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DFT Study of the Regioselectivity of Addition of Sulfenylchloride to Ethenes

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ABSTRACT: *The electrophilic addition reactions of methylsulfenyl chloride to the double bonds of functionalized ethenes have been studied theoretically. Density functional theory (DFT) calculations have been applied for starting species and ethene-based sulfonium intermediates bearing substitutes at α-carbon atom to study geometrical parameters and electronic states of plausible intermediate forms. The quantum chemical optimizations of intermediates indicate that the episulfonium ion is the most likely methyl- or carboxyl-substituted ethane-based intermediate. However, with phenyl substituents the intermediate is more like a carbonium than an episulfonium ion. The role of sulfur appears to be that of directing the stereochemistry of the addition reaction of chloride, forming the trans product upon nucleophilic attack on the C–C bond of the episulfonium ion. The regioselectivity features of the opening of the episulfonium ion by the chloride anion depend on the LUMO and LUMO+1 of the episulfonium ion and the approaching HOMO of chlorine. The results of the theoretical investigations are in agreement with experiment.* Heteroatom Chem 18:695–703, 2007; DOI 10.1002/hc.20378

INTRODUCTION

Bifunctional thioalkylhalogenides are versatile agents for applications in medicinal chemistry as anticancer and therapeutically active agents [1]. They are also desirable targets in biochemistry due to their ability to activate chromosomal enzymes, mainly *poly(ADP-ribose)polymerase,* subsequently causing selective breakup of DNA [2].

Many research groups are using electrophilic addition reactions of sulfenyl halogenides to the double bonds of functionalized bicyclic compounds, heterocycles, or bulky-substituted alkenes [3] as the principal synthetic route to these compounds. As shown in Scheme 1, the reaction mechanism involves two main steps: first the formation of a stable intermediate followed by nucleophilic displacement of halide to give the chloroalkyl sulfide product. It was determined experimentally that the reaction occurs in a stereospecific trans manner, with the nucleophile (halide) attacking one of the unsaturated carbon atoms [4]. The first step is usually reversible, so it is the second step that determines the stereochemistry of the products. It is well known that the addition reactions of sulfenyl chlorides to unsymmetrical alkenes give two isomeric adducts, the Markownikoff adduct (**M**) and the anti-Markownikoff adduct (**aM**). The ratio of the amounts of these isomeric adducts formed is characteristically different, according to the type of the unsymmetrical alkene used. It was shown (Scheme 1) that when the α-carbon substituent R of an intermediate structure type **1** is alkyl, the predominant ring-opening

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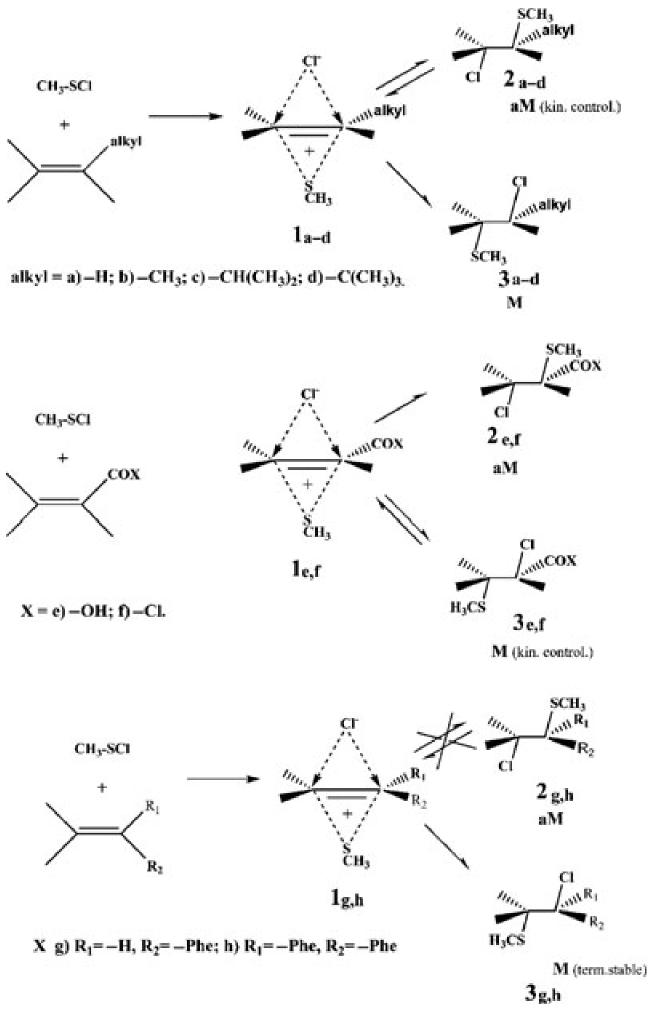

SCHEME 1 The addition reaction of methylsulfenyl chloride to the double bonds of functionalized ethenes

reaction occurs by attack at the terminal β carbon atom, giving the kinetically controlled **aM** products with structures **2b–d**, which undergo further rearrangement to the thermodynamically stable **M** adduct, of structure type **3**. In contrast, the addition of sulfenylchloride to conjugated olefins, when the α-carbon substituents R are phenyl, vinyl, and carboxyl, gives products with the Markownikoff orientation, of type **3**, directly. The phenyl-substituted olefins did not show any tendency to rearrange to give thermodynamically stable oriented structures **3g,h** in one step, whereas olefins with carboxylic groups as substituents first gave the kinetically controlled **M** oriented adducts **3e,f**, which undergo further rearrangement to the thermodynamically stable **aM** products with structures **2e,f**. The ratios of the amounts of the two isomers formed are believed to result from competition between steric and electronic effects [5].

Much of the discussion of electrophilic addition reaction mechanisms is concerned with the stable conformations of sulfonium ion intermediates: carbonium like—open classical, symmetrical bridged and unsymmetrical bridged [6,7].

In contrast to those formed by the usual atomic electrophiles such as H^+, Hg^+, Ag^+, the sulfonium-type intermediates differ in the geometric configuration of substituents on the double bond and particularly in the nature of the sulfur atom, which have major consequences for the bonding properties and the stability of intermediates.

The sulfenyl compounds are usually the preferred kind of electrophiles for the investigation of reaction mechanisms, since the addition reactions proceed in a stereospecific trans manner, forming cyclic episulfonium intermediates, which can even be detected in special cases [3,4]. An investigation of the kinetics and NMR spectroscopy of the reactions of methyl and 2,4-dinitrobenzenesulfenyl chlorides with cyclohexene are consistent with σ-type tetracovalent sulfur of the cyclic episulfonium intermediates [7]. In addition, experimental results reported for the reactions of 2,4-dinitrobenzenesulfenyl chloride with styrene and propylene reflect carbonium ion character in the transition structures [5]. Nevertheless, strong evidence against nonrotating open carbonium ions has recently been supplied by the stereospecific uniformity of this reaction over a wide temperature range [6,7].

Recent experimental studies [5,8] of addition reactions of sulfenyl chlorides to substituted olefins have investigated the effects of the sulfonium ion intermediates using kinetics and NMR spectroscopy methods, and have confirmed the reaction mechanism. These investigations indicate that the electronic structures and configurational features of episulfonium ion intermediates should be examined using molecular orbital approaches to these problems. We have therefore investigated the regioselectivity features of addition reactions of methylsulfenyl chlorides to methyl-, carboxyl-, and phenyl-substituted ethenes using quantum chemical density functional theory (DFT) methods. The results are reported here.

RESULTS AND DISCUSSION

In the present paper, we discuss stable forms of methanesulfenyl chloride and sulfonium ion intermediates formed by addition of methanesulfenyl cations to ethylene **1a**, prop-1-ene **1b**, 4-methylpent-1-ene **1c**, 3,3-dimethylbut-1-ene **1d**, acrylic acid **1e**, and its chloroanhydride **1f**, styrene **1g**, and 1,1-diphenylethene **1h**, performing DFT calculations

TABLE 1 Lowdin Charge Densities of Methanesulfenyl Chloride and Its Cation, Calculated in Vacuum and with CCl_4 and CH_2Cl_2 Solvent Models

	Methanesulfenyl Chloride			*Methanesulfenyl Cation/Radical*	
	C	*S*	*Cl*	*C*	*S*
Charges in vacuum	−0.701	+0.251	−0.240	−0.816/−0.450	+0.846/+0.041
Charges in CCl_4	−0.695	+0.275	−0.273	−0.820	+0.851
Charges in CH_2Cl_2	−0.691	+0.290	−0.305	−0.846	+0.855

TABLE 2 Bond Orders and Bond Dissociation Energies (kcal/mol) of Methanesulfenyl Chloride, Calculated in Vacuum and with CCl_4 and CH_2Cl_2 Solvent Models

	Bond Energies		*Bond Orders*	
	C—S	*S—Cl*	*C—S*	*S—Cl*
In vacuum	379.02	198.98	0.92	0.83
In CCl_4	247.78	76.50	0.90	0.81
In CH_2Cl_2	245.98	73.42	0.91	0.70

with the 6-31G basis set and the B3LYP method in vacuum and using the PCM solvent model.

In the first place, to elucidate the significance of solvent effects on the initiation of addition reactions, we performed calculations for the starting reactants, the methanesulfenyl chloride, its cation, and ethylene, both in appropriate solvents and in vacuum.

Subsequently, we investigated reaction intermediates that could be the most stable ones formed by addition. The calculations showed that in the ethylene-based episulfonium ion, the most stable form of intermediate, the most plausible configuration of valence electrons in the S atom is closer to the p configuration than sp^3. Further calculations were performed to elucidate the bonding nature of C(α)=C(β) and S—C(α), S—C(β) bonds of intermediate episulfonium ion, and the regioselectivity of the this ion ring opening. After full geometry optimizations in vacuum and with the solvent model, we calculated electronic states and the molecular orbitals (MOs) of the ethylene-based episulfonium ion intermediate **1a**, and compared them with fully optimized geometries and MOs of intermediates **1b–h**, obtained by the additions to prop-1-ene, 3,3-dimethylbut-1-ene, 4-methylpent-1-ene, styrene, 1,1-diphenylethene, and acrylic acid.

Electronic States of Methanesulfenyl Chloride and Methanesulfenyl Cation

Most experimental studies pertaining to the electrophilic addition mechanism have been conducted with sulfenyl chlorides, but it is known that in theory the molecule methylsulfenyl chloride could react in at least three distinct ways with an olefin: either as a source of electrophilic sulfur or of chlorine, or as a source of free radicals by homolytic cleavage [9]. We therefore investigated the electronic state of methanesulfenyl chloride and compared it with the methanesulfenyl cation and radical.

The charges of methanesulfenyl chloride presented in Table 1 show that the positive charge is mainly located on the sulfur atom, whereas the negative charge is on the chlorine atom. The charge polarization between these atoms is enhanced by the influence of solvation effects; the positive charge on sulfur increases from +0.25 up to +0.29, resulting in an increase of electron density on the chlorine atoms from −0.24 to −0.31. Moreover, the increase of positive charge density on the sulfur atom in the methylsulfide cation compared to that in methylsulfenyl chloride is so significant that it becomes +0.8 and solvation effects show slight tendencies to increase it. Meanwhile, there is a considerable decrease of positive charge, to +0.04, on the sulfur atom of the methylsulfide radical, compared to that in its cation. The bond energies and bond orders in the methylsulfenyl chloride molecule, as shown in Table 2, are considerablly smaller between the S and Cl atoms than in the C—S bond, and the solvation effects reflect tendencies to lower the dissociation energy and bond order for both the bonds. The calculated charge distribution and geometric parameters of the ethylene molecule in vacuum did not show changes comparing to those calculated for the solvated medium. These results imply that the polarization of the S—Cl bond in the methylsulfenyl chloride molecule is expected to be sensitive to the polarity of the solvent. This is important for electrophilic addition reactions, which may therefore occur fairly easily in polar solvents.

We also calculated the distribution of the frontier molecular orbitals of the methylsulfide cation, which is one of the possible starting species of the addition reaction. In Fig. 1, it is shown that the electrons of the highest occupied molecular orbital (HOMO) are mainly localized in the p_y atomic

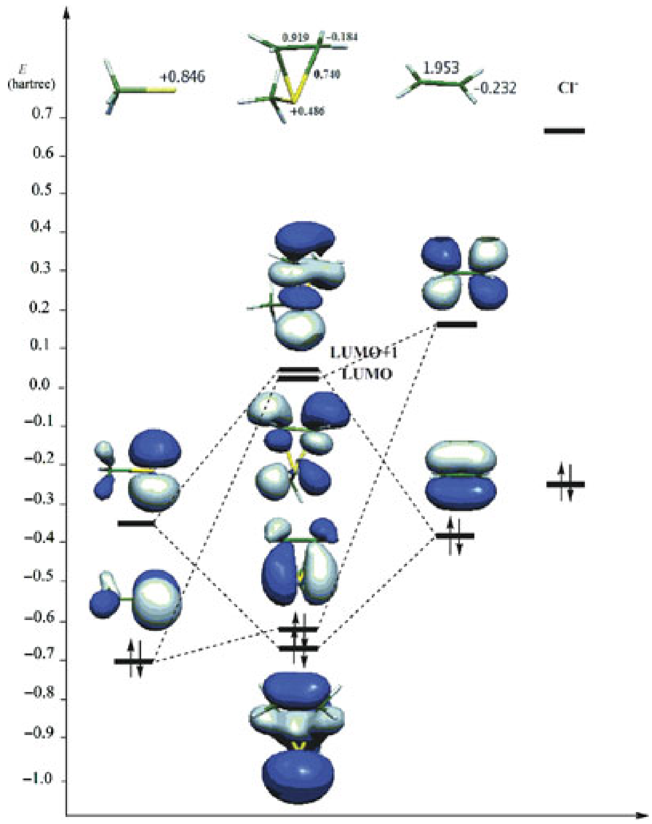

FIGURE 1 MO diagram for interacting electrophile–MeS cation, nucleophiles–ethylene, and chloride anion together with the episulfonium cation reaction intermediate. Lowdin charges on sulfur and carbon atoms and S—C and C—C bond orders are also presented.

orbital (AO) of the S atom and the LUMO is localized in the p_z of the S atom, which implies that the methylsulfide cation can easily react with various olefins or nucleophiles forming the cationic $p\sigma$-type intermediates. Therefore, for further calculations, we considered the methylsulfide cation as most plausible electrophilic starting species for the initiation of electrophilic addition reaction to olefins.

Stable Conformations of Substituted Ethylene Episulfonium Ion Intermediates

To get more insight into the nature of the observed regioselectivity of addition reaction and of factors controlling ring opening, we optimized most plausible structures of addition reaction intermediates using 6-31G basis set and the PCM solvent model to study the geometry and electronic structure of the ethylene-based episulfonium intermediate **1a** as the model compound and its substituted ones **1b–h**. To get better energy description, the energies were calculated for optimized starting species and intermediates **1a–h** using $6\text{-}311G^{**}$ basis set in the PCM solvent model and are presented in Table 3. These results explain that formation of episulfonium ion via the addition of methylsulfide cation to ethenes is thermodynamically favorable process.

The geometry of plausible structures of cationic intermediates may be considered to be either the open form or symmetrically cyclic. Also in the cyclic form, there are three typical and plausible electronic configurations of the S atom: p, sp^2, and sp^3. The dihedral angles $C(\alpha)—C(\beta)—S—C$ and $C(\beta)—C(\alpha)—S—C$ mostly reflect the hybridization of the S atom in the episulfonium fragment and should be 90° for p, 180° for sp^2, and 125.5° for sp^3 hybridizations, respectively. Usually, it is considered that in compounds such ethylene oxide or sulfide the lone pair of electrons of heteroatoms takes sp^3-type configuration. By analogy, the sp^3 configuration may also be seen to be plausible for episulfonium ion intermediates, which have similar structures. In the fully optimized structures of ethylene-based episulfonium ion intermediates **1a**, the dihedral angles are about 93°. It follows that sp^2 geometry for the S atom is not acceptable, but that the S atom loses sp^3 character and more closely relates to p hybridization. Therefore, as pictured in the MO diagrams of interacting electrophile–methylsulfide cation, nucleophile–ethene, and the reaction intermediate episulfonium cation (Fig. 1), the geometric and electronic features suggest that in the electrophilic addition the double bond transfers to the S atom, to neutralize almost completely the positive charge on the S atom and then form a fairly strong bond between the S and C atoms, resulting in weakening of the C═C double bond. This stabilization is caused by the delocalization among the p_x orbitals of C(α), C(β), S, and C atoms in the same plane. Deformation of the double bond is also caused in the process

TABLE 3 Relative Energies and Total Energies *E* (kcal/mol) of Starting Species (Methylsulfide Cation + Ethane and Its Analogues) and Episulfonium Ion Intermediates **1 a–h** for Electrophilic Addition Reaction

Intermediate Number	*E of Starting Species*	*E of Intermediate*	*Relative Energies*
1a	−323080.50	−323154.37	−73.87
1b	−347575.80	−347653.76	−77.96
1c	−396564.05	−396643.12	−79.07
1d	−421058.08	−421136.41	−78.33
1e	−440799.66	−440858.03	−58.37
1f	−681775.85	−681828.25	−52.40
1g	−467114.80	−467194.07	−79.27
1h	−611124.86	−611225.79	−100.93

of the methylsulfide group approaching the double bond to form the π-complex episulfonium ion intermediate. The comparison of HOMO and LUMO shapes for the reacting ethene and methylsulfide cation and the episulfonium product indicates that the charge of π electrons in the double bond transfer to the vacant orbital on the S atom, and otherwise the positive charge of the isolated methanesulfenyl cation, wholly distributes over the intermediate. Such charge delocalization makes a contribution to the stabilization of the intermediate. Furthermore, we discuss about the process in which the nucleophile (chloride anion) attacks α or β carbon atoms of cationic intermediate causing regioselective ring opening reaction. In this process, the lowest vacant orbitals of the episulfonium ion intermediates play an important role in predicting the reaction path and the stability of the final adducts. As pictured in Fig. 1, the lowest vacant MOs, that is, the LUMO and LUMO+1 of the stabilized episulfonium ion intermediate, are the Walsh-type orbitals [10], which are very close in energy. Moreover, the LUMO+1 is energetically highly separated from other higher lying LUMOs. The LUMO+1 is symmetrically delocalized π-type orbital on the C=C bond, and the LUMO orbital is antisymmetrical π-type orbital on the C=C bond, presenting the greatest extension along the p_z direction. According to Klopman's charge and frontier orbital control concept [11] and as shown in the Fig. 1 for both reactions (electrophilic addition with methylsulfide cation and nucleophilic displacement of episulfonium ion by chloride anion), the energy gap between the HOMO of the nucleophile and the LUMO of the electrophile is small compared to that between the orbitals of individual reagents, and so the reaction could be frontier-orbital controlled rather than charge controlled, which would require a progressively increasing energy gap between the HOMO of the nucleophile and the LUMO of the electrophile. Also, as the episulfonium ion LUMO and the next higher vacant orbital LUMO+1 present the greatest extension around the C—C bond along the p_z direction, they offer the greatest interaction with an occupied orbital of the nucleophile (chloride anion) when the nucleophile approaches the intermediate along this direction. Ring opening may, therefore, occur in the trans manner, as described in the experimental investigation in the literature [4]. In addition, the regioselective features of episulfonium ring-opening reactions with the chloride anion may be governed by the small energy gap between the LUMO and LUMO+1 of the intermediates [12]. The interaction between an occupied orbital of the nucleophile (chloride anion) approaching the C—C atoms of the intermediate could in some cases be predominantly with the LUMO+1, and if this is stronger than the LUMO interaction with the nucleophile it will control the course of the reaction.

The Electronic Structures and Geometry of Propylene, 3,3-Dimethylbut-1-ene, 4-methylpent-1-ene, Styrene, 1,1-Diphenylethene, Acrylic Acid, and Its Chloroanhydride-Based Episulfonium Ion Intermediates **1b–h***, and the Orientation of Ring-Opening Reaction by Chloride Anion*

The effects of α-carbon substituents on the C—C bond of the episulfonium ion on its ring-opening regioselectivity were considered. We compared geometries, charges, and LUMOs of the methyl, carboxyl, and aryl-substituted episulfonium ion intermediates **1b–h** with the ethene-based one **1a**. From Figs. 2 and 3 and Table 4, it may be seen that ions **1b–f** and the ethene-based ion **1a** (Fig. 1) have quite similar bond lengths, angles, and torsion angles.

The positive charge (+0.5) for ethene-based intermediates **1a** and **1b–f** is mainly located on the sulfur atom. The two bond angles between α or β carbons and the sulfur atom, S—C(α)—C(β) and S—C(β)—C(α), are about ∼70°, which may be favor the episulfonium ion. The C(α)—S and C(β)—S bonds are almost equivalent, that is bond lengths are both about 1.9 Å and their bond orders are both ∼0.8. It appears that the geometries of **1b–f** support the episulfonium character of the intermediates. From the data for **1g** and **1h** in Fig. 4 and Table 4, it is apparent that the effect of phenyl group is noteworthy from a geometrical standpoint. In contrast to the geometrical parameters for the episulfonium ion substituted with methyl **1b–d** and carboxyl **1e–f**, when carbon is substituted with a phenyl group significant changes in the geometry of ions **1g** and **1h** are observed. The angle S—C(α)—C(β) (41.9°) becomes smaller than angle S—C(β)—C(α) (106.5°) upon replacement of hydrogen with phenyl groups. The angle S—C(β)—C(α) still appears to be too large for this to be considered an intermediate having episulfonium ion character. There are changes in the carbon–sulfur bonds; the S—Cα bond is lengthened significantly, up to 2.74 Å (bond order 0.05), whereas S—C(β) is shortened to 1.85 Å (bond order 0.87). Also, in the case of substitution with phenyl the positive charge is equally delocalized between sulfur (+0.2) and the α carbon (+0.26). Both of these phenomena allow for the possibility that when the hydrogen of the α-carbon atom replaced by an aryl group, the structure of the intermediate may be even more carbonium-like than of the episulfonium type.

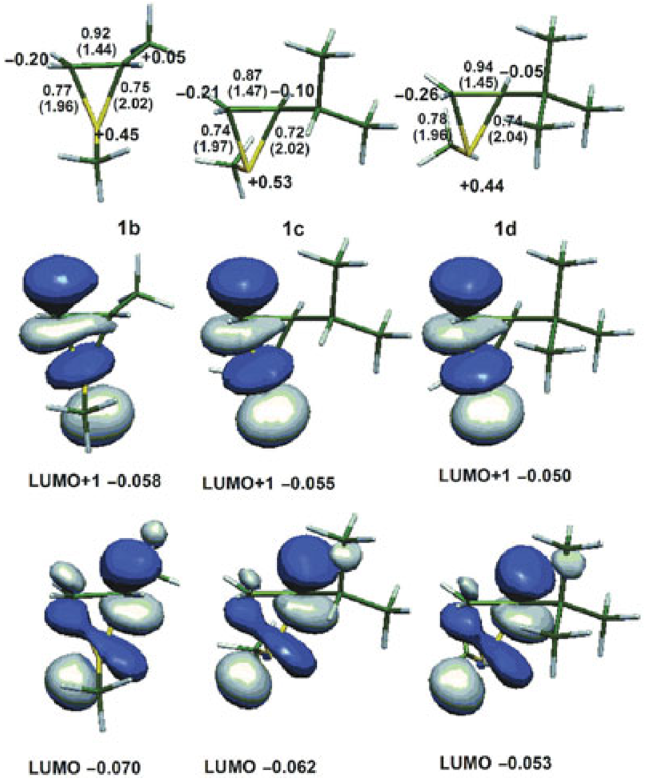

FIGURE 2 The LUMO and LUMO+1 shapes and energies (in hartrees), Lowdin charges, and bond orders (bond lengths) for episulfonium ion intermediates **1b–d**, derived from propylene, 3,3-dimethylbut-1-ene, and 4-methylpent-1-ene.

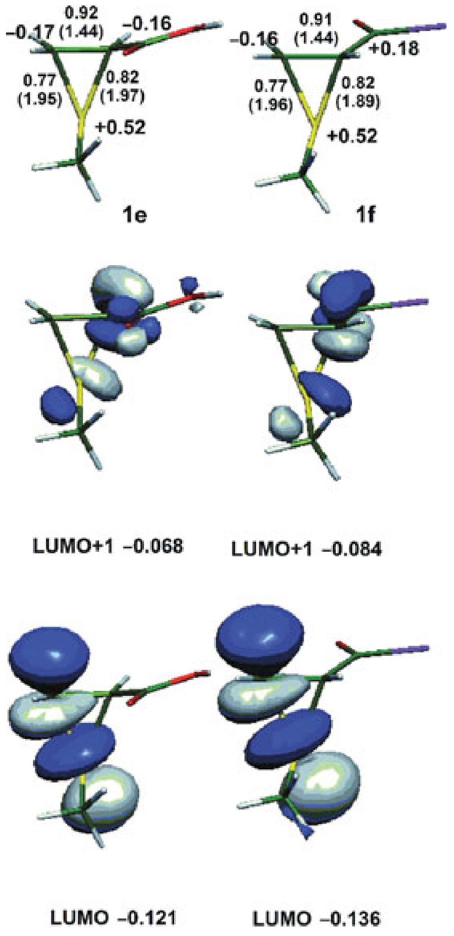

FIGURE 3 The LUMO and LUMO+1 shapes and energies (in hartrees), Lowdin charges, and bond orders (bond lengths) for episulfonium ion intermediates **1e,f**, derived from acrylic acid and its chloroanhydride.

To develop further a qualitative understanding of the regiochemistry of episulfonium ring opening by nucleophilic displacement with chloride anion, it was of interest to examine different reactivities of the C(α)—C(β) carbon atoms of substituted ions **1b–h**, estimating the local atomic charges and shapes of the LUMOs. Lowdin charges were obtained for structures **1a–h**, and they are presented in Figs. 2–4. We expected to find that the isolated molecule approach would show the highest rates of nucleophilic reagent attack at the mostly positively charged or lowest electron density centers. The calculated Lowdin charges of α and β carbon atoms for **1b–h** show that the β carbon is more negatively charged than α, suggestting that the position of the α carbon is more favorable for nucleophilic attack by chloride anions. However, experimental results revealed the opposite situation. When hydrogen is replaced with methyl, a ring-opening reaction occurs at the β carbon by chloride attack at the terminal β carbon, giving the kinetically controlled **aM** product with structure **2b–d**, whereas replacement of hydrogen with phenyl or carboxyl gives the Markownikoff orientation **3e–h**, leading to ring-opening reaction at the α carbon. This implies that episulfonium ring-opening regioselectivity cannot be fully explained by attractive electrostatic interactions between the reacting centers. This is in agreement with the results outlined in the preceding paragraph, which are consistent with the reaction being frontier-orbital controlled. We therefore

TABLE 4 Comparison of Geometrical Parameters for Episulfonium Ion Intermediates **1 b–h**

	Bond Length/(Å)		*Bond Angle/(°)*	
Compound	*C(α)—S*	*C(β)—S*	*S—C(α)—C(β)*	*S—C(β)—C(α)*
1b	2.02	1.96	66.57	71.35
1c	2.02	1.97	65.99	71.55
1d	2.04	1.96	65.58	71.94
1e	1.97	1.95	68.42	68.31
1f	1.89	1.96	68.38	67.97
1g	2.65	1.93	47.31	98.87
1h	2.74	1.90	41.88	106.50

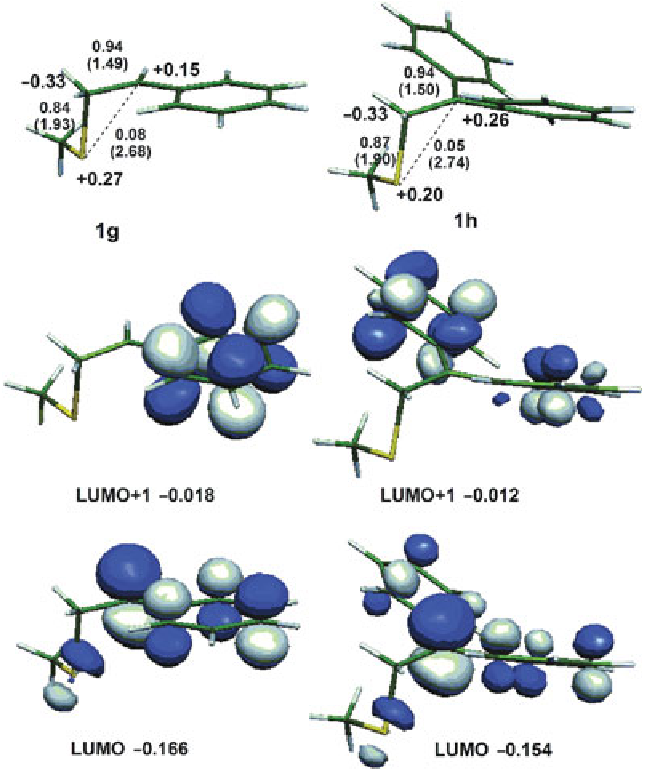

FIGURE 4 The LUMO and LUMO+1 shapes and energies (in hartrees), Lowdin charges, and bond orders (bond lengths) for episulfonium ion intermediates **1g,h**, derived from styrene and 1,1-diphenylethene.

concentrated efforts on the examination of the shapes and locations of the LUMOs of **1b–h**, which are important for interpretation of nucleophilic displacements in episulfonium ions, comparing them with data for the ethylene-based system (**1a**).

In this article we have pictured the two lowest vacant orbitals, LUMO and LUMO+1, which are accepted as being the most important for the interpretation of observed regioselectivity. These orbitals are formed from out-of-plane p_z orbitals, which result in π-complex character for all intermediates **1a–h**. Replacement of hydrogen with methyl, carboxyl, and phenyl substituents on the α carbon of the C—C bond resulted in distortions of vacant orbital shapes for all substituted intermediates **1b–h**, compared to ethylene-based episulfonium **1a**. The episulfonium ion ring-opening regioselectivity is governed by whether the chloride ion attacks C(α) or C(β) of the intermediate, and so is considered to be determined by unsymmetrical extension of the vacant orbital on C(α) or C(β); the larger the extension, the easier the chloride anion attack at that site.

Otherwise, as the energy differences between the LUMO and LUMO+1 are very small for all intermediates, it implies that nucleophilic attack could be determined by interactions controlled by the energy gap or orbital overlap, that is, depending on the greater impact of LUMO or LUMO+1 for nucleophilic addition of chloride [12]. In the case of methyl-substituted intermediates, it is easy to see that the LUMO+1 shape is more localized on terminal C(β) than on the methyl-substituted atom C(α), and accordingly the experiments show that the chloride anion may more easily attack the terminal C(β) to give the **aM** kinetically controlled adduct **2b–d**. On the other hand, in the case of carbonyl-substituted episulfonium ion intermediates **1e** and **1f**, the LUMO+1 is delocalized between the C(α) atom and the carboxylic group, as shown in Fig. 3. This leads to the opposite conclusion to that for the methyl substitution case, that is, carbonyl-substituted intermediates **1e** and **1f** give kinetically controlled adducts with **M** orientation **3e,f**, governed by the addition of chloride to the α-carbon atom. Furthermore, LUMO+1 shape of phenyl-substituted intermediates **1g,h** are delocalized between two adjacent C—C phenyl atoms instead of expected localization on episulfonium C(α) or C(β) carbons, whereas no kinetically controlled adducts were observed experimentally. The extension of the LUMO+1 for all **2b–h** is in agreement with the experimental possibility of forming kinetically controlled adducts.

The shapes of the LUMOs for episulfonium intermediates **1b–h** are consistent with the possibility of rearrangement to the thermodynamically stable products via the formation of episulfonium ion intermediates. The localization of the LUMO shape on α carbon, compared to localization on C(β) in the phenyl-substituted episulfonium **1g,h**, implies that the C(α) position is more susceptible to nucleophilic addition of a chlorine atom. This result is in agreement with experimental observations showing exceptional formation of **M**-oriented products **3g,h**, which are thermodynamically stable and did not show any tendency to rearrange. The LUMO shape of carboxyl substituted episulfonium **1e,f** located on β-carbon. This result corresponds to experimental finding that nucleophilic displacement process of carboxyl-substituted **M**-oriented kinetically controlled adducts **3e,f** undergoes rearrangement to **aM** products **2e,f**, which are thermodynamically stable. In the case of nucleophilic addition of chloride to the methyl-substituted episulfonium, ion subsequent rearrangement of kinetically controlled **aM** adducts **2b–d** to stable **M** products **3b–d** was observed experimentally. Accordingly, the calculated LUMO shapes for **1b–d** show enlarged extension along the p_z direction of the α-carbon atom, which supports attraction to form **M**-oriented products **3**.

The formation of kinetically controlled adducts is favored by the possibility of interaction of the episulfonium ion C—C bond with chloride, between the HOMO of nucleophile and the LUMO+1 vacant symmetrical orbital of electrophile. While the formation of thermodynamically stable products is favored by the interaction of the HOMO of nucleophile (chloride anion) with the LUMO of electrophile (episulfonium ion C—C bond).

Summarizing, we can note that the quantum chemical optimizations of the most likely intermediates for electrophylic addition reaction of sulfenyl chloride to the double bond of ethane and its functionalized derivatives indicate that the episulfonium ion is an intermediate structure for reactions of ethylene, propylene, 3,3-dimethylbut-1-ene, 4-methylpent-1-ene, acrylic acid, and its chloroanhydride. However, in the cases where ethylene hydrogens are replaced by a phenyl group, that is styrene and 1,1-diphenylethene, there may be a significant change in the geometries of the intermediates, which are significantly more like nonrotating carbonium ions than episulfonium ions.

For the intermediate ions in this study, the role of sulfur appears to be that of directing the stereochemistry of the addition reaction of chloride, in this case forming trans products upon nucleophilic attack on the C—C bond of the episulfonium ion. This is in agreement with experimental results.

The comparison of calculated results in vacuum and in solvated media shows that ionization of the MeSCl molecule by polar solvents could affect electrophylic addition reaction.

The investigation of the addition of the methylsulfide cation to ethylene with subsequent attack of chloride anion shows the reaction to be frontier-orbital controlled. The regioselectivity features of episulfonium ion opening by chloride anion depend on the LUMO and LUMO+1 of episulfonium ion and the HOMO of the approaching chloride. The LUMO+1 of episulfonium ions has greatest interaction with the nucleophile approaching along p_z direction, leading to kinetically controlled adduct formation, whereas the episulfonium ion in LUMOs have greater interaction—leading to subsequent thermodynamically stable product formation.

EXPERIMENTAL

Full geometry optimization and other quantum chemical calculations were carried out using the GAMESS program package [13]. All calculations were performed within the DFT framework using the 6-31G basis set and B3LYP hybrid functional. Calculations were performed for molecules in vacuum and also using the PCM approach, to treat solutions for both polar (CH_2Cl_2) and nonpolar (CCl_4) solvents. Default value of parameter optoll $= 10^4$ (hartree/bohr) was used for finding potential energy surface. The root mean square gradient value is less then 1/3 of optoll. The stationary points were checked by frequency analysis. All frequencies obtained were real for all compounds mentioned here. This indicates that we obtained minimum points for reactants and intermediates.

For obtained geometries, 6-311G** basis set energies were calculated to have better energy description concerning the molecules under consideration. The visualization of optimized geometries and orbitals was performed with the MOLEKEL [14] program package (version 4.3).

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