

Article

Symmetry Analysis in Mechanistic Studies of Nucleophilic Substitution and β -Elimination Reactions

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Abstract: A mechanistic study of the bimolecular nucleophilic substitution (S_N2) reaction for halomethane CH_3X ($X = Cl, Br, \text{ or } I$) is approached by using symmetry principles and molecular orbital theory. The electrophilicity of the functionalized sp^3 -carbon is attributable to a 2p-orbital-based antibonding MO along the C–X bond. This antibonding MO, upon accepting an electron pair from a nucleophile, gives rise to dissociation of the C–X bond and formation of a new Nuc–C bond. Correlations are made between the molecular orbitals of reactants (Nuc[−] and CH_3X) and products (Nuc CH_3 and X^-). Similar symmetry analysis has been applied to mechanistic study of the bimolecular β -elimination (E2) reactions of haloalkanes. It well explains the necessity of an anti-coplanar arrangement of the C_α –X and C_β –H bonds for an E2 reaction (anti-elimination). Having this structural arrangement, the bonding C_α –X (σ_{C-X}) and antibonding C_β –H (σ_{C-H}^*) orbitals become symmetry-match. They can partially overlap resulting in increase in electron density in σ_{C-H}^* , which weakens and polarizes the C_β –H bond making the β -H acidic. An E2 reaction can readily take place in the presence of a base. The applications of symmetry analysis to the S_N2 and E2 reactions represent a new approach to studying organic mechanisms.

Keywords: S_N2 reaction; E2 reaction; molecular orbital (MO); symmetry, electrophilicity

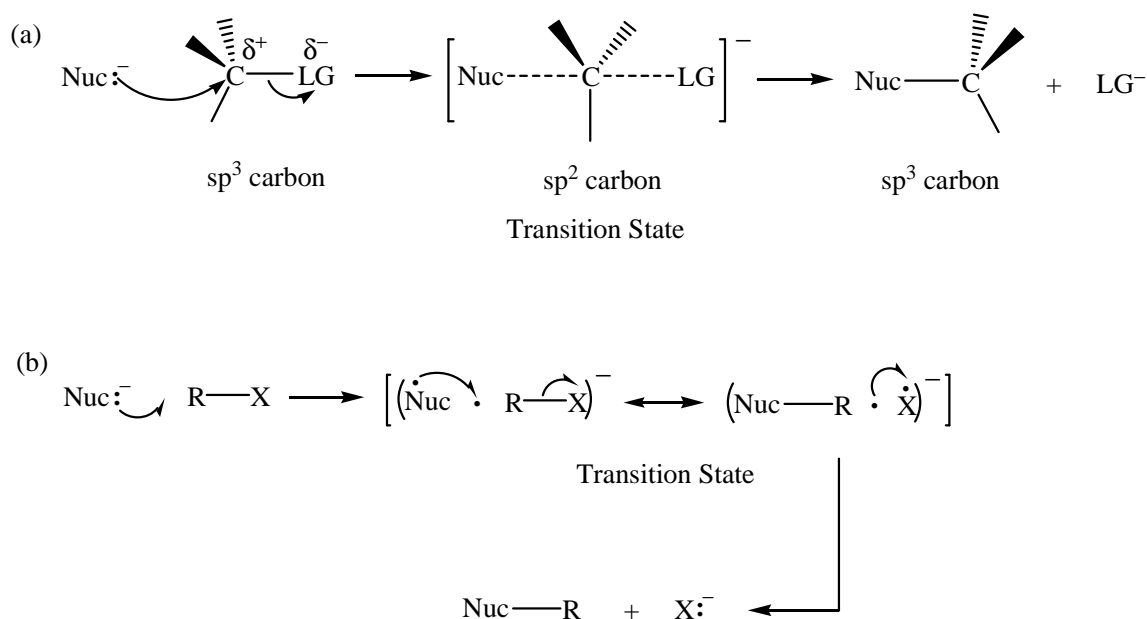
1. Introduction

The bimolecular nucleophilic substitution (S_N2) reactions are among the fundamental and most important organic reactions. Traditionally, the mechanism of the S_N2 reactions is studied using qualitative transition state theory [1–5]. The functionalized sp^3 hybridized carbon in a substrate

molecule functions as an electrophilic center. This electrophilicity is considered due to a partial positive charge created on carbon by the electronegative functional group. A nucleophile (Nuc^-) attacks the sp^3 hybridized carbon from the opposite side of the leaving group ($-\text{LG}$). This nucleophilic attack results in a transition state in which the carbon atom becomes sp^2 hybridized with the $\text{C}-\text{LG}$ bond partially broken and the $\text{Nuc}-\text{C}$ bond partially formed (Figure 1a). Finally, the $\text{C}-\text{LG}$ bond is broken completely coincident with formation of the $\text{Nuc}-\text{C}$ bond, giving the nucleophilic substitution product.

The explanation of the $\text{S}_{\text{N}}2$ mechanism by qualitative transition state theory is intuitive and readily understandable. It has a great merit in chemical education. However, its explanation on nature of the transition state is vague. While steric effect is employed to explain why nucleophilic attack proceeds from the opposite side of the leaving group resulting in a configuration change in the product, the argument is less overwhelming. In addition, this approach does not explain why the $\text{S}_{\text{N}}2$ reactions do not occur readily on functionalized organic compounds that contain two or more leaving groups on the central sp^3 hybridized carbon (e.g., CH_2Cl_2 , which only undergoes nucleophilic substitution with extremely strong nucleophiles such as silylphosphine, but inert to most of common nucleophiles.) [6]. Harcourt [7], on the other hand, argued that an $\text{S}_{\text{N}}2$ reaction is effected via consecutive one-electron transfers (Figure 1b). Accordingly, the transition state contains a delocalized one-electron intermolecular bond. This single electron transfer mechanism has been well reviewed in journal articles [8,9] and well discussed in a physical organic chemistry textbook [10]. This model is developed by rigorous molecular orbital calculations and appears to better reflect nature of the $\text{S}_{\text{N}}2$ reactions. However, it does not explain either of the above issues regarding the origin of electrophilicity of a functionalized sp^3 hybridized carbon and the properties of CH_2Cl_2 .

Figure 1. (a) Nucleophilic attack on the partially positively charged sp^3 hybridized carbon in a functionalized molecule forming a transition state with the central carbon sp^2 hybridized. (b) Nucleophilic attack on a functionalized molecule forming a postulated transition state containing a delocalized one-electron intermolecular bond (See ref. [7]).



In an earlier article [11], this author developed an alternative approach to the S_N2 mechanism using symmetry rules and qualitative molecular orbital theory, demonstrating that the reaction can be well effected by transfer of a lone pair of electrons from the nucleophile to the antibonding C–LG orbital. Since then, the author has established further detailed orbital correlations between the reactant and product molecules for the S_N2 reaction on the basis of symmetry principles. The new results are presented in the present article. The origin of electrophilicity for haloalkanes has been well accounted for. Such a model is often employed in studying inorganic compounds [12–15], but so far not common for organic compounds.

Bimolecular β -elimination (E2) reactions represent another important type of fundamental organic reactions [1–5]. Although the stereochemistry, transition state, and energy profile for the E2 reactions have been well established by sophisticated experimental and theoretical investigations [16,17], the origin for acidity of the β -hydrogen is unclear, and interpretation on this matter is unavailable. The understanding of the β -hydrogen acidity in a functionalized substrate molecule such as a haloalkane is the key to study of the E2 reaction mechanism. Recently, this author has examined the E2 reactions using symmetry analysis on the reacting molecular orbitals. Possible frontier molecular orbital interactions have been identified. The activation of the β -hydrogen by the functional group in a haloalkane, which makes it slightly acidic, is well accounted for by examining these orbital interactions on the basis of symmetry-match. Such an approach to understanding of E2 reactions by symmetry analysis is unprecedented and has not been reported elsewhere prior to this work. The results are presented in this article.

The applications of symmetry analysis to the S_N2 and E2 reactions represent a new method to study organic mechanisms. This adequately simplified model appeals to the interests and needs of general audiences in chemical science. The reactivity of different types of functionalized organic compounds is well accounted for by using symmetry principles.

2. Results and Discussion

2.1. The S_N2 Reaction of Halomethane CH_3X ($X = Cl, Br, \text{ or } I$)

Halogen atoms (other than fluorine) are among the most common good leaving groups in organic chemistry [1–5]. In this article, symmetry analysis on reacting molecular orbitals for the S_N2 reaction of halomethane has been developed by the aid of character tables. The orbital interactions identified in the course of the S_N2 reaction of CH_3X represent the general mechanism for bimolecular nucleophilic substitution reactions.

A halomethane molecule CH_3X ($X = Cl, Br, \text{ or } I$) possesses the C_{3v} symmetry. Its principal three-fold axis is along the C–X bond. Therefore, this direction is defined as z-axis (Figure 2a). The carbon atom in the molecule can be regarded as the central atom, while the three hydrogen and halogen atoms are considered four ligands coordinating to the central carbon atom. According to molecular orbital theory, the linear combination of the four ligand orbitals forms four molecular orbitals called *ligand group orbitals* (LGO's) [12]. Then bonding in CH_3X can be treated by further linear combination of LGO's with valence orbitals in the central carbon atom ($2s, 2p_x, 2p_y, \text{ and } 2p_z$) based on symmetry-match, forming a set of molecular orbitals (MO's). This method has been widely used in transition

metal coordination compounds [12] as well as in tetracoordinated, pentacoordinated, and hexacoordinated main group compounds [13–15].

Figure 2. (a) Molecular orbitals (MO's) in CH_3X ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) which are formed by linear combination of ligand group orbitals (LGO's = $2a_1 + e$) and $2s, 2p_x, 2p_y,$ and $2p_z$ in the central carbon based on symmetry-match. The four MO's on the top are occupied bonding orbitals. Each of them has a counterpart of an unoccupied antibonding MO. Only one antibonding MO ($2p_z$ -based LUMO $2a_1^*$ along the C–X bond) is displayed. (b) Molecular orbital diagram of CH_3X , showing correlations of LGO's to the carbon atomic orbitals and qualitative energy levels of related orbitals.

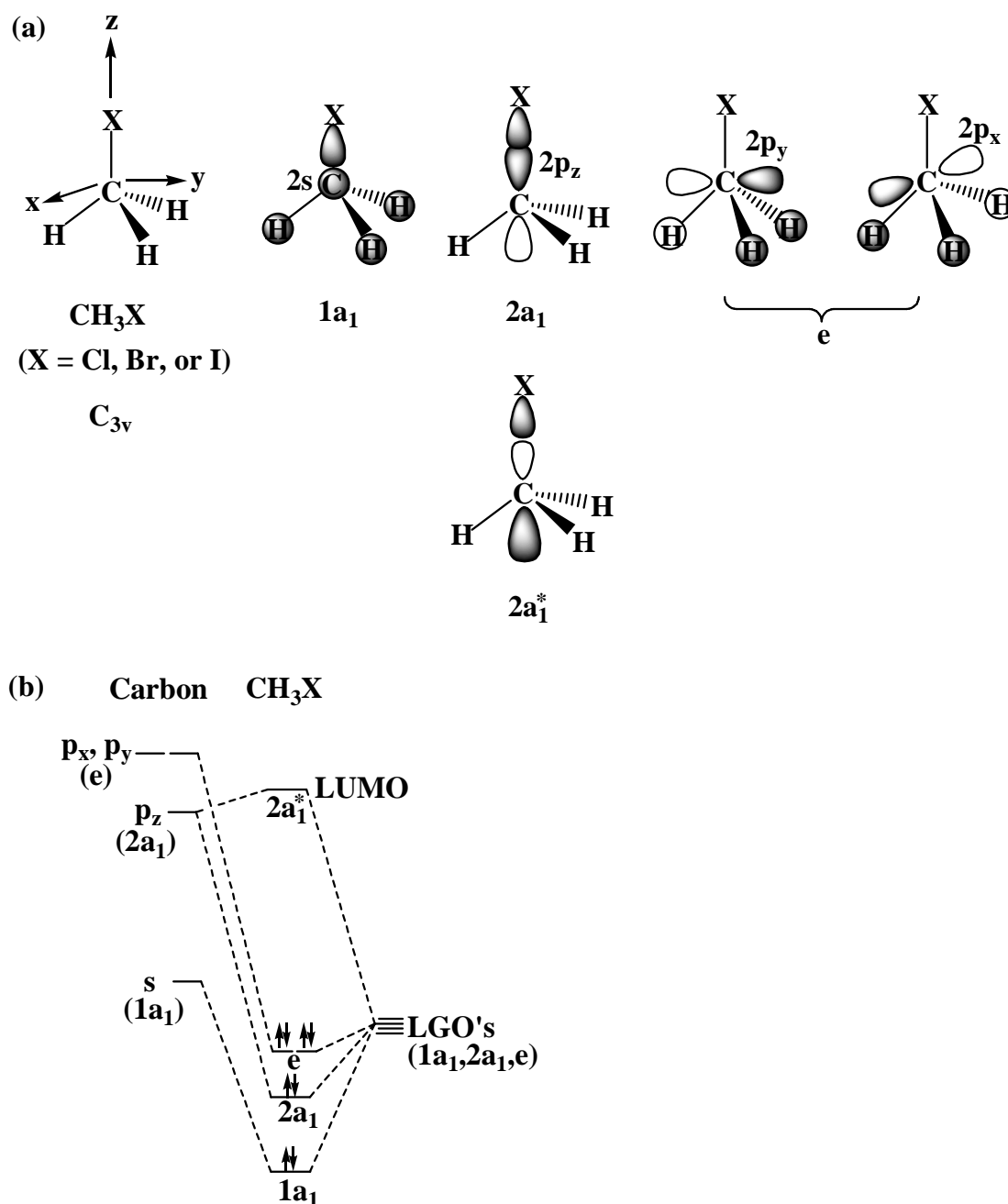
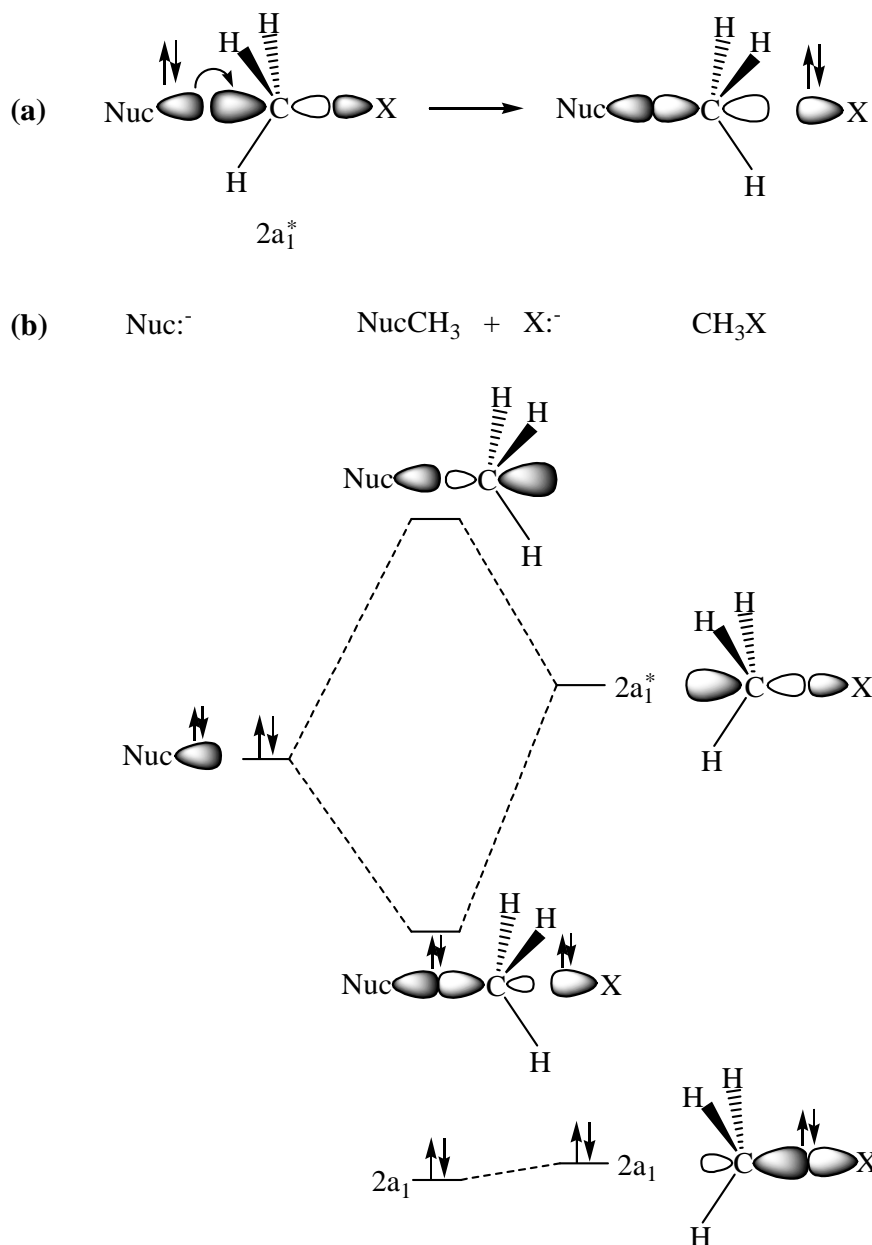


Figure 3. (a) Maximum overlap of a nucleophile orbital with the $2p_z$ -based LUMO $2a_1^*$ in the opposite side of the leaving group $-X$ in CH_3X ($X = Cl, Br, \text{ or } I$) results in electron transfer to $2a_1^*$ breaking the $C-X$ bond and effecting an S_N2 reaction. (b) Correlations of frontier molecular orbitals for the S_N2 reaction of CH_3X .



The LGO's in CH_3X can be established by using the C_{3v} character table [12] and symmetry rules, and they are formulated as follows (See details in Supplemental Materials S1):

$$\text{LGO's} = 2a_1 + e$$

where a_1 (a singlet) correlates to $2s$ or $2p_z$ orbital and e (a doublet) correlates to $2p_x$ and $2p_y$ orbitals in the central carbon atom according to the C_{3v} character table. As a result, four bonding MO's are formed in the entire molecule (Figure 2a). The predominant MO responsible for formation of the $C-X$ bond is $2a_1$, a carbon $2p_z$ -based bonding orbital along the $C-X$ bond. Its counterpart antibonding

orbital $2a_1^*$ is LUMO (Lowest Unoccupied Molecular Orbital). A qualitative molecular orbital diagram for CH_3X is shown in Figure 2b.

In an $\text{S}_{\text{N}}2$ reaction of CH_3X , the carbon atom functions as the electrophilic center (electron-pair acceptor). Therefore, the $2p_z$ -based LUMO ($2a_1^*$) should be the reacting orbital. It is an antibonding orbital along the C–X bond, responsible for cleavage of the C–X bond upon being filled with a pair of electrons. A vulnerable lobe of $2a_1^*$ is identified along z-axis, just being positioned in the opposite side of the halogen atom. When a nucleophile (Nuc^-) is approaching the central carbon from the opposite side of the C–X bond, the filled Nuc^- orbital has the maximum overlap with $2a_1^*$ (Figure 3a). This effects electron transfer into $2a_1^*$, which leads to breaking of the C–X bond and formation of a new Nuc–C bond. The nucleophilic attack from any other orientations would generate less effective orbital overlap and thus, it would be kinetically unfavorable. The correlations of frontier molecular orbitals between reactants (Nuc^- and $\text{CH}_3\text{–X}$) and products (Nuc–CH_3 and X^-) for the $\text{S}_{\text{N}}2$ reaction of a halomethane CH_3X are shown in Figure 3b.

2.2. The E2 Reactions of the Chain-Like Haloalkanes

The bimolecular β -elimination (E2) reactions of haloalkanes are among fundamental and most important organic reactions. They take place in the presence of a base [1,5,16–18]. For chain-like haloalkanes, the E2 reaction requires a staggered conformation for the haloalkane substrate molecule, namely that the $\text{C}_{\alpha}\text{–X}$ and $\text{C}_{\beta}\text{–H}$ bonds to be cleaved in the molecule must be anti-coplanar (Figure 4) [16–18]. An eclipsed conformation, in which the $\text{C}_{\alpha}\text{–X}$ and $\text{C}_{\beta}\text{–H}$ bonds stay syn-coplanar (see below), usually does not lead to an E2 reaction. Such a structural feature for the E2 reaction is necessary to make the β -H acidic via polarization of the $\text{C}_{\beta}\text{–H}$ bond. This can be accounted for by a symmetry analysis on the related reacting molecular orbitals.

Figure 4 shows that when the $\text{C}_{\alpha}\text{–X}$ and $\text{C}_{\beta}\text{–H}$ bonds in a haloalkane molecule are anti-coplanar in a staggered conformation, the C–H bonding ($\sigma_{\text{C–H}}$) orbital and the C–X antibonding ($\sigma_{\text{C–X}}^*$) orbital are of symmetry-match and they partially overlap; and the C–H antibonding ($\sigma_{\text{C–H}}^*$) orbital and the C–X bonding ($\sigma_{\text{C–X}}$) orbital are of symmetry-match and they partially overlap. The interaction (partial overlap) of the $\sigma_{\text{C–H}}$ (filled) and $\sigma_{\text{C–X}}^*$ (empty) orbitals increases the electron density in $\sigma_{\text{C–X}}^*$ weakening the C–X bond and easing the leave of the halo ($-\text{X}$) group. The interaction (partial overlap) of the $\sigma_{\text{C–X}}$ (filled) and $\sigma_{\text{C–H}}^*$ (empty) orbitals increases the electron density in $\sigma_{\text{C–H}}^*$ weakening and polarizing the C–H bond and making the β -H slightly acidic. As a result, the β -H can be effectively attacked by a base (B^-) on the $\sigma_{\text{C–H}}^*$ antibonding orbital (Figure 4c), while simultaneously, the C–X bonding ($\sigma_{\text{C–X}}$) orbital partially populates $\sigma_{\text{C–H}}^*$ with electrons. The combination leads to a concerted E2 elimination reaction. The correlations of frontier molecular orbitals between reactants and products for the E2 reaction of a haloalkane are shown in Figure 5.

Figure 6 shows that when the $\text{C}_{\alpha}\text{–X}$ and $\text{C}_{\beta}\text{–H}$ bonds in a haloalkane molecule are syn-coplanar in an eclipsed conformation, the $\sigma_{\text{C–H}}$ and $\sigma_{\text{C–X}}$ bonding orbitals (both filled) are of symmetry-match. However, the $\sigma_{\text{C–H}}$ bonding orbital (filled) and the $\sigma_{\text{C–X}}^*$ anti-bonding orbital (empty) are of symmetry-conflict (anti-symmetric). The $\sigma_{\text{C–H}}^*$ anti-bonding orbital (empty) and the $\sigma_{\text{C–X}}$ bonding orbital (filled) are also of symmetry-conflict (anti-symmetric). Neither the $\text{C}_{\alpha}\text{–X}$ bond nor the $\text{C}_{\beta}\text{–H}$ bond can be activated by effective orbital overlap as demonstrated above. As a result, a haloalkane in an eclipsed

conformation with the $C_{\alpha}-X$ and $C_{\beta}-H$ bond syn-coplanar usually does not lead to an E2 reaction. The unfavorable effect of the eclipsed conformation on the E2 reaction has been accounted for previously as that the Pauli repulsion between lone pairs of electrons in the attacking base (B^-) and the halogen $-X$ atom enhances the energy of the transition state, making the syn-elimination process energetically difficult [16].

Figure 4. (a) Anti-coplanar arrangement of the $C_{\alpha}-X$ and $C_{\beta}-H$ bonds in a haloalkane molecule ($X = Cl, Br, \text{ or } I; R_1, R_2, R_3, R_4 = H \text{ or alkyl}$) in staggered conformation. Bonding and antibonding molecular orbitals for the anti-coplanar $C_{\alpha}-X$ and $C_{\beta}-H$ bonds. (b) Effective interactions (partial overlap) of the molecular orbitals for the $C_{\alpha}-X$ and $C_{\beta}-H$ bonds due to symmetry-match. (c) Proposed interactions and transformations of reacting molecular orbitals in the course of an E2 reaction. The configuration (geometry) of the transition state has been established earlier [16,17].

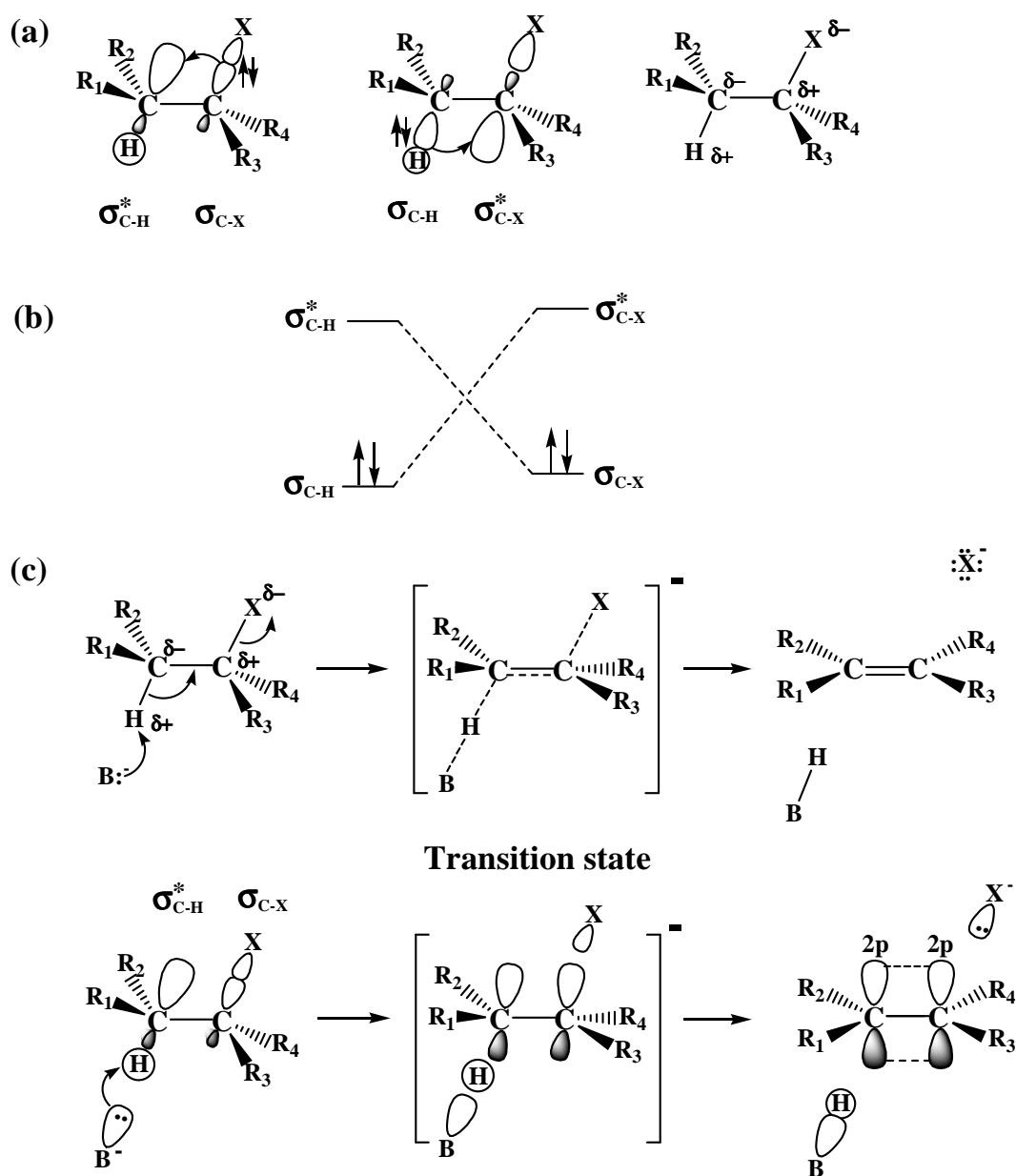


Figure 5. Correlations of frontier molecular orbitals for E2 reaction of haloalkane.

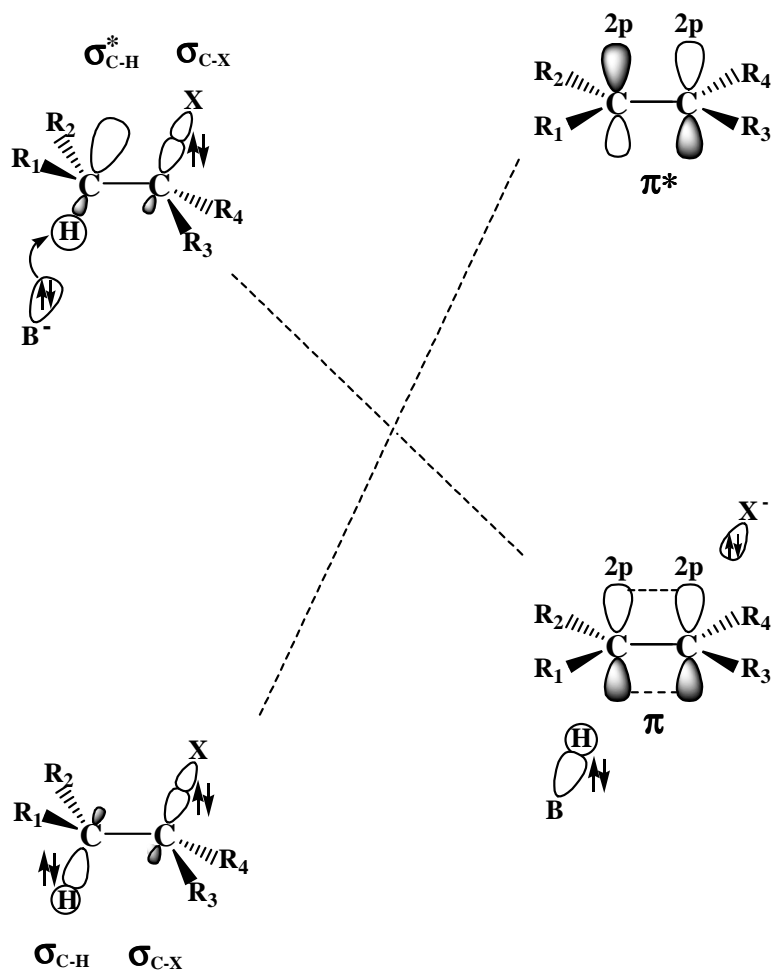
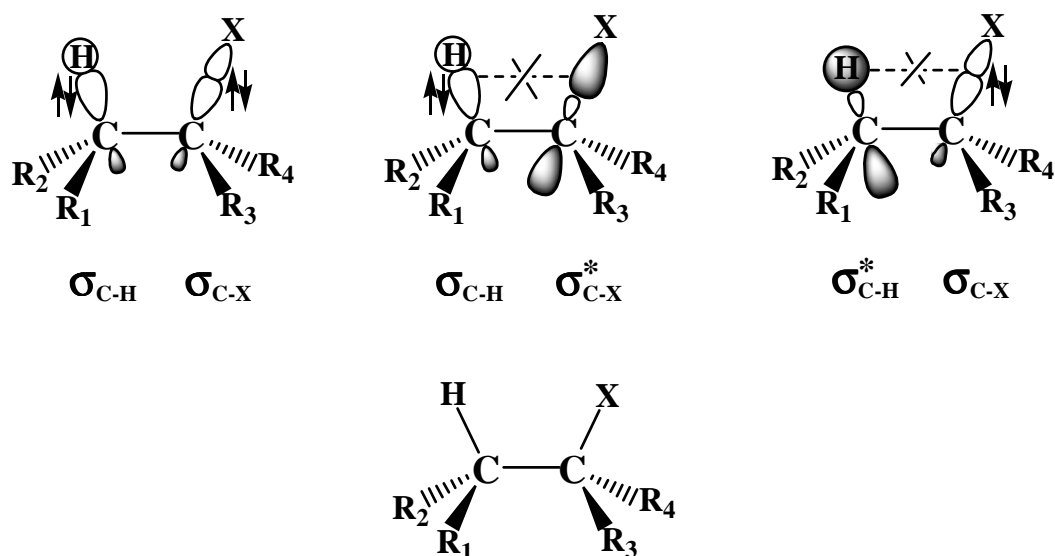


Figure 6. Syn-coplanar arrangement of the C_{α} -X and C_{β} -H bonds in a haloalkane molecule in eclipsed conformation. Bonding and antibonding molecular orbitals for the syn-coplanar C_{α} -X and C_{β} -H bonds.



2.3. The E2 Reactions of Halocyclohexanes

The major conformation for halocyclohexanes is the chair-conformation as shown in Figure 7. The E2 reaction of a halocyclohexane requires that the halo ($-X = -Cl, -Br, \text{ or } -I$) group be on an axial position, while an equatorial halo $-X$ group cannot be eliminated. Only when a halo $-X$ group is equilibrated to an axial position, can the $C_{\alpha}-X$ and $C_{\beta}-H$ (also in axial position) bonds to be cleaved stay anti-coplanar, which makes the reacting molecular orbitals interact effectively.

Figure 7 shows that the axial $C_{\alpha}-X$ bonding (σ_{C-X}) orbital (filled) and the axial $C_{\beta}-H$ antibonding (σ_{C-H}^*) orbital (empty) are of symmetry-match and they can partially overlap each other. The axial $C_{\beta}-H$ bonding (σ_{C-H}) orbital (filled) and the axial $C_{\alpha}-X$ antibonding (σ_{C-X}^*) orbital (empty) are of symmetry-match and they can partially overlap each other. As seen in the case of the chain-like haloalkanes, the interaction (partial overlap) of the filled σ_{C-H} and empty σ_{C-X}^* orbitals increases the electron density in σ_{C-X}^* weakening the $C-X$ bond and easing the leave of the halo ($-X$) group. The interaction (partial overlap) of the filled σ_{C-X} and empty σ_{C-H}^* orbitals increases the electron density in σ_{C-H}^* weakening and polarizing the $C-H$ bond and making the $\beta-H$ slightly acidic. As a result, the $\beta-H$ can be effectively attacked by a base (B^-) on the σ_{C-H}^* antibonding orbital (Figure 7c) leading to a concerted E2 elimination reaction.

3. Conclusions

Traditionally, the S_N2 mechanism has been studied by a qualitative transition state theory. The electrophilicity of the reacting functionalized sp^3 hybridized carbon in a substrate molecule is considered due to a partial positive charge on the carbon created by the electronegative functional group. In this article, a new approach to the S_N2 mechanism is developed. The mechanism is examined using symmetry rules and qualitative molecular orbital theory. This approach has led to better understanding of nature of the reaction and explained some related issues that cannot be explained by the traditional method.

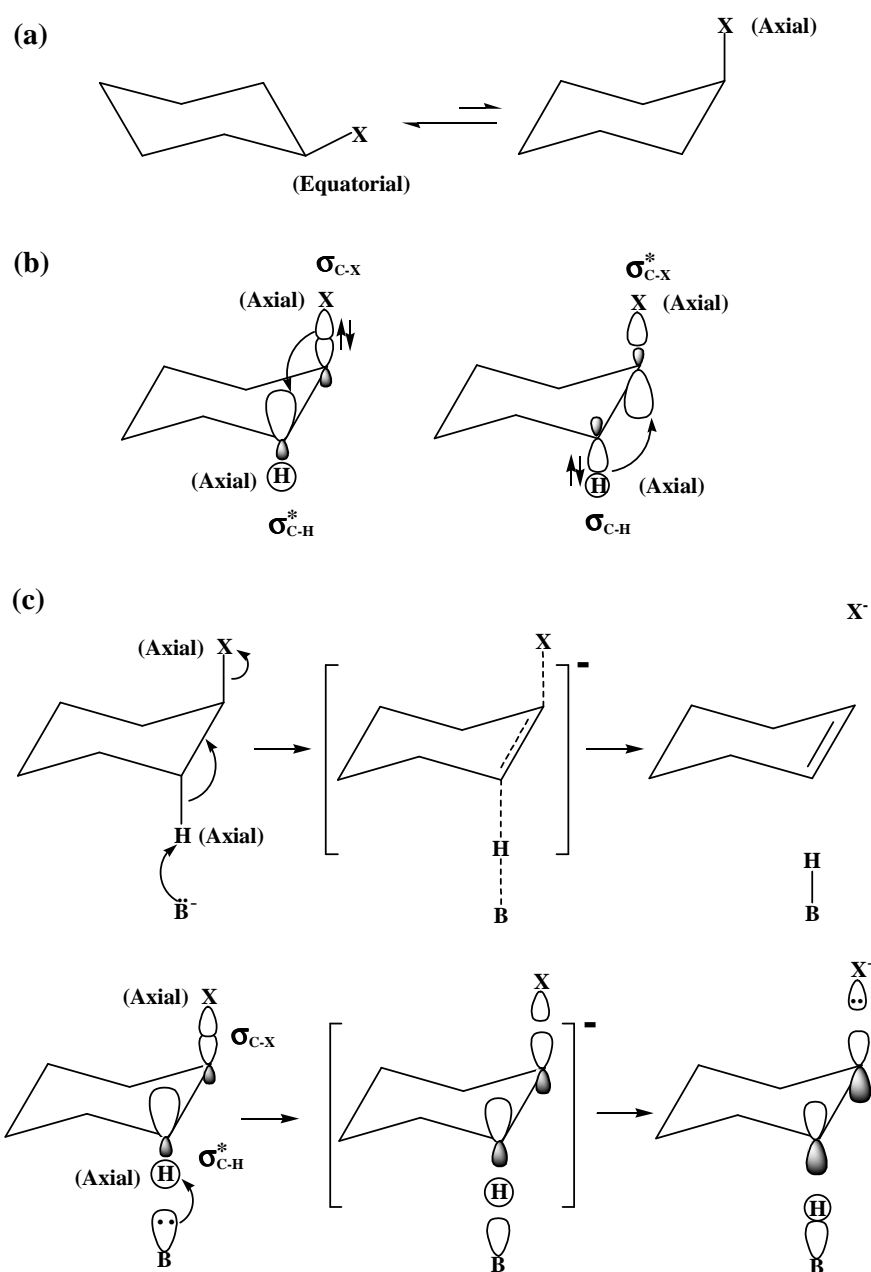
According to the model developed in this article, the key to electrophilicity of a functionalized sp^3 hybridized carbon lies in presence of a carbon 2p-orbital based antibonding MO along the $C-X$ bond ($X = Cl, Br, \text{ or } I$ – a good leaving group). This antibonding MO, upon accepting a pair of electrons from a nucleophile, gives rise to dissociation of the $C-X$ bond and formation of a new Nuc-C bond. The presence or absence of such an antibonding MO in functionalized organic molecules can be identified readily by a symmetry analysis aided by character tables. The overall orbital interactions and correlations in the course of an S_N2 reaction have been established by a qualitative molecular orbital analysis.

In this article, symmetry analysis has been applied to mechanistic studies of the E2 reaction, another type of fundamental organic reactions. It shows that only when the $C_{\alpha}-X$ and $C_{\beta}-H$ bonds to be cleaved in a haloalkane molecule are anti-coplanar, can the reacting molecular orbitals be of symmetry-match. As a result, the positive overlap of σ_{C-H} and σ_{C-X}^* orbitals increases the electron density in σ_{C-X}^* weakening the $C-X$ bond and easing the leave of the halo ($-X$) group. The positive overlap of σ_{C-X} and σ_{C-H}^* orbitals increases the electron density in σ_{C-H}^* weakening the $C-H$ bond and making the $\beta-H$ acidic. All this leads to an E2 reaction in the presence of a strong base. Although

sophisticated mechanistic studies of the E2 reaction have been performed previously [16,17], prior to this work, no explanation on the origin of acidity for the β -H in functionalized organic compounds such as haloalkanes has been found. The author believes that understanding of the β -H acidity is the key to study of the E2 reactions.

Usually, symmetry rules are used in studying transition metal based inorganic compounds. This work shows that the combination of symmetry rules and qualitative molecular orbital theory is also a powerful tool for studying organic mechanisms.

Figure 7. (a) Chair-conformations of a halocyclohexane ($X = \text{Cl, Br, or I}$). (b) Symmetry-match for the reacting molecular orbitals on the $\text{C}_\alpha\text{-X}$ (axial) and $\text{C}_\beta\text{-H}$ (axial) bonds in a halocyclohexane. (c) The molecular orbital interactions in the course of an E2 reaction of a halocyclohexane.

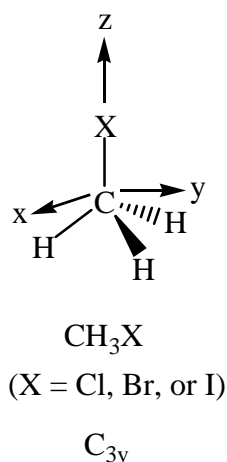


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Supplemental Materials—Symmetry Analysis and Ligand Group Orbitals (LGO's) for Various Functionalized Molecules

S1 CH_3X (X = Cl, Br, or I)



C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	$(x^2 - y^2, xy)$ (xz, yz)
Γ_r	4	1	2		

The reducible representation (Γ_r) for each of the symmetry operations (E, C_3 , and σ_v) in the C_{3v} point group equals the total number of the bonds that do not move under the corresponding operation. Under the operation of E, all the four bonds in the molecule do not move ($\Gamma_r = 4$ for E). Under the operation of C_3 , only the C–X bond does not move ($\Gamma_r = 1$ for C_3). Under the operation of σ_v , the C–X bond and one C–H bond do not move ($\Gamma_r = 2$ for σ_v).

The number of each of irreducible representations (A_1 , A_2 , and E) in the four bonds can be calculated based on the character table and reducible representations as follows:

$$N(A_1) = 1/6 (4 \times 1 \times 1 + 1 \times 1 \times 2 + 2 \times 1 \times 3) = 2$$

$$N(A_2) = 1/6 (4 \times 1 \times 1 + 1 \times 1 \times 2 + 2 \times (-1) \times 3) = 0$$

$$N(E) = 1/6 (4 \times 2 \times 1 + 1 \times (-1) \times 2 + 2 \times 0 \times 3) = 1$$

Therefore, the ligand group orbitals (LGO's) of CH_3X can be formulated by symmetry as follows:

$$\text{LGO's} = 2a_1 + e$$

According to the C_{3v} character table, a_1 (singlet) correlates to s or p_z on the central C; and e (doublet) correlates to p_x and p_y on the central C.