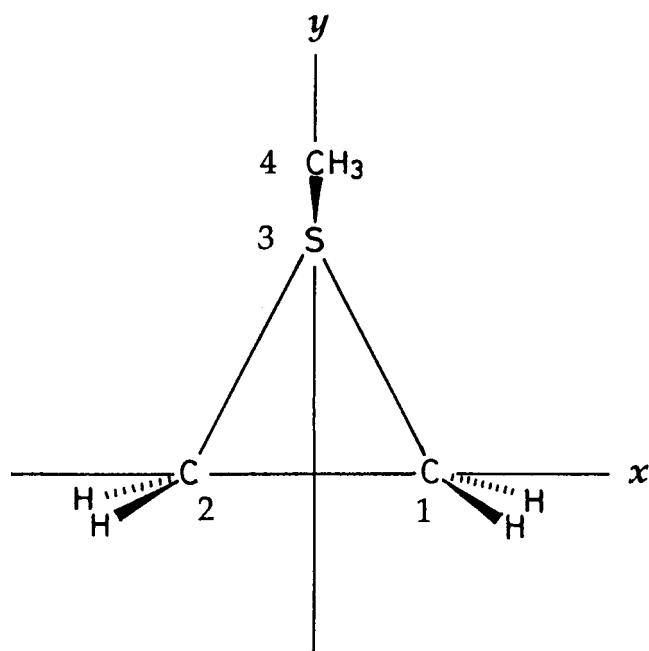


FIGURE 2 The definition of coordinates and numbering of atoms for **1**.

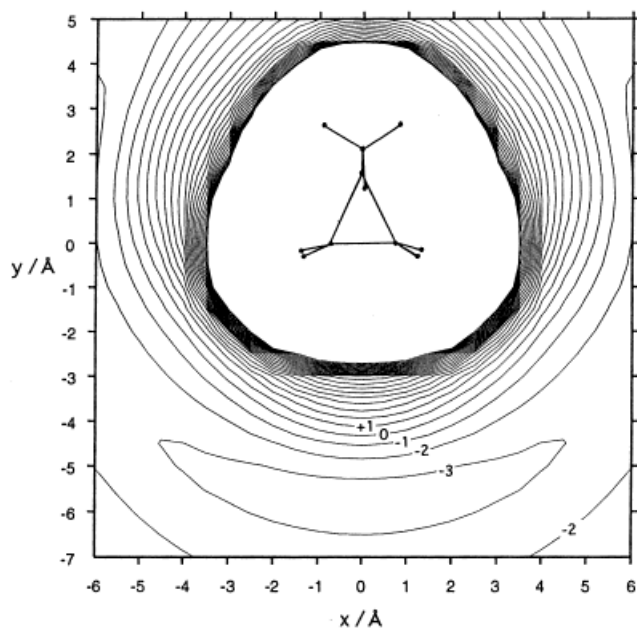


FIGURE 3 The interaction energy between **1** and Cl^- on the xy plane. The contour lines are drawn in steps of 1 kcal/mol, and the numbers cited are in kcal/mol.

atoms and stabilizes the cyclic structure in comparison with the $3-21+G^*$ basis set in which polarization functions are included only in the S and Cl atoms. The stabilization by the polarization functions is larger in the strained compound **1** than in **2**.

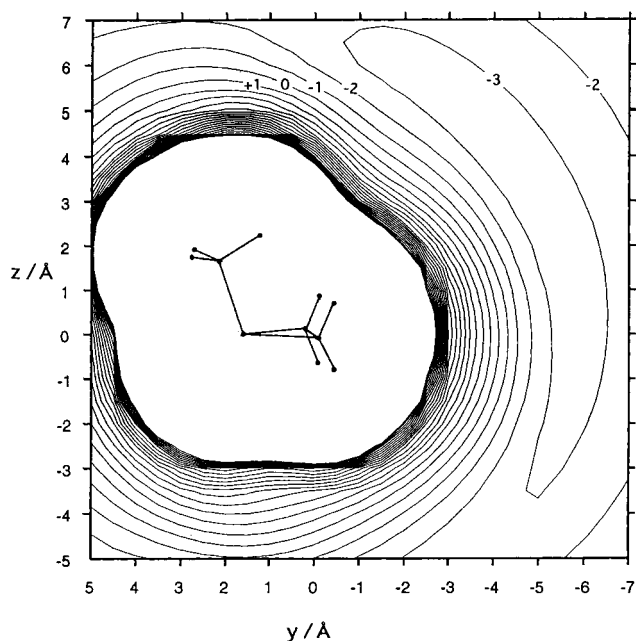


FIGURE 4 The interaction energy between **1** and Cl^- on the yz plane. The contour lines are drawn in steps of 1 kcal/mol, and the numbers cited are in kcal/mol.

TABLE 2 Ab Initio GB Energies (hartree) and Relative Energies^a (kcal/mol, in parentheses) of the Cyclic Sulfonium Ion (**1**), CEMS (**2**), and Related Species in Aqueous Solution

Species	$3-21+G^*$	$6-31+G^*$
$\text{CH}_3\text{S}^+\text{CH}_2\text{CH}_2$ 1	-512.51952	-515.02887
1 + Cl^-	-970.10751 (0.0) ^a	-974.68865 (0.0) ^a
1 + H_2O	-588.14818 (0.0) ^b	-591.06593 (0.0) ^b
1 + OH^-	-587.67992 (0.0) ^c	-590.57953 (0.0) ^c
$\text{CH}_3\text{SCH}_2\text{CH}_2\text{Cl}$ 2	-970.11557 (-5.1) ^a	-974.68171 (+4.4) ^a
$\text{CH}_3\text{SCH}_2\text{CH}_2\text{O}^+\text{H}_2$ 3	-588.15405 (-3.7) ^b	-591.04040 (+16.0) ^b
$\text{CH}_3\text{SCH}_2\text{CH}_2\text{OH}$ 4	-587.74954 (-43.7) ^c	-590.64077 (-38.4) ^c
$\text{CH}_3\text{SCH}_2\text{CH}_2 \dots \text{Cl}^-$ 5 transition state	-970.08060 (+16.9) ^a	-974.64940 (+24.6) ^a
$\text{CH}_3\text{SCH}_2\text{CH}_2 \dots \text{H}_2\text{O}$ 6 transition state	-588.13331 (+9.3) ^b	-591.02466 (+25.9) ^b

^aThe energies relative to the separated reactant **1** + Cl^- .

^bThe energies relative to the separated reactant **1** + H_2O .

^cThe energies relative to the separated reactant **1** + OH^- .

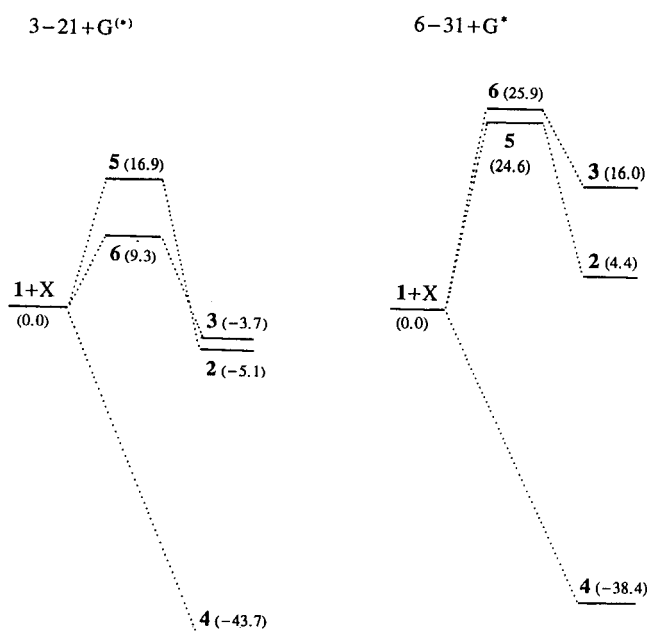


FIGURE 5 The energy diagrams for the S_N2 -type reactions of the cyclic sulfonium ion **1** and three nucleophiles. The energies are in kcal/mol and are relative values to $1 + X$, where X is Cl^- , H_2O , and OH^- for the formations of **2**, **3**, and **4**, respectively.

This effect is also reflected in the activation energy for the $1 + Cl^- \rightarrow 2$ process; the $6-31+G^*$ barrier height (24.6 kcal/mol) is larger than the $3-21+G^{(*)}$ value (16.9 kcal/mol). However, it is interesting to notice that the basis set dependence of the barrier height for the reverse $2 \rightarrow 1 + Cl^-$ reaction is small; the values are 20.2 and 22.0 kcal/mol for the $6-31+G^*$ and $3-21+G^{(*)}$ calculations, respectively. The calculated barrier height, 20.2 kcal/mol, agrees well with the experimental enthalpy of activation for the hydrolysis of CEMS, 19.7 kcal/mol [2] and 19.3 kcal/mol [6].

McManus et al. [3] and Yang et al. [8] confirmed that the sulfonium ion is an intermediate in the hydrolysis of **2**, and the sulfonium ion formation from CEMS is reversible. These studies have indicated that the relative energies between $1 + Cl^-$ and **2** are small, and the barrier for the interconversion between them is not very large. The present energy profile for the $1 + Cl^- \rightleftharpoons 2$ reaction agrees well with these experimental facts.

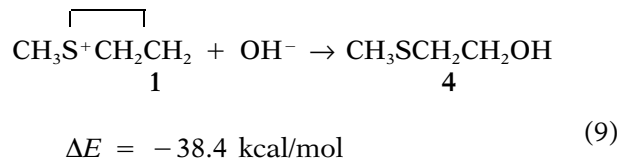
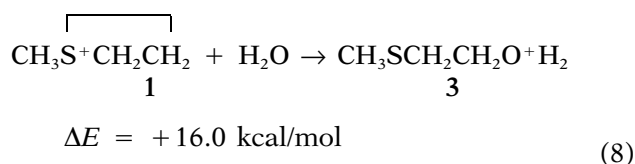
Donovan [13] calculated the parameters of the $2 \rightarrow 1 + Cl^-$ reaction in solution by ab initio $6-31G^*$ SCRFF theory; the energy of **1** plus Cl^- is higher than that of **2** by 31.1 kcal/mol, and the activation energy is 31.8 kcal/mol for the $2 \rightarrow 1 + Cl^-$ reaction [13], suggesting that the cyclic sulfonium ion **1** can hardly exist in aqueous solution, which is against the ex-

perimental evidence. In order to reproduce the experimental barrier correctly, an appropriate mixing of energy components was required [13]. These energetic properties are reflected at the transition state structure; the SCRFF transition state is located on the sulfonium side (the SC_2C_1 angle is 82.5° , and the C_1-Cl distance is 2.601 Å) [13].

The Löwdin charge populations of **1**, **2**, and **5** are shown in Figure 6. In the transition state **5**, the electrons in the breaking S-C bond are mostly withdrawn by the sulfur atom, and the positive charge on the sulfur atom is significantly reduced, although most of the negative charge remains on the Cl atom. This trend is similar to the transition state calculated for the reaction between trimethylsulfonium and Cl^- in aqueous solution [30].

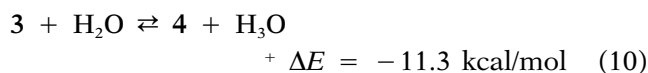
Hydrolysis of **1**

The S_N2 reactions of **1** with H_2O and OH^- were examined.



The heats of reactions were calculated from the energies for each species that are shown in Table 2. The energy diagrams for the $1 + H_2O \rightarrow 3$ and $1 + OH^- \rightarrow 4$ reactions are shown in Figure 5.

The formation of **3** from $1 + H_2O$ is calculated to be endothermic by 16.0 kcal/mol ($6-31+G^*$), and the reverse reactions $3 \rightarrow 1 + H_2O$ is expected to occur easily. For the $1 + OH^- \rightarrow 4$ reaction, the product is much more stable than the reactant, and the transition state could not be found. In basic solution, **4** is expected to form easily from $1 + OH^-$. In the neutral aqueous solution, **3** is formed first, and then **4** will be formed from **3** by assistance of an H_2O molecule; the proton transfer from **3** to H_2O is exothermic by 11.3 kcal/mol ($6-31+G^*$).



This process is a simple proton transfer reaction and proceeds with a small activation energy. In other words, **3** is difficult to form from **4** by the reverse reaction, and thus the reaction of **1** with a nucleo-

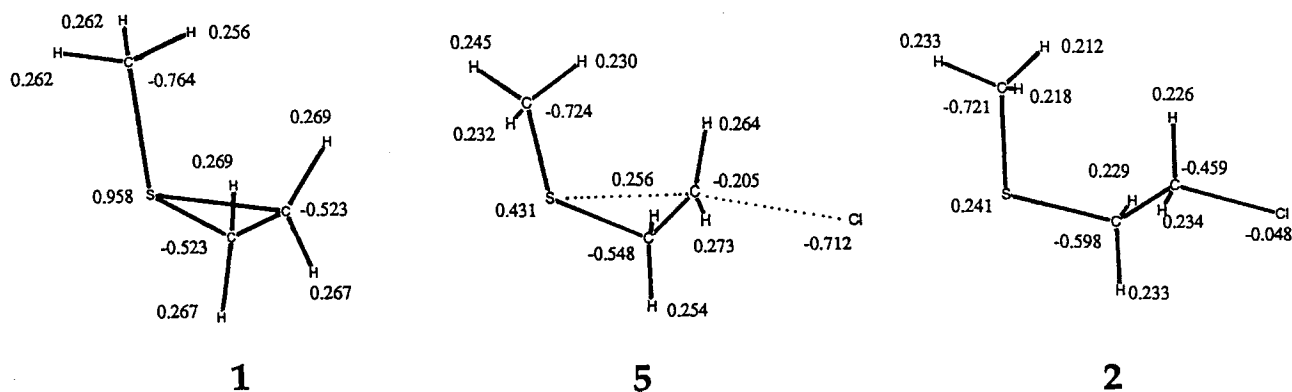


FIGURE 6 Löwdin charge populations for three species: 1, 2, and 5.

phile such as H_2O leads to a stable ring-opened compound that will not easily be converted to the cyclic sulfonium ion. This mechanism is consistent with that proposed by Bartlett and Swain [1] in their pioneering work on the hydrolysis of sulfur mustard.

CONCLUSION

An ab initio MO study including the solvent effect determined for the first time the molecular and electronic structure of methyl ethylenesulfonium ion in solution, and the reactivities of the cyclic sulfonium ion with nucleophiles in aqueous solution were revealed. The cyclic sulfonium ion is stable and reacts with nucleophiles in the standard $\text{S}_\text{N}2$ -type mechanism. The cyclic sulfonium ion is confirmed as an intermediate in the hydrolysis reaction of monochloro derivatives of sulfur mustard. It is suggested that the sulfur mustard and the cyclic sulfonium ion are in equilibrium, and the cyclic sulfonium ion reacts with water to give the hydroxyethyl sulfide as a stable species. These conclusions are in good agreement with experimental facts, and the present ab initio GB model describes well the structure and reactivity of the cyclic sulfonium intermediate in solution.

ACKNOWLEDGMENTS

This research was supported by a Grant-in-Aid for Scientific Research (C) No. 08640633 from the Ministry of Education, Science, Sports, and Culture and by a Tsukuba University Research Project A.

REFERENCES

[1] P. D. Bartlett, C. G. Swain, *J. Am. Chem. Soc.*, **71**, 1949, 1406.

[2] M. J. Blandamer, H. S. Golinkin, R. F. Robertson, *J. Am. Chem. Soc.*, **91**, 1969, 2678.
 [3] S. P. McManus, N. Neamati-Mazraeh, B. A. Hovanes, M. S. Paley, J. M. Harris, *J. Am. Chem. Soc.*, **107**, 1985, 3393.
 [4] S. P. McManus, R. M. Karaman, R. Sedaghat-Herati, B. A. Hovanes, X.-T. Ding, J. M. Harris, *J. Org. Chem.*, **58**, 1993, 6466.
 [5] S. P. McManus, R. M. Karaman, R. Sedaghat-Herati, J. M. Hariss, *J. Org. Chem.*, **60**, 1995, 4764.
 [6] Y.-C. Yang, J. R. Ward, T. Luteran, *J. Org. Chem.*, **51**, 1986, 2756.
 [7] Y.-C. Yang, J. R. Ward, R. B. Wilson, W. Burrows, J. S. Winterle, *Thermochim. Acta*, **114**, 1987, 313; from Mustard to chlorohydrin, 18.5 kcal/mol enthalpy of activation.
 [8] Y.-C. Yang, L. L. Szafraniec, W. T. Beaudry, J. R. Ward, *J. Org. Chem.*, **53**, 1988, 3293.
 [9] C. Sosa, R. J. Bartlett, K. KuBulat, W. B. Person, *J. Phys. Chem.*, **93**, 1989, 577.
 [10] H. Bruch, R. Viani, D. Vasilescu, *Int. J. Quant. Chem.*, **43**, 1992, 511.
 [11] P. Politzer, D. Habibollahzadeh, *J. Phys. Chem.*, **98**, 1994, 1576.
 [12] W. H. Donovan, G. R. Famini, *J. Phys. Chem.*, **98**, 1994, 3669.
 [13] W. H. Donovan, *Struct. Chem.*, **6**, 1995, 243.
 [14] W. H. Donovan, W. E. White, *J. Mol. Struct. (Theochem.)*, **370**, 1996, 209.
 [15] V. M. Csizmadia, G. H. Schmid, P. G. Mezey, I. G. Csizmadia, *J. Chem. Soc. Perkin II*, 1977, 1019.
 [16] M. Born, *Z. Phys.*, **45**, 1920, 1.
 [17] G. J. Hoijtink, E. De Boer, *Recl. Trav. Chim. Pays-Bas*, **75**, 1956, 487.
 [18] I. Jano, *C. R. Acad. Sci.*, **261**, 1965, 103.
 [19] O. Tapia: in R. Daudel, A. Pullman, L. Salem, A. Veillard (eds): *Quantum Theory of Chemical Reactions*, vol. 2, Reidel, Dordrecht, p. 25 1981.
 [20] T. Kozaki, K. Morihashi, O. Kikuchi, *J. Mol. Struct. (Theochem.)*, **168**, 1988, 265.
 [21] T. Kozaki, K. Morihashi, O. Kikuchi, *J. Am. Chem. Soc.*, **111**, 1989, 1547.
 [22] C. J. Cramer, D. G. Truhlar, *J. Am. Chem. Soc.*, **113**, 1991, 8305, 8552.
 [23] C. J. Cramer, D. G. Truhlar, *J. Comput. Chem.*, **13**, 1992, 1089.
 [24] O. Kikuchi, T. Matsuoka, H. Sawahata, O. Takahashi, *J. Mol. Struct. (Theochem.)*, **305**, 1994, 79.

- [25] O. Takahashi, H. Sawahata, Y. Ogawa, O. Kikuchi, *J. Mol. Struct. (Theochem)*, 393, 1997, 141.
- [26] O. Kikuchi, T. Watanabe, Y. Ogawa, H. Takase, O. Takahashi, *J. Phys. Org. Chem.*, 10, 1997, 145.
- [27] (a) J. S. Binkley, J. A. Pople, W. J. Hehre, *J. Am. Chem. Soc.*, 102, 1980, 939; (b) M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, W. J. Hehre, *J. Am. Chem. Soc.*, 104, 1982, 2797; (c) W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. Defrees, J. A. Pople, J. S. Binkley, *J. Am. Chem. Soc.*, 104, 1982, 5039; (d) The exponents of diffuse functions were taken from: W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople: *Ab Initio Molecular Orbital Theory*, Wiley, New York (1986).
- [28] (a) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.*, 56, 1972, 2257; (b) The polarization and diffuse functions were taken from: W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople: *Ab Initio Molecular Orbital Theory*, Wiley, New York (1986).
- [29] R. G. Pearson, *J. Am. Chem. Soc.*, 108, 1986, 6109.
- [30] O. Kikuchi, Y. Sano, O. Takahashi, K. Morihashi, *Heteroatom Chem.*, 7, 1996, 273.