

A theoretical study of styrene and sulfenyl chloride reaction mechanism

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The classical description of sulfenyl halides additions to olefins proposes the formation of an episulfonium ion intermediate during the reaction path. However, a careful analysis of experiments performed in the past suggests that there should not be a single mechanistic picture of sulfenyl halide additions to substituted olefins. Our work is the first theoretical study of detailed insights into the mechanism of methylsulfenyl chloride addition to styrene. The reaction potential energy profile has been calculated by means of the B3LYP functional with the 6-31++G(d, p) basis set. Mixing of the molecular orbital shapes of reaction stationary points has been described. The addition proceeds as a single step reaction from the methylsulfenyl chloride and styrene reactants via the concerted transition state (TS) to the final product along the reaction path estimated by the calculation of the intrinsic reaction coordinate. The reaction intermediate was not detected by calculations. The polar solvent has a significant effect on the decrease of reaction activation energy barriers. The large charge separation of the S–Cl bond in TS implies that the addition reaction should proceed through the ionic TS.

Keywords: density functional theory, reaction mechanism, molecular orbital, addition, styrene, sulfenyl chloride

INTRODUCTION

The sulfur-functionalized organic compounds involving natural products play an important role in biologically relevant processes and biocatalytic reactions [1–3]. A variety of methods exist aiming to obtain new and physiologically interesting, sulfur atom containing derivatives. Among them, the functionalization of olefins by the addition of electrophilic sulfur groups [4–5] represents a powerful approach leading to new desirable products [6–7]. The addition of sulfenyl halides to double bonds has been known for many years and has received a considerable attention [1, 7–14]. Along with extensive studies of the reaction mechanism the presence of non-rotated episulfonium intermediates on the reaction path has been postulated. The classical descrip-

tion of the sulfenyl halides interaction with olefins suggests the rate-determining formation of an episulfonium ion intermediate. Hereafter, the episulfonium ion undergoes trans-stereoselective nucleophilic addition affording 1,2-difunctionalised products with a defined configuration [8]. The scheme of this process is presented in Fig. 1.

The structure of episulfonium ion intermediate (I) has been proposed to explain the anti-Markovnikov (aM) orientation of products from the addition of sulfenyl halides to alkyl substituted olefins. The predominant ring opening occurs by the attack at the terminal carbon C2 giving a kinetically controlled aM adduct. A steric factor of the methyl group appears to be quite important since halogen attacks the least hindered carbon atom giving kinetically controlled adducts [14]. Therefore, it was suggested that the halogen trans-addition to alkyl substituted olefins is more consistent with the non-rotating episulfonium ion intermediate of structure I as shown in Fig. 1 [14]. Intensive kinetics

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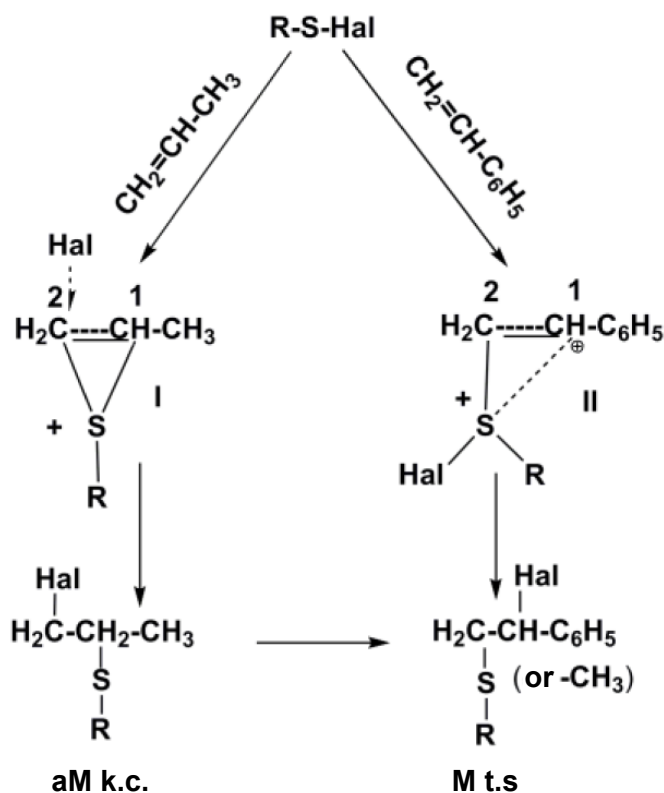


Fig. 1. The scheme of classical description of the addition of sulfenyl halides to alkyl and aryl substituted olefins: the anti-Markovnikov adduct (aM), Markovnikov product (M), kinetically controlled adduct (k.c), thermodynamically stable product (t.s)

investigations of the sulfenyl chlorides addition to a diversity of alkyl substituted olefins, however, have not been sufficient to completely confirm the general postulate of an episulfonium ion intermediate I [8, 14]. More recently, the theoretical investigations of the reaction potential energy profile of the sulfenylchloride addition to propene confirmed the episulfonium ion intermediate formation on the reaction path [15–16]. Two transition states corresponding to two possible directions of the addition of halide forming a kinetically controlled aM adduct and a thermodynamically stable Markovnikov (M) product as well as an isomerization transition state from the aM kinetically controlled to the thermodynamically stable M product have been detected by computations as presented in Fig. 2 taken from [15–16].

Molecular orbital (MO) studies of the episulfonium intermediate [17–20] demonstrated that the direction of the nucleophile attack by chloride anion was sensitive to the shapes of two lowest unoccupied MOs (LUMO) Walsh orbitals that were observed for an episulfonium cation by calculations.

In contrast to the addition of sulfenylhalides to alkyl substituted olefins, the addition of sulfenyl chlorides to conjugated olefins ($\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$, $\text{CH}_2=\text{CH}_2-\text{CH}_2=\text{CH}_2$) gives an exclusive product of the M orientation [8–21]. Therefore, the presence of an unsymmetrical episulfonium ion intermediate II (Fig. 1) was proposed by experiments [8–21]

aiming to explain the exclusive M oriented product formation.

Despite extensive experimental studies, a detailed reaction mechanism study, however, has not been described for the addition of sulfenyl chlorides to conjugated olefins. Moreover, in most experimental applications the presence of the episulfonium intermediate is only assumed to be known. Thus, the analysis of extensive experimental studies done in the past suggests that there is no single mechanistic picture for all observations of sulfenyl chloride addition to substituted olefins. The nature of the substitutes should significantly influence the mechanism of such reactions. Therefore the qualitative estimation of the sulfenyl halide interaction with conjugated olefin should be clarified by calculations of the reaction potential energy (or free energy) based on the transition state theory [22].

This work was the first theoretical study of detailed insights into the mechanism of methylsulfenylchloride ($\text{CH}_3\text{-S-Cl}$) addition to styrene ($\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$). Based on the selected model, an attempt was made to illuminate charge and bond character changes in the transformation from starting reactants to transition states and products. Mixing of the molecular orbital (MO) shapes of reaction stationary points on the minimal energy path estimated by the intrinsic reaction coordinate (IRC) as a molecular system proceeding from the reactants to transition state has been described.

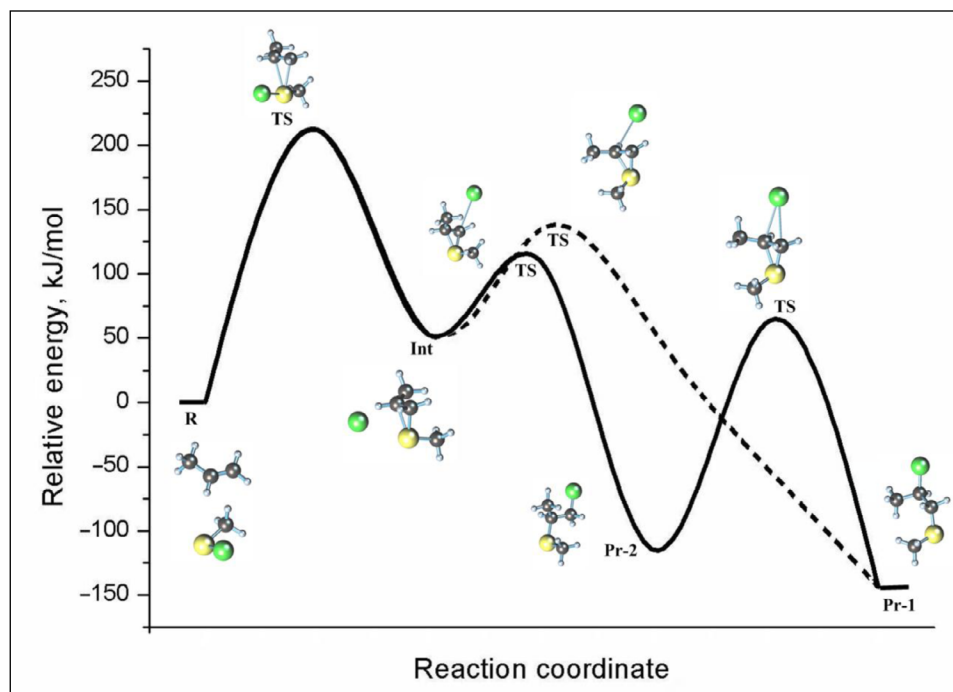


Fig. 2. The schematic reaction energy profile of the sulfenyl halide addition to propene: R is reactants, TS is transition state, Pr-1 and Pr-2 are reaction products [15–16]

METHODS

All calculations were carried out with the Gaussian 09 suite of a computational program [23].

The geometry optimizations of molecules at the reaction stationary points were performed with the density functional theory (DFT) B3LYP functional in conjunction with the 6-31G(d, p) and 6-31++G(d, p) basis sets. The addition of diffuse basis functions to the 6-31G(d, p) basis set ensured a much more rapid and smooth convergence to the optimal geometries at the reaction stationary points and progression of IRC calculations up to the ends. So further in the text, the results of the B3LYP method in conjunction with 6-31++G(d, p) basis sets is presented. The hybrid B3LYP functional [24–25] is one of the most popular density functionals for molecular calculations. It yields suitable structural and thermochemical characters in the computational studies of cyclic molecules [26–31].

The intrinsic reaction coordinate (IRC) calculations were performed to confirm the connectivity of transition state with reactants and the product at the same level of theory. The frequency analysis was performed following each optimization to characterize reaction stationary points. The implicit continuum solvent – a polarizable continuous media (PCM) model has been used in molecular simulations in addition to gas phase calculation. The reaction stationary points of solvated molecules were optimized on the basis of gas-phase optimized structures using the PCM at the B3LYP/6-31++G(d, p) level of theory including polar (water) and non-polar (heptane) solvation media.

RESULTS AND DISCUSSION

Structures and energy

The methylsulfenchloride addition to styrene gives the exclusive M orientation products by the attack of chlorine at a phenyl substituted carbon atom as it was shown by the experiment [8–14]. The reaction solvation media polarity plays an important role in the reaction rates raising [8–21]. Thus, aiming to simulate the experimental conditions and the influence of solvent polarity on the reaction stationary points, the gas phase computation result was compared with the results of the implicit solvent model – the PCM method for heptane (non-polar) and water (polar) solvents. The schematic free energy profile and structures of reaction stationary points are shown in Figs. 3 and 4. The Gibbs free energies of reaction stationary points are presented in Table 1.

As seen from Figs. 3 and 4, the addition of methylsulfenchlorides to styrene proceeds differently as in the case of the addition to propene (Fig. 2) [15–16]. The important for reaction progress bond lengths S–Cl, S–C2, S–C1, C1–Cl and the dihedral Cl–C1–C2–S angle changes along IRC are presented in Figs. 5 and 6. The charges obtained by natural population analysis on the essential atoms, the Wiberg bond index (WI) and MO transformations at the reaction stationary points are presented in Table 2 and 3, and Fig. 7.

It was somewhat surprising to detect a single step reaction proceeded from the reactants (R) via the concerted transition state (TS) to the M orientation final product (P).

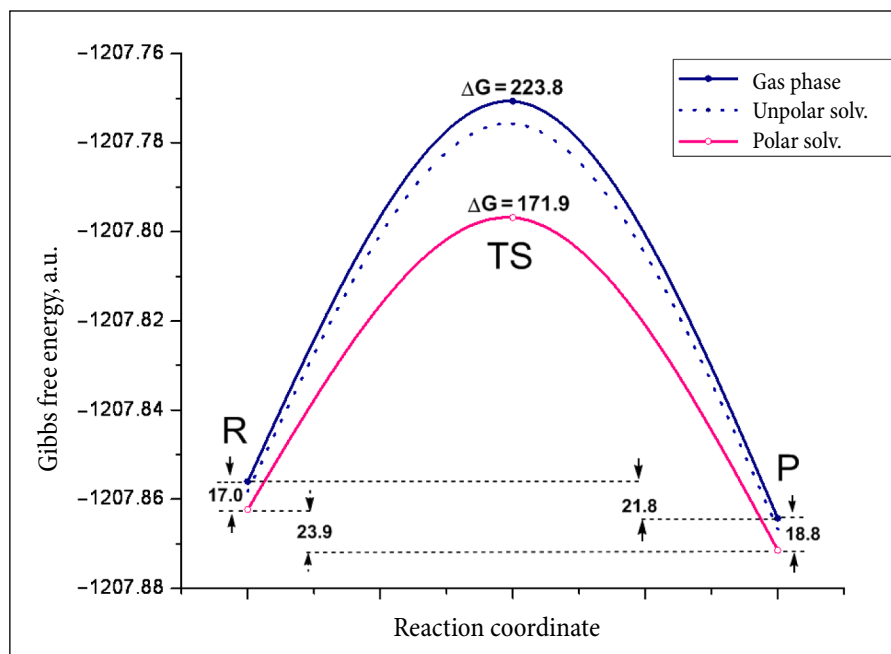


Fig. 3. A schematic Gibbs free energy profile (in a.u.) for the sulfenyl chloride interaction with styrene: the gas phase (a blue solid line), non-polar solvent phase (a blue dashed point line), polar solvent phase (a red solid line). The differences of Gibbs energies are presented in kJ/mol. The reaction stationary points: R is reactants, TS is transition state, P is product. Calculations were done at the B3LYP/6-31++G(d, p) level

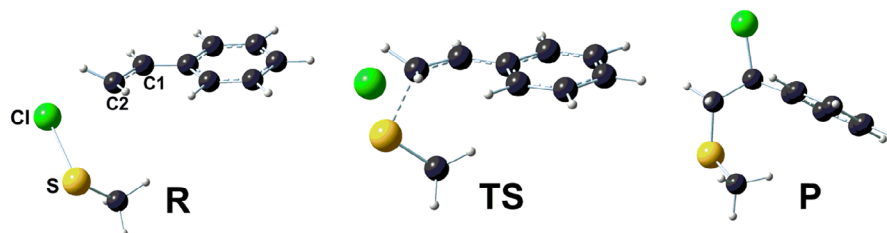


Fig. 4. The optimized geometries of the reaction stationary points: R is reactants, TS is transition state, P is product. Calculations were done at the B3LYP/6-31++G(d, p) level

Table 1. The Gibbs free energies in a.u. for the reaction stationary points: methylsulfenylchloride and styrene reactants (R), transition state (TS), products (P) in the gas phase and in the polar and non-polar solvents calculated at the B3LYP/6-31++G(d, p) level. The imaginary frequencies (in cm^{-1}) of transition structures are shown in parentheses

	R	TS	P
Gas phase	-1207.856024	-1207.770718 (i364.8044)	-1207.864307
PCM for polar solvent (water)	-1207.862343	-1207.79686 (i416.7439)	-1207.871442
PCM for unpolar solvent (heptane)	-1207.858227	-1207.775734 (i390.2032)	-1207.866774

The attempts to obtain the geometry of the reaction intermediate from calculations were unsuccessful.

The reaction starts with the interaction of methylsulfenylchloride and the π bond of styrene. This process leads to the increase of energy until the TS forms. As the system

moves along the reaction coordinate, important structural changes occur. First, the sulfur atom approaches perpendicularly towards the C2 atom of the π bond of styrene. The considerable shortening of the S–C2 bond to 2.16 Å occurs as the reacting system approaches TS. At the TS

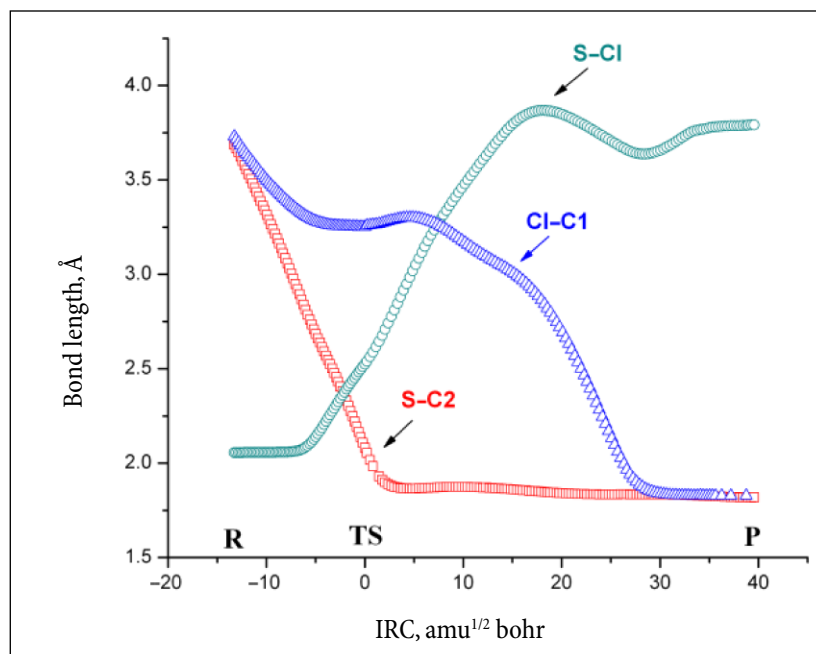


Fig. 5. The selected bond lengths along the IRC. Calculated by IRC following the method at the B3LYP/6-31++G(d, p) level for the gas phase

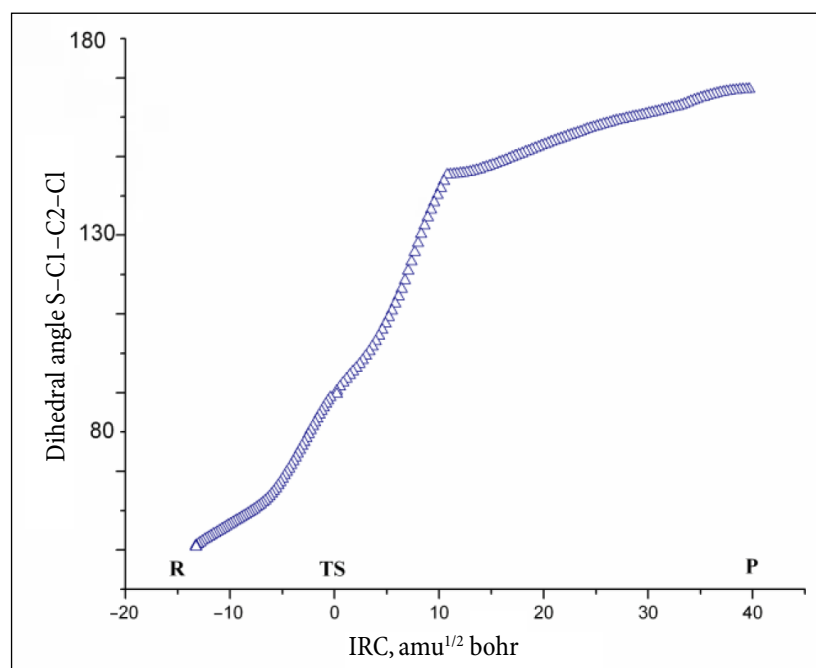


Fig. 6. The S-C1-C2-Cl dihedral angle along the IRC. Calculated by IRC following the method at the B3LYP/6-31++G(d, p) level for the gas phase

the S-C2 bond almost completely forms with the Wiberg bond index (WI) of 0.7.

Second, the S-Cl increases from 2.1 to 2.6 Å indicating the S-Cl bond polarization and weakening with the WI changes from 1.0 to 0.5. Third, with these structural changes the chlorine atom migrates towards the π bond. The distances between the Cl atom and S atom become close to

the van der Waals distance, with the reactive chlorine atom almost perpendicularly facing the double bond. The migration of the chlorine atom was estimated by the S-C1-C2-Cl dihedral angle changes along the reaction coordinate (Fig. 6). The significant changes in the dihedral angle from 29.0 to 79.6° occur as the reaction proceeds to TS along IRC.

Table 2. The Wiberg bond index for the reaction stationary points: methylsulfenchloride and styrene reactants (R), transition state (TS), products (P) in the gas phase and in polar solvent calculated at the B3LYP/6-31++G(d, p) level

	R		TS		P	
	Gas phase	Solvent	Gas phase	Solvent	Gas phase	Solvent
S-Cl	0.97	0.96	0.46	0.43	0.00	0.00
S-C1	0.00	0.00	0.64	0.67	1.00	1.00
C2-C1	1.90	1.90	1.31	1.31	1.00	1.00
C2-Cl	0.00	0.0	0.05	0.05	0.96	0.96
C2-Phe	1.11	1.01	1.26	1.26	1.00	1.00

Table 3. The natural population analysis charges on selected atoms and dipole moments (μ , D) of the reaction stationary points: methylsulfenchloride and styrene reactants (R), transition state (TS), products (P) in the gas phase and in polar solvent (water) media calculated at the B3LYP/6-31++G(d, p) level

	R		TS		P	
	Gas phase	Solvent	Gas phase	Solvent	Gas phase	Solvent
μ	2.97	3.49	6.09	9.47	2.72	3.45
S	+0.07	+0.23	+0.36	+0.28	+0.19	+0.16
Cl	-0.08	-0.20	-0.45	-0.53	-0.10	-0.13
C1	-0.22	-0.23	-0.19	-0.18	-0.23	-0.23
C2	-0.41	-0.41	-0.49	-0.49	-0.59	-0.60

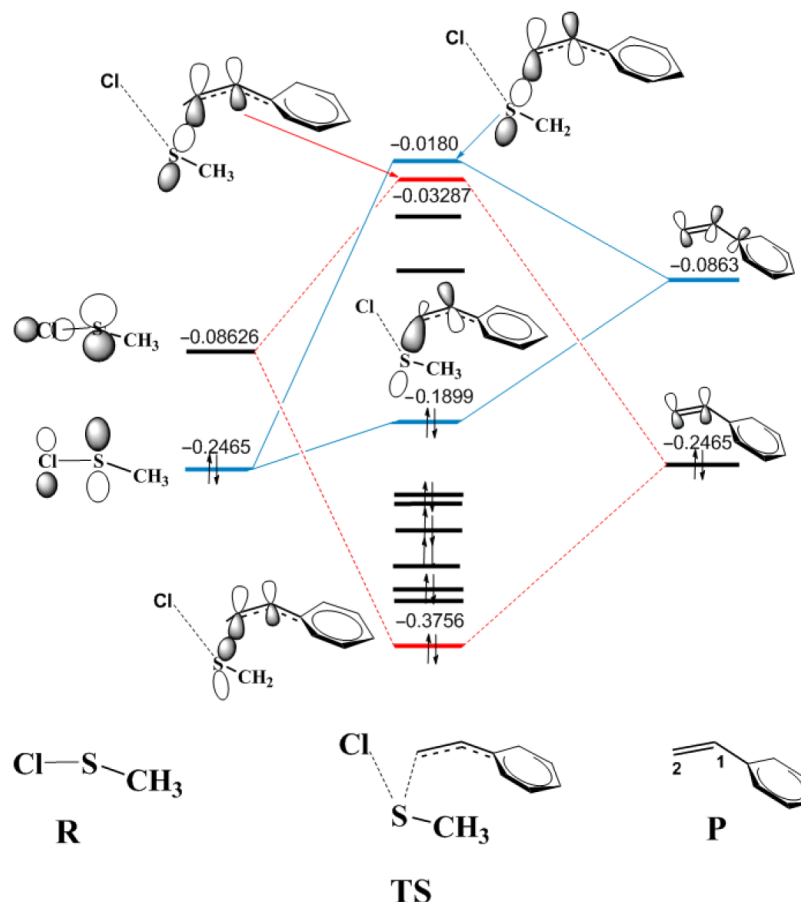


Fig. 7. The Kohn-Sham molecular orbitals (energies in a.u.) interaction diagram for the reactants (R), transition state (TS), natural charges on the relevant atoms, dipole moments (in D) and Wiberg bond indexes for the reaction stationary points R, TS, P determined in the gas phase at the B3LYP/6-31++G(d, p) level

The transition of R to TS requires free activation energy of 223.8 kJ/mol. This comparatively high activation energy barrier testifies that the addition process proceeds slowly which supports the experimental assumptions [8–21] that the reaction is irreversible and the solvent polarity may play an important role in reducing an energy barrier. Behind this barrier, the reacting molecular system moves to the P product. The stabilization energy of P is 21.8 kJ/mol lower compared to that of R. The most significant changes from TS to P are the complete migration of the Cl atom to the C1 atom with the C1–Cl bond lengths shortening to 1.8 Å, the elongation of S–Cl distance to 4.0 Å and the dihedral angle changes from 79.6 to 180.

In summary, the calculated reaction free energy profile shows that the reaction proceeds in a single step. During this process, the essential structural changes involve the transfer of the chlorine atom to the carbon C1 atom and the migration of the S atom to the C2 atom. The S–C2 bond is formed and the S–Cl bond weakens as reacting molecular systems move from R to TS. Below the TS going to P the C1–Cl bond is formed and the S–Cl breaks. The high energy barrier indicates that the solvent effects may be important in reducing of the reaction activation barrier.

Charge transfer

The charges on the relevant atoms obtained by natural population analysis for all stationary points are summarized in Table 3.

At the starting stage, the almost neutral S–Cl unit becomes more polarized in TS as sulfenyl chloride approaches the double bond. The positive charge on the S atom increases from +0.07 to +0.36, while the Cl atom becomes more negative, from –0.07 to –0.45 in TS. With this charge separation the S–Cl bond weakens and becomes polarized. The S atom approaches the π bond and simultaneously transfers electron density to the chlorine atom. The π electrons of the phenyl ring becomes conjugated with the π orbital electron density of the double bond in TS (see WI changes as the system transfers from R to TS in Table 2).

This electron density delocalization increases the negative charge on the C2 atom to –0.49 at TS and stimulates the interaction between C2 and S as the system goes to TS. Behind the TS the reversible electron density transfer from the Cl atom to the π bond of styrene moiety occurs on the reaction paths. The C1 and C2 atoms become more negative from –0.19 and –0.49 to –0.23 and –0.59, respectively, while the Cl atom loses the negative charge from –0.45 to –0.10 as the system goes from TS to P. Together with this charge transfer the C1 and C2 atoms change hybridization from sp^2 to sp^3 as the reaction proceeds to P.

In summary, the charge separation effect of the S–Cl bond in TS implies that the addition reaction should proceed through the ionic TS. On the other hand, the charge transfer during chlorine atom migration confirms breaking of S–Cl and formation of C1–Cl covalent bonds in the whole

transformation of the reacting molecular system, which requires a sufficient overlap between the electron-donating orbital and electron-withdrawing orbitals. Therefore, the ionic and covalently bonded TS may exist and the real bonding nature of TS should depend on the polarity of the solvent.

Molecular orbital transformations

Charge transfer and electron density changes can also be estimated through the molecular orbital transformations along the reaction coordinate. In this article, the sulfenyl chloride and styrene interaction was examined on the basis of frontier and perturbation molecular orbital (FMO) approaches [32–35]. The Kohn–Sham (KS) MO shapes and energies for TS and R have been evaluated at the B3LYP/6-31++G(d, p) level. We expected that the interaction between sulfenyl chloride and styrene involves the electrophilic sulfur and nucleophilic π double bond of styrene interaction as generally suggested by a classical mechanistic study of sulfenyl halogenes addition to olefins [8–21]. The relevant KS MOs involved in the formation of TS are presented in Fig. 7.

Thus, applying FMO theory the HOMO shape of TS is expected to form a bonding combination consisting of sulfenyl chloride LUMO and styrene HOMO molecular orbital fragments. This two-electron HOMO-LUMO bonding combination, as usual, should lower energy with the stabilizing effect on the molecular system. However, this effect was not detected for the interaction under study. The HOMO energy values of the reactants are equal to –0.2465 a.u. which reveals the equal ability to lose electrons as suggested by Koopman's theorem. The HOMOs of the sulfenyl chloride and styrene Rs are involved in the two main MO transformations as the reaction proceeds from R to TS. First, the HOMO of TS is formed from the bonding interaction of the HOMO orbital of sulfenyl chloride located on the sulfur atom and the LUMO orbital of styrene located on the double bond as shown in Fig. 7. Hereupon, this orbital mixing induces the LUMO+3 of TS formed in an antibonding way, accordingly. This bonding raises the energy of the TS system as compared to the frontier orbitals of R. Second, the HOMO+7 of TS is formed from the bonding interaction of the styrene HOMO located on the double bond and the LUMO of sulfenyl chloride consisting of the p orbital mainly located on the sulfur atom. Thus, the LUMO+2 of TS is formed in an antibonding way, accordingly. This interaction results in the decrease in the energy of TS HOMO as compared to the frontier orbitals of R. The MO analysis reveals that the HOMO and LUMO orbitals of both reactants are essential for the electron density transfer from R to TS. This transformation raises the HOMO energy of TS which is compatible with the high reaction activation barrier. The forthcoming chlorine addition may reduce the reaction energy barrier with the stabilizing effect on the molecular system.

Solvent effects

Solvent effects on the reaction stationary points were determined by the PCM method with water (polar) and heptane (non-polar) solvents. The Gibbs free energies in the gas phase and the solvating media of reaction stationary points are presented in Fig. 2. The relevant bond WI values, charges obtained by natural population analysis on atoms, dipole moments of reaction stationary points for the gas phase and in the polar solvent phase are presented in Table 2 and 3.

The TS possess a large dipole moment (6.09 D for the gas phase), a strong charge separation between the S (+0.36) and Cl (-0.45) atoms as compared to R sulfenyl chloride bearing a dipole moment of 2.79 D for the gas phase, almost neutral charges on the S (+0.08) and Cl (-0.07) atoms, and the P product (2.72 D for the gas phase).

The solvent polarity strongly influences the charge separation and dipole moment values of the TS (9.47 D for the polar solvent) as compared to R (3.23 D for the polar solvent) and P (3.45 D for the polar solvent). This suggests that stabilization of TS should be strongly influenced by polar solvents. Meanwhile, the solvation might have a slight influence on the stabilization energy of the R and P as compared to that of TS. The comparison of the calculated Gibbs free energy of activation in the gas phase and solvating media confirms this assumption, indicating that the solvation influences stabilization of TS to a greater extent as compared to the solvated media influence in stabilization of R and P. The decreased free activation energy for polar solvent reaction conditions compared to the gas phase of TS is 51.88 kJ/mol. The free stabilization energies of R and P calculated for polar solvent media decreases by 17.0 and 18.8 kJ/mol, respectively. The values of reaction stationary points calculated for non-polar solvation media are almost equal to the gas phase calculated values. This means that the polar solvent can have a significant effect on the lowering of reaction activation energy barriers.

CONCLUSIONS

The mechanism of methylsulfenylchloride addition to styrene has been presented by DFT calculations. The reaction potential energy profile has been calculated by means of the B3LYP functional in conjunction with the 6-31++G(d,p) basis set. The relevant charges on atoms, bond character changes and frontier molecular orbital shapes mixing on the minimal energy path estimated by the intrinsic reaction coordinate method have been described.

A single-step reaction mechanism with one transition state and no intermediates has been suggested. During this process the essential structural changes involve transfer of the chlorine atom to the C1 atom and migration of the S atom to the C2 atom. The S-C2 bond is formed and the S-Cl bond weakens as reacting molecular systems move from the reactant to transition state. Below the transition state going to the product the C1-Cl bond is formed and the S-Cl breaks.

The charge separation effect of the S-Cl bond in the transition state implies that the addition reaction should proceed through the ionic transition state. The polar solvent has a significant effect on the reduction of reaction activation energy barriers and increases the charge separation of the S-Cl bond. Thus, the ionic or covalently bonded TS may exist and the real bonding nature of TS should depend on the polarity of reaction media. The molecular orbital analysis reveals that the HOMO and LUMO orbitals of both reactants are essential for electron density transfer from the reactant to transition state.

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STIRENO IR SULFENCHLORIDO REAKCIJOS MECHANIZMO TEORINIS TYRIMAS

Santrauka

Sulfenhalogenidai su įvairiai pakeistais alkenais gali reaguoti ne tik regio- bet ir stereoselektyviai. Siekiant paaiškinti šio tipo reakcijų selektyvumo priežastis, dažniausiai remiamasi klasikiniu episulfonio tarpinio reakcijos komplekso susidarymo postulatu. Tačiau atliktų sintezės darbų analizė parodė, kad sulfenhalogenidų ir alkenų sąveiką gali lemti ir kiti molekuliniai mechanizmai. Šis darbas yra skirtas detaliam metilsulfenchlorido ir stireno reakcijos mechanizmo analizei. Potencinės energijos paviršiaus profilio skaičiavimams buvo pasirinktas tankio funkcionalo metodas B3LYP ir atominių bazinių funkcijų rinkinys 6-31++G(d, p). Taikant solvatacinės aplinkos metodą PCM buvo apskaičiuota ir įvertinta solvatacinių efektų įtaka analizuojamai reakcijai. Naudojant vidinės reakcijos koordinatės skaičiavimus nustatyta viensistadinės reakcijos eiga. Reakcijai būdingas vienas pirmos eilės balno taškas – pereinama būseną, kuri mažiausios energijos trajektorijomis jungiasi su dviem reakcijos minimumais: reaktantais (metilsulfenchloridu ir stirenu) ir produktu 1-chlor-1-feniletil-2-(metil)sulfidu. Remiantis vidinės reakcijos koordinatės skaičiavimais, darbe aprašyti reaguojančių molekulių geometrijos, elektroninės sandaros ir molekulių orbitalių pokyčiai reakcijos vyksmo metu.

