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MO CALCULATIONS OF EPISULFONIUM ION INTERMEDIATES AND REGIOSPECIFICITY IN THE ADDITIONS OF Cl^-

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Abstract—The calculations were carried out for the ethylene, propylene, iso-butylene and butadiene episulfonium ion intermediates by CNDO/2 method to optimize the geometric parameters and investigate the electronic states of the intermediates, resulting that the p-form intermediates were unexpectedly most stable. It was shown that the differences in extension of the lowest unoccupied molecular orbitals on ethylenic carbon atoms in the intermediates have an important role on the regiospecificity of the ring-opening additions of Cl^- to the intermediates.

INTRODUCTION

In many cases, electrophilic additions to olefins are known to proceed by the formation of olefin-electrophile intermediates which subsequently undergo nucleophilic attack to afford the addition products. Much of the discussions of the mechanism of these reactions are concerned with stable conformations of the intermediates, e.g., open classical, symmetrical bridged or unsymmetrical bridged form, and recent molecular orbital approaches to these problems[1] have given considerable successes for prediction of their stable forms. Furthermore, σ-sulfurans have recently been proposed as a possible structure of tetracovalent sulfur intermediate.[2-4] Especially, Owsley *et al.*[4] have shown the presence of such an intermediate by PMR spectroscopy and suggested that it may also be a plausible intermediate in the addition reactions of methanesulfenyl chloride to olefins. However, their conclusion seems to be deduced from the results of not the addition reaction of sulfenyl chloride but the anion exchange reaction of episulfonium ion intermediate.

Of various kinds of electrophiles, the sulfenyl compounds (RSCl) may be a favourable reagent for investigation of the reaction mechanism since the addition reaction proceeds in stereospecific trans manner at fairly low temperature ($-20 \sim 0°$) without considerable subreaction nor strong solvent effects,[5] forming the cyclic episulfonium ion intermediate which is even detected in a special case.[6] Contrast to usual atomic electrophiles such as H^+, Ag^+, Hg^+ or X^+, the episulfonium ion, however, has a difference concerning to the geometric configuration of alkyl or aryl groups bonded to the S atom, which may cause large differences in the properties of bonding and the stability of the cyclic intermediates. Moreover, it is well known that the addition reactions of sulfenyl chloride to unsymmetrical terminal olefins give two isomeric adducts, i.e., Markownikoff adduct (M-adduct) and anti-Markownikoff adduct (aM-adduct), and the ratio of amounts of these isomeric adducts is charactertistically different according to the kind of the unsymmetrical olefin, i.e., conjugated olefins such as butadiene and stylene give M-adduct, while non-conjugated ones such as propylene and iso-butylene give aM-adduct.[7]

Concerning these orientations, Thaler *et al.* tried to explain the ratio of the adducts of two isomers as the resultants of the competition between the steric and the electronic effect[8] as schematically shown in Fig 1. The electronic effect contends that the π-electron density on the terminal carbon atom (C_1) in the episulfonium ion intermediate increases with the conjugation effect between the double bond and the substituent R′ and subsequently Cl^- attacks on the less negative inner carbon atom (C_2) rather than the terminal one. This is a usual explanation for Markownikoff adduct. While, if the substituents R′ is aliphatic, the addition occurs conversely as mentioned above, and they introduced the steric factor between Cl^- and aliphatic R′ to explain the resulting orientation of the adducts.

In the recent study of addition reaction of ArSCl (Ar = p-chlorophenyl and 2,4-dinitrophenyl) to *cis* and *trans*-1-phenyl propene, Schmidt *et al.*[9] have confirmed the reaction mechanism and investigated the electronic effect of the episulfonium ion intermediate. Their conclusion suggests inevitably to investigate the electronic state of the episulfonium ion intermediate to explain the orientation of the adduct.

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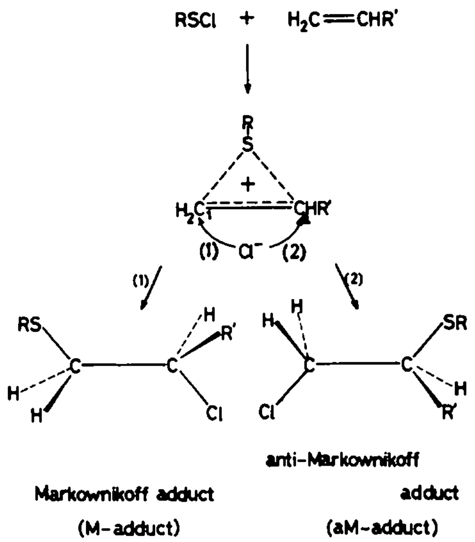

Fig 1. Addition mechanism of RSCl to olefins.

In the present paper, we try to discuss some of the stable configurations and their electronic states of the methanesulfenyl chloride and of the episulfonium ion intermediates formed by the additions of methanesulfenyl cation to ethylene, by using CNDO/2 method excluding d-orbitals of the S atom and then these of propylene, iso-butylene and butadiene to explain the large difference in the adducts as mentioned above.

In the first place, we calculated the methanesulfenyl chloride and its cation in order to compare the difference of the electronic states between them. Subsequently, we investigated various configurations of the ethylene episulfonium ion intermediate, giving the results that the plausible configuration of valence electrons in S atom is p-form but not sp^3 or sp^2 as so far supposed. Succeeding calculations of adducts propylene (iso-butylene) and butadiene revealed that the main reason to make such a difference of coefficients on C_1 and C_2 in the lowest unoccupied molecular orbitals (LUMO) of their intermediates, i.e., the contrast difference in their orbital extension of LUMO.

Method of calculations. Semiempirical SCF-MO calculations by means of CNDO/2 method[10] by Pople *et al.* were carried out for methanesulfenyl chloride, its cation, and various configurations of ethylene, propylene, (iso-butylene) and butadiene episulfonium ion intermediates by considering up to 3p orbitals of S atom.*

In these calculations, the configurations of methanesulfenyl chloride was adopted from the result of microwave spectroscopy[11] and the structure of CH_3S^+ is assumed to be the same as CH_3S group of dimethyl sulfide.[12]

At the outset of the calculations of the intermediates, we first take the open structure of the intermediates and set the distances between S and C=C as R=1·92 Å which is longer by 12% than that of ethylene sulfide, referring to the fact that the distance between Ag^+ and the double bond in the Ag^+-olefin complex gets loose by 12% in comparison with the normal Ag–C covalent bond from the result of X-ray diffraction.[13]

Next, we varied the geometric parameters of R, r, α, β, and d in Fig 2, keeping constant the other parts of the distances and angles in parent olefins and methyl sulfide group in order to find out the stable structures of intermediates.

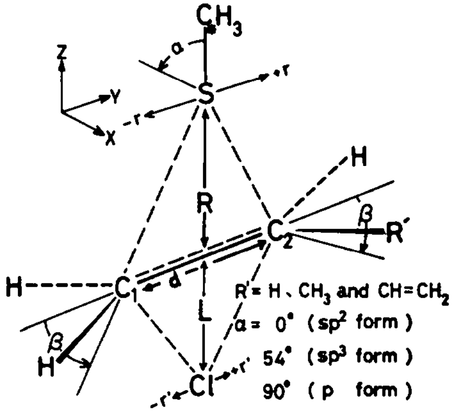

Fig 2. Geometrical parameters of olefin-episulfonium ion intermediates.

RESULTS AND DISCUSSION

(1) *Electronic states of methanesulfenyl chloride and methanesulfenyl cation.* According to the results of microwave experiments,[11] methanesulfenyl chloride has a rotational barrier of 2·5 Kcal/mole around the C–S bond in the bulk system. The electronic state of this compound shows from Table 1 that the bond energy between S and Cl is considerably smaller than that of other bonds and the charge polarization is enlarged with increase of the distance R(S–Cl) between S and Cl as e.g., at R(S–Cl) = 3·0 Å the net charge on Cl becomes −0·222. These results imply that the ionic dissociation may occur fairly easily in polar solvents.[14]

In order to compare with CH_3SCl, we then calculate the electronic state of the methanesulfenyl cation as one of the partners of the isolated systems and the results were presented in Tables 1 and 2, showing that the electrons of the highest occupied molecular orbital (HOMO) mainly localizes in p_y AO of the S atom and the LUMO localizes in p_z of the S atom, which implies that CH_3S^+ easily reacts with various olefins or nuc-

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*In our preliminary calculations including d-orbitals of S atom, it was found that the contribution of the d-orbitals to the energy is negligibly small.

Table 1. Bond energies and net charge densities of methanesulfenyl chloride and its cation

	Net Charge Density					Bond Energy (A.U.)			
	Q_s	$Q_{C\cdot}$	Q_H^*	Q_{H_1}†	Q_{Cl}	E_{S-Cl}	$E_{S-C\cdot}$	$E_{C\cdot-H}$	$E_{C\cdot-H_1}$
Methanesulfenyl chloride	+0·068	−0·003	+0·018	+0·019	−0·119	−0·481	−0·611	−0·762	−0·760
Methanesulfenyl cation	+0·652	−0·024	+0·115	+0·142	*	*	−0·625	−0·754	−0·733

*The two hydrogen atoms (H) of Me group ($C\cdot H_3$) are the mirror image to each other to the plane containing the atoms of C·, S and Cl.

†The H atom (H_1) is on the plane described above.

Table 2. Eigenvalues (A.U.) and eigenvectors of methanesulfenyl cation

Molecular orbital		HOMO	LUMO
Eigenvalue		−0·840	−0·399
C·	S	−0·000	0·001
	X	−0·000	−0·000
	Y	−0·245	0·000
	Z	0·000	0·085
S	S	−0·000	0·000
	X	−0·000	0·001
	Y	0·924	0·000
	Z	0·000	−0·974

leophiles to form the pσ-type intermediates. The net charge density of protons of methyl group in CH_3SCl is a little larger than those of the normal hydrocarbons and the PMR chemical shift of this compound (δ2·91 ppm)[15] supports the result of the present calculation. In the case of MeS^+, however, the increase of the net charge density is so remarkable that the chemical shift of the MeSCl is expected to be sensitively affected by the polarity of the solvents.*

(2) *Stable conformations of ethylene episulfonium ion intermediates.* Generally speaking, the plausible structure of the cationic intermediate may be considered to be either open or cyclic one.[16] According to our preliminary calculation, the latter was much more stable than the former by *ca* 50 Kcal/mole even for conjugated olefin (butadiene) and therefore in the present calculations, we consider only the latter form as the intermediate. This is quite acceptable from the experimental aspect, too, because, otherwise, the stereospecificity that the addition reaction proceeds in the trans manner could not be hold.

In the cyclic form, there are three typical and plausible electronic configurations of S atom in the intermediate, i.e., sp^2, sp^3, and p type as illustrated in Fig 2 (R′=H). For these geometries, MO calculations were carried out to get results listed in Table 3, showing that the double bond transfers to the S atom so as to neutralize almost completely the positive charge on S atom and then form fairly strong bond between S and C atoms, resulting to weaken C=C double bond. This stabilization is caused by the delocalization among p_x orbitals of C_1, C_2, S and C· on the same plane. The geometry of sp^2, however, is not accepted from energetical point of view as previously pointed out by Bach,[1] even though it is preferable for local bonding as the bond energy between C_1 (C_2) and S is larger than those of other geometries. The reason may be attributed to that the double bond is weakened much more than other cases. Thus, we mainly restrict the geometries to both sp^3 and p forms.

Usually it is considered that in the compounds such as ethylene oxide and imine, the lone pairs of the hetero atoms take sp^3 type configuration. Analogously, the sp^3 configuration may also seem to be plausible form even for episulfonium ion intermediates which have the similar structures. However, it is seen from Table 3 that the p-form is much more stable than sp^3-form from the energetical point of view if the ethylenic configuration is

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*According to our preliminary experiments for the solvent effect of *p*-toluenesulfenyl chloride, chemical shifts of protons on benzene-ring from TMS linearly increases to the increase of the polarity of the solvents, as shown below.

Chemical shift (δ) of protons on benzene-ring from TMS for the solvent effect of *p*-toluenesulfenyl chloride

Solvent	Dielectric Constant	Chemical Shift (δ) H_a	H_b
n-Hexane	1·890	7·409	7·008
n-Heptane	1·924	7·409	7·008
Carbon Tetrachloride	2·238	7·422	7·036
Ethyl Ether	4·335	7·481	7·095
Dichloromethane	9·08	7·528	7·143

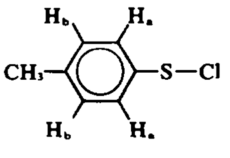
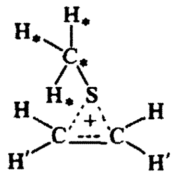


Table 3. Net charge densities and bond energies in ethylene episulfonium ion intermediates

		Total Energy		Net Charge Density					Bond Energy (A.U.)			
α	β	(A.U.)	Q_S	Q_C	Q_{C*}	Q_H Q'_H	Q_{H*} Q_{H*}	E_{S-C}	E_{S-C*}	E_{C-C}	E_{C-H} $E_{C-H'}$	E_{C*-H*} E_{C*-H*}
0°(sp²)	0°	−36·5890	+0·021	+0·145	+0·042	+0·090 +0·090	+0·090 +0·090	−0·349	−0·575	−1·349	−0·743 −0·743	−0·680 −0·680
54°(sp³)	0°	−36·9221	+0·251	+0·086	+0·020	+0·078 +0·084	+0·082 +0·071	−0·294	−0·585	−1·430	−0·746 −0·747	−0·760 −0·760
54°	15°	−36·9276	+0·256	+0·080	+0·020	+0·079 +0·086	+0·082 +0·071	−0·308	−0·585	−1·416	−0·746 −0·747	−0·760 −0·760
90°(p)	0°	−36·9330	+0·292	+0·084	+0·006	+0·075 +0·087	+0·078 +0·055	−0·288	−0·579	−1·430	−0·747 −0·746	−0·760 −0·762
90°	15°	−36·9401	+0·298	+0·078	+0·006	+0·077 +0·088	+0·078 +0·055	−0·301	−0·579	−1·416	−0·748 −0·746	−0·760 −0·762
Ethylene		−17·0533	*	−0·025	*	+0·013	*	*	*	−1·714	−0·754	7*

*The structures of the intermediates are defined as the following figure.



not deformed. It may be understood by considering the result of calculation by extended Hückel method with ω-technique that the direction of the protonation to the ethylene sulfide is perpendicular to the ring plane.[17] This will be essentially attributed to the fact that π-type lone pair orbital of the S atom is in the higher energy level than σ-type as shown in the result of the ab initio MO calculation.[18] It should be noticed here that the two lone pairs in ethylene oxide are not so clearly separated as in ethylene sulfide and then the energy difference is smaller.[19]

In these calculations, the distance R between the center of double bond and S atom was fixed in R = 1·92 Å. However, it should be determined so as to optimize the total energy. Then we calculated both configurations (sp^3 and p) by varying the distance R between the ethylene and the methanesulfenyl cation with the results of Fig 3.

It is easily seen from Fig 3 that there is a similarity with respect to the relation of the energy and the distance R for configurations sp^3 and p, and almost R = 1·92 Å gives the minimum value of the total energy for both configurations as is expected.

Furthermore, such calculations for propylene and butadiene episulfonium ion intermediate were carried out by using the same configurations (sp^3 and p), and led to almost the same results to the both olefins as that of ethylene. Therefore, we fix the distance R = 1·92 Å for the stable episulfonium ion intermediates of propylene and butadiene for further calculations.

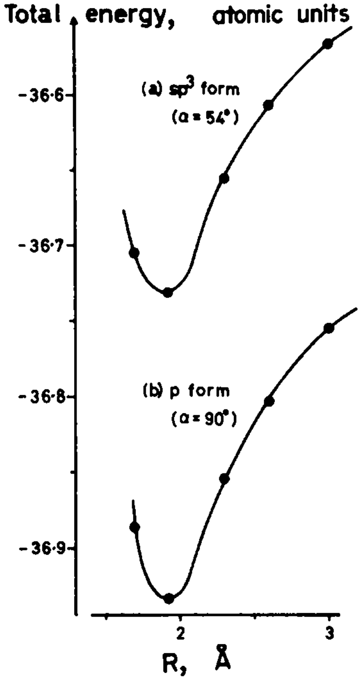


Fig 3. Total energies of episulfonium ion intermediates of ethylene by changing the distance R ($r = 0{\cdot}0$ Å and $\beta = 0°$).

In the next, the deformation of the double bond may be caused in the process that the MeS^+ group approaches to the double bond to form the episulfonium ion intermediate. As the variable for describing such deformation, we took up the angle β between the olefinic plane and the plane of HC_1H and HC_2R', and calculated the angle dependence with respect to each intermediates. As the result, the intermediate of the ethylene is stabilized at about 15° of β, whose value was very close to each other in the case of propylene and butadiene episulfonium ion intermediates, as is shown in Table 4. In the case of ethylene sulfide, the optimal value of β equals to 28°17′ and the values obtained above for the episulfonium ion intermediates are considerably smaller. This is attributed to the difference in the hybridization of the C atoms (C_1 and C_2), that is, the C_1–(C_2–)S bond of the episulfonium ion intermediates is fairly weaker than that of ethylene sulfide, and hence the hybridizations of them may be nearly between sp^2 and sp^3 forms.*

The results of Table 3 show that the p-type intermediate was still energetically more stable than the sp^3-type by 7·2 Kcal/mole, although the sp^3-type obtains considerable stabilization energy at the optimal β (15°). The stabilization at β = 15° for the sp^3-type may be caused by the decrease of the structural strain, which prefers to form ethylene sulfide.

The Table 5 indicates that there are no essential differences in the coefficients of the HOMO and the LUMO for both configurations and that the S–C_1 (C_2) bonds are formed by the charge-transfer of the π-electrons in the double bond to the vacant orbital p_z on the S atom. However, for the coefficient of p_z on C_1 (C_2) of the LUMO, the value is larger for the p-type than the sp^3-type, which suggests that the p-type intermediate is more profitable over the

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*We also tried to vary the double bond distance d in the intermediate, i.e., d = 1·40, 1·45 and 1·50 Å, and found that in each intermediates of the olefins the change of the total energy accompanying the slight elongation of the double bond is very small, even though the total energy is formally minimalized at d = 1·40 Å, that is, in the case of propylene the difference of the total energy as a standard of d = 1·353 Å is −4·1 (d = 1·40), +0·3 (d = 1·45) and +10·0 Kcal/mole (d = 1·50), while in the case of butadiene it is, as a standard of d = 1·370 Å, −2·4 (d = 1·40), +2·3 (d = 1·45), and +12·5 Kcal/mole (d = 1·50). In every case, the other parameters except for d is fixed as R = 1·92 Å, r = 0·0 Å, α = 0° and β = 15°. Therefore, even if d = 1·40 Å is formally employed, the electronic states may not be appreciably affected and consequently we fixed the double bond distance one of each parent olefins' d = 1·353 Å for propylene and d = 1·370 Å butadiene, and hereafter discuss the intermediates by using the original double bond distance, in particular for the orientations of the ring-opening addition of Cl^-.

Table 4. Total energies (A.U.) of episulfonium ion intermediates for three olefins

β*	0°	7°	15°	28°17′
Ethylene	−36·9330	−36·9392	−36·9401	−36·9278
Propylene	−45·6498	−45·6564	−45·6577	−45·6462
Butadiene	−52·6012	−52·6080	−52·6096	−52·5985

*The other geometric parameters are as follows: R = 1·92 Å, r = 0·0 Å and α = 90°.

Table 5. Eigenvalues (A.U.) and eigenvectors of ethylene, methanesulfenyl cation and ethylene episulfonium ion intermediates for various configurations

		Ethylene† and CH_3S^+		Episulfonium ion intermediate			
		HOMO′	LUMO	HOMO α = 54°*	LUMO (sp^3)	HOMO α = 90°*	LUMO (p)
Eigenvalue				−0·749	−0·227	−0·758	−0·207
C_1	S	0·000	0·000	0·026	−0·115	0·022	−0·128
	X	0·000	0·000	0·008	0·002	0·035	−0·002
	Y	0·000	−0·000	−0·032	−0·047	−0·028	−0·054
	Z	0·707	−0·707	−0·155	−0·332	−0·148	−0·356
C_2	S	−0·000	−0·000	−0·026	−0·115	−0·022	−0·128
	X	0·000	0·000	−0·008	0·002	−0·035	−0·002
	Y	−0·000	−0·000	−0·032	0·047	−0·028	0·054
	Z	0·707	0·707	0·155	−0·332	0·148	−0·356
S	S	−0·000	0·000	0·000	0·321	−0·000	0·215
	X	−0·000	0·001	−0·000	−0·363	−0·000	−0·000
	Y	0·924	0·000	0·904	−0·000	0·901	−0·000
	Z	0·000	−0·973	0·000	−0·621	0·000	−0·806

*The other geometric parameters are R = 1·92 Å, r = 0·0 Å and β = 0°.
†The CNDO/2 calculation of ethylene gives the result that the π-MO is not HOMO but the next HOMO by the nature of the calculation method itself. Since it is unacceptable, we took the π-MO as the HOMO′.

subsequent nucleophilic attack of Cl^-. From the Table 3, no essential differences are also found in the values of net-charge densities and bond energies for each configurations of the intermediate, showing that the positive net-charge of the isolated methanesulfenyl cation wholly distributes over the intermediate. Such charge-delocalization seems to make a contribution to the stabilization of the intermediates.

(3) *The electronic states of propylene and butadiene episulfonium ion intermediates and the orientation of the ring-opening addition of* Cl^-. Apparently, in the case of the ethylene episulfonium ion intermediate, it needs no consideration about the deviation r of the MeS group along the double bond direction since it is the symmetrical olefin. However, in the unsymmetrical olefins like propylene and butadiene, it is necessary to take the effect of unsymmetrical factor into account. We checked out the approach of MeS group closer to the substituent R′ by taking the r = −0·2, 0·0, and +0·2 Å for two olefins, respectively. The calculations led to the results of Table 6 which shows that both intermediates are stable still at the point of the r = 0·0 Å, i.e., when the MeS group exists about the center of the double bond in Fig 2. It should be noticed here that the differences in total energy between the structure of the intermediate of r = −0·2 Å and that of r = 0·0 Å is smaller of 10^{-1} order than that between its r = 0·0 and +0·2 Å for each olefins. It may be worthwhile to investigate whether or not this is caused by the repulsion between the MeS group and the substituent R′ in olefins (*cf* Fig 2). In order to estimate the repulsive energy, let us compare with the sum of bond energy between the substituent R′ and MeS group, and the results are shown in Tables 7 and 8. However, it seems not to be affirmative because the interaction energy between them is rather less repulsive by approaching of the MeS group to the substituent R′ for each olefins, implying, in other words, bonding in nature, although the Me group in propylene interacts much

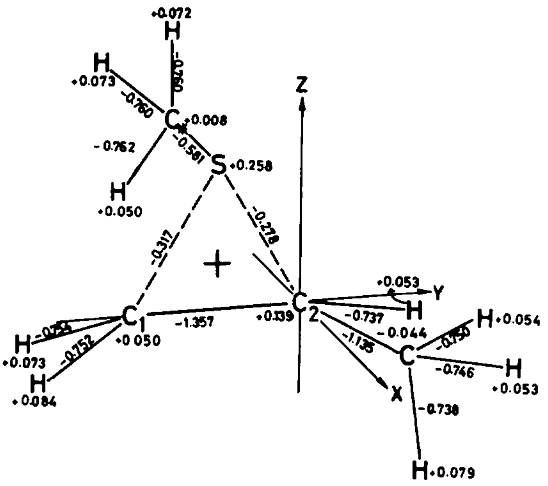

Fig 4. Net-charge densities and bond energies (A.U.) of propylene episulfonium ion intermediate.

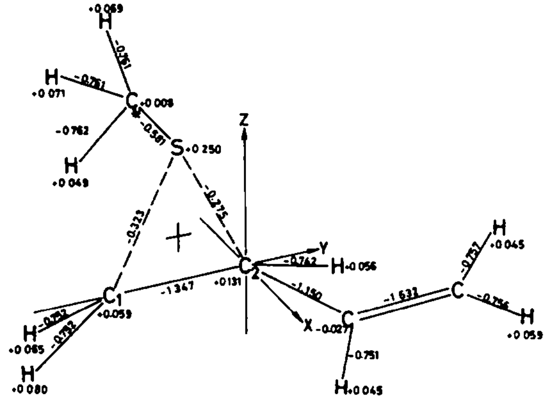

Fig 5. Net-charge densities and bond energies (A.U.) of butadiene episulfonium ion intermediate.

Table 6. Total energies (A.U.) of episulfonium ion intermediates by changing the parameter r

r(Å)*	−0·2	0·0	+0·2
Propylene	−45·6491	−45·6498	−45·6397
Butadiene	−52·6006	−52·6012	−52·5909

*The other geometric parameters are R = 1·92 Å, α = 90° and β = 0°.

Table 7. Repulsive energies (kcal/mol) between the substituent R′ and the groups or atom of the electrophile in the propylene episulfonium ion intermediate

r(Å)	−0·2	0·0	+0·2
CH_3–C.H_3	+ 1·743	+ 1·575	+ 1·275
CH_3–S	+ 19·979	+ 17·911	+ 17·387
CH_3–C.H_3S	+ 21·722	+ 19·486	+ 18·662

Table 8. Repulsive energies (kcal/mol) between the substituent R′ and the groups or atom of the electrophile in the butadiene episulfonium ion intermediate

r(Å)	−0·2	0·0	+0·2
CH_2=CH–C.H_3	+ 1·856	+ 1·583	+ 1·368
CH_2=CH–S	+ 3·644	+ 2·485	+ 0·414
CH_2=CH–C.H_3S	+ 5·500	+ 4·068	+ 1·783

more repulsively than vinyl group in butadiene as shown in Tables 7 and 8. Accordingly, it may not be attributed to the repulsion between the substituent R′ and the MeS group that the MeS group tends to incline the direction of r = −0·2 Å. Both intermediates have an energetical minimum at about r = 0·0 Å, where the MeS group is at the center of the double bond, although this minimum is a shallow one to the deviation of the direction r = −0·2 Å. It may be reasonable because the open form intermediate is less stable than the cyclic one as discussed above. Subsequently, we discuss about the process, in which the nucleophile (chloride anion) attacks the cationic intermediate to cause the ring-opening addition. In this process, it is the LUMO's of the episulfonium ion intermediates that play an important role to predict the reaction path and therefore it is worthwhile to figure out the LUMO's. It is easily seen from Figs 6 and 7 that the LUMO extends to the opposite direction of the z-axis of the C atoms (C_1 and C_2) and hence that the chloride anion attacks the intermediate from the opposite direction of the z-axis, i.e., the ring-opening addition occurs in the trans manner as shown by the experimental results. The orientations of the adducts are governed by the result

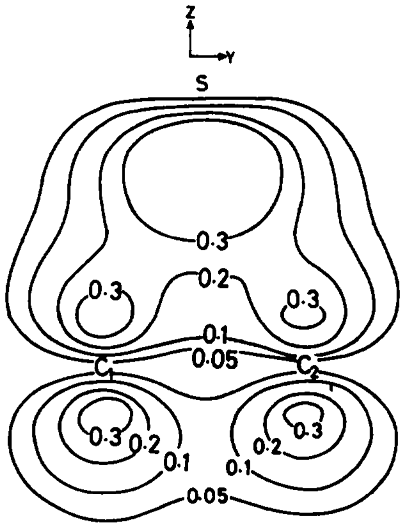

Fig 6. Density map of the LUMO of propylene episulfonium ion intermediate.

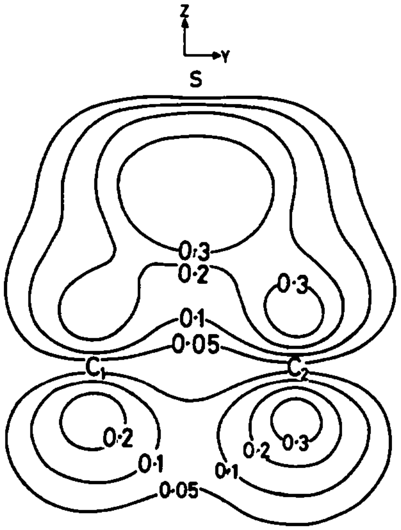

Fig 7. Density map of the LUMO of butadiene episulfonium ion intermediate.

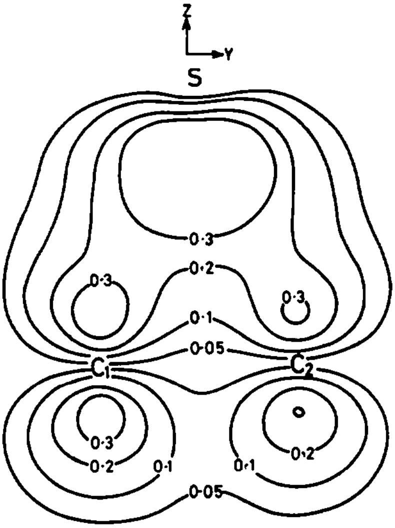

Fig 8. Density map of the LUMO of iso-butylene episulfonium ion intermediate.

whether the chloride anion attacks on the C_1 or C_2 atom of the intermediates and hence considered to be determined by the unsymmetrical extension of the LUMO on C_1 and C_2, i.e., the larger the extension is, the easier the chloride anion attacks there. In the case of propylene episulfonium ion intermediate, it is easily seen from Fig 6 that the LUMO amplitude on the terminal C atom C_1 is larger than that of Me substituted one C_2, and it shows that the chloride anion may attack more easily the terminal C atom C_1 to give anti-Markownikoff adduct. On the other hand, in the case of butadiene episulfonium ion intermediate, the LUMO extension on the vinyl substituted C atom C_2 is larger than C_1 as shown in Fig 7, and this leads the conclusion to the contrary of the propylene, i.e., butadiene gives Markownikoff adduct as many other conjugated olefins do it.

Furthermore, we figured out the LUMO of iso-butylene episulfonium ion intermediate and the result of Fig 8 shows that the chloride anion attacks the terminal C atom C_1 to give the anti-Markownikoff adduct in agreement with experimental results likely to the case of the propylene.

In order to confirm these results, we further calculated the energy of the systems which include the cationic intermediates and the additional chloride anion in various configurations of a distance L (Fig 2) between chloride anion and episulfonium ion intermediate at L = 2·0 and 2·5 Å, and of a deviation r′ (see also Fig 2) of − 0·2, 0·0 and + 0·2 Å. In the Tables 9 and 10, the results of only a value of the deviation r of MeS group, i.e., r = 0·0 Å for the propylene and − 0·2 Å for the butadiene are listed. We checked, however, all the values of r = − 0·2, 0·0 and + 0·2 Å for both olefins, and the described ones are energetically the lowest of them.

Table 9. The relative stability of the direction of the chloride anion addition to propylene episulfonium ion intermediate

L(Å)*	r′(Å)*	Total Energy Difference (kcal/mol)	CH_3–Cl Repulsion (kcal/mol)
	− 0·2	− 3·140	+ 0·711
2·0	0·0	0·0	+ 2·154
	+ 0·2	+ 3·642	+ 3·525
	− 0·2	− 1·005	− 7·121
2·5	0·0	0·0	− 7·236
	+ 0·2	+ 1·068	− 7·360

*The other geometric parameters are R = 1·92 Å, r = 0·0 Å, α = 90° and β = 15°.

Table 10. The relative stability of the direction of the chloride anion addition to butadiene episulfonium ion intermediate

L(Å)*	r′(Å)*	Total energy difference (kcal/mol)	CH_3–Cl Repulsion (kcal/mol)
	− 0·2	+ 2·763	− 5·549
2·0	0·0	0·0	− 7·770
	+ 0·2	− 2·512	− 10·554
	− 0·2	+ 1·382	− 6·013
2·5	0·0	0·0	− 9·362
	+ 0·2	− 1·382	− 10·113

*The other geometric parameters are R = 1·92 Å, r = − 0·2 Å, α = 90° and β = 15°.

Moreover, we calculated the configuration of β = 0° and this result is left out here because of its similarity to β = 15°.

In the case of propylene, it is pointed out from Table 9 that the total energy of the system at $r' = -0\cdot2$ Å in both $L = 2\cdot5$ and $2\cdot0$ Å is lower than that of $r' = 0\cdot0$ Å by 1·005 and 3·140 kcal/mole, respectively. It means that in the process of the nucleophilic attack to the cationic intermediates, the chloride anion attacks the terminal C atom C_1 rather than the inner one (C_2) in agreement with the result developed above. According to the discussion by Thaler *et al.*[20], the main factor to produce aM-adducts is attributed to the repulsion between the chloride anion and the substituent (Me group). The present calculation, however, shows that the interaction between the Cl^- and the Me group is rather attractive at $L = 2\cdot5$ Å, while it becomes repulsive at $L = 2\cdot0$ Å. It may be attributed to the following consideration. The negative charge on the chloride anion (i.e., -1 when L is infinite) removes by 0·288 to the cationic intermediate at $L = 2\cdot5$ Å to be $-0\cdot712$ of the net-charge density on Cl atom, and the Me group (R′) becomes $\delta+$ by $+0\cdot104$ of net-charge density, then the interaction between them is considered to be coulombically attractive. On the other hand, the negative charge on the Cl^- at $L = 2\cdot0$ Å moves by 0·509 to the cationic intermediate to be $-0\cdot491$ of the net-charge density on the Cl atom and it decreases the positive charge on the Me group to be $+0\cdot042$ of the net-charge density, hence the interaction between them may come to be repulsive.

However, if the differences of the total energies to the deviation r′ are compared with those of the repulsive energies between them, it is seen that the contribution of the repulsion to the total energies is not decisive, and that the electronic effect in the episulfonium ion intermediate is rather important. Especially, in the process for the chloride anion to approach to the intermediate, the parameter β is considered to decrease from 15° and we checked at $\beta = 0°$ to be the same tendency in both systems. It may support the discussion described here.

In the case of the butadiene, when S atom is on the symmetrical position ($r = 0\cdot0$ Å), the stable position of Cl^- becomes to be the left hand side ($r' = -0\cdot2$ Å) rather than the right hand side ($r' = +0\cdot2$ Å) from the energetical point of view, while when S atom is on the left hand side ($r = -0\cdot2$ Å), the right hand side is more stable than the left hand side. However, the total energy of the former ($r = 0\cdot0$ Å, $r' = -0\cdot2$ Å) is higher than that of the latter ($r = -0\cdot2$ Å, $r' = +0\cdot2$ Å) by 2·01 kcal/mole at $L = 2\cdot0$ Å and 1·51 kcal/mole at $L = 2\cdot5$ Å, and it means that the trend of the latter is preferable path for the attack of the Cl^-. Moreover, the interaction between the chloride anion and the vinyl group is attractive at both $L = 2\cdot0$ and $2\cdot5$ Å, and interestingly the differences of the attractive energies correspond nearly to those of the total energies. It implys that the episulfonium ion intermediate of butadiene is deformed to the unsymmetrical 3-membered ring by the approach of the chloride anion. The main reason of such attractive interaction is attributed to the situation that the positive charge on C_2 to increase, and it spreads over the vinyl group to be coulombically attractive with the chloride anion.

From these discussions, it concludes that although there are considerable indirect interactions between the chloride anion and the substituents R′, attractive or repulsive, the direction of the nucleophilic attack by the chloride anion is decided by the out-spread (represented by the LUMO's) of the episulfonium ion intermediates of propylene and butadiene. In other words, the main factor to determine the orientation seems to be not simply the steric hindrance of substituents but the delicate electronic states of the intermediates.

Furthermore, in consequence of the calculations, 1,2-additions of sulfenyl chloride to olefins are allowed from the view-point of the orbital symmetry as shown in Fig 9, where only the symmetry of HOMO of ethylene and LUMO of sulfenyl cation is considered because the predominant contributions comes from this combination although the alternative is also allowed. On the contrary, 1,4-additions are forbidden in agreement of the experimental results.[21,22] Likewise, 1,6-additions, for example, to cycloheptatriene may be allowed as shown in Fig 9, although we have no definite experimental result.

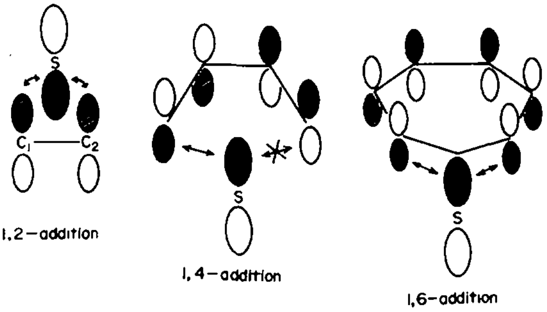

Fig 9. Orbital symmetry of HOMO on olefins and LUMO on sulfenyl cation in the formation of episulfonium ion intermediates.

CONCLUSION

Considering the orbital extensions and their directions of the LUMO's related to the ring opening addition reactions in the episulfonium ion intermediates, we could well explain the experimental results concerning to the regiospecificity in the addition reactions of sulfenyl chloride.

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