

An MO Study on Reaction Mechanism and Reactivity of *p*-Substituted Phenylchloroethylsulfones

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Abstract

The molecular orbital theory (EHT) has been applied to the discussion of the reaction mechanism and reactivity of *p*-substituted phenyl- β -chloroethylsulfones, $R-\text{C}_6\text{H}_4-\text{SO}_2\text{CH}_2\text{CH}_2\text{Cl}$, where R are CH_3O , CH_3 , Cl , H .

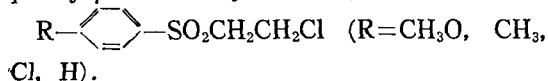
The theoretical conclusion derived are in good agreements with the experimental order.

요 약

p-Substituted phenyl- β -chloroethylsulfones, $R-\text{C}_6\text{H}_4-\text{SO}_2\text{CH}_2\text{CH}_2\text{Cl}$, 에서 R이 CH_3O , CH_3 , Cl , H 인 화합물들의 반응기수와 반응성을 EHT 방법으로 계산하고 실험값과 비교 검토 하였다.

INTRODUCTION

The molecular orbital (MO) theory has been used successfully to account for chemical reactivities of both conjugated and saturated organic compounds¹⁻⁵. In particular, Fukui and his collaborators⁶ were able to predict reactivities of saturated carbon compounds using the extended Hückel theory (EHT) developed by Hoffmann⁷. In this work, we have used EHT throughout to investigate theoretically the relative nucleophilic reactivities on the *p*-substituted phenyl- β -chloroethylsulfones,



In the approximate sigma MO method dealing with large molecules, the computa-

tional simplicity of the EHT method is one of the more important factors to be taken into consideration at the outset, especially when only semiquantitative results are required.

In the EHT method the molecular orbitals are expressed as a linear combination of the Slater type atomic orbitals (AO) ϕ_i ,

$$\Phi_i = \sum_{j=1}^n C_{ij} \phi_j \dots \dots \dots (1)$$

which is in turn given as,

$$\phi_i = N r^{n-1} \exp(-rZ) Y_{l,m}(\theta, \phi) \dots \dots \dots (2)$$

where Z is the orbital exponent for the AO's and other terms have their usual significances.

The summation in (1) is over all valence orbitals used in constructing the molecular orbital (MO), namely the 1s orbital for

hydrogen, 2s, 2p_x, 2p_y, and 2p_z orbitals for the second row elements, and 3s, 3p_x, 3p_y, and 3p_z orbitals for the third row elements.

In solving the usual secular equation (3) in this method, the Coulomb integrals H_{ii} are chosen as the negative of valence state ionization potential (VSIP) and

$$\sum_{i=1}^m (H_{ii} - ES_{ii}) C_{ij} = 0, \quad (j=1, 2, \dots, m) \quad (3)$$

for estimating the off-diagonal matrix elements H_{ij} the Wolfsberg-Helmholtz approximation⁸⁾ (4) is used.

$$H_{ij} = 1/2K (H_{ii} + H_{jj}) S_{ij} \quad (4)$$

The value of K has been chosen as 1.75 in accordance with earlier works^{6-7, 21-22)}.

CALCULATIONS

The computer input data consisted of the orbital exponents $Z^{(9)}$, valence state ionization potential¹⁰⁾ and accurate coordinates of atoms.

The Z and VSIP valences are summarized in table I.

Table I. The Slater Exponents, Z , and Valence State Ionization Potential, $-I$.

AO	Z	$-I$ (eV)
H 1s	1.00	13.60
C 2s	1.59	21.01
C 2p	1.59	11.27
N 2s	1.92	26.92
N 2p	1.92	14.42
O 2s	2.24	36.07
O 2p	2.24	18.53
S 3s	1.98	20.08
S 3p	1.98	13.32
Cl 3s	2.20	24.02
Cl 3p	2.20	15.03

The geometry of molecules were determined by using interatomic distances and valence angles obtained from Interatomic Distances and Configuration in Molecules and Ions, edited by L.E. Sutton, Special publications No. 11 and 18, The Chemical Society London.

Precise atomic coordinates of various atoms in molecules were calculated by Vector method.

In order to interpret the experimental data, the Mulliken population analysis¹¹⁾ has been employed and the following MO theoretical quantities are calculated.

The partial valence-inactive AO population¹²⁾ of AO in the j th MO;

$$Pr^j = 2(Cr^j)^2$$

The partial valence-inactive atom population of the atom A in the j th MO;

$$P_A^j = \sum_r^A Pr^j$$

The partial atom bond population between the atoms A and B in the j th MO;

$$M_{AB}^j = 2 \sum_r^A \sum_s^B Cr^j Cs^j Srs$$

The gross atomic population of the atom A ;

$$M_A = \sum_r^A N_r$$

Atomic bond population;

$$M_{AB} = \sum_r^A \sum_s^B N_{rs}$$

Formal charge;

$$Q_A = n_A - M_A$$

Where Cr^j stands for the coefficient of AO in the j th MO and where \sum_r^A signifies the summation over all the AO's belonging to the atom A , and n_A is the number of electrons in atom A .

The geometry of molecules were determined by the following interatomic distances

and bond angles.

C — H	=1.09Å	∠OSO=128°
C — Cl	=1.78Å	∠CCCl=110°
C(sp ³)—C(sp ³)	=1.54Å	∠CSC=119°
C(sp ³)—C(sp ²)	=1.50Å	∠CSO=106°
C—C (benzene)	=1.40Å	∠COC=121°
S = O	=1.44Å	

Results and Discussion

The various molecular orbital approaches have been used in predicting reactivities and these can be classified into polarized state and activated state approximations¹³⁾. These activity indices used in the first category are charge, self-polarizability and free valence while those in the second are localization energy, reactivity number and frontier electron densities.¹⁴⁻¹⁸⁾

In this work, we will only be concerned with those reactivity parameters which are normally derived from the EHT analysis.

As the results of calculation, the total electronic energies E and energies for the highest occupied (HO) and the lowest unoccupied (LU) levels of molecules, ϵ , are summarized in table II. In this table, $\Delta\epsilon$ is the difference in energy between HO and LU orbitals.

$\Delta\epsilon$ indicate that stabilities are in the order




But, the rate constant of these compounds which is E_2 type experimental data are



Therefore, $\Delta\epsilon$ are unsuitable for the activity indices.

Fig. I shows the atom and atom bond populations for *p*-substituted phenyl- β -chloroethylsulfones. In these compounds, when gross atom population of $H_1(H_2)$ compared with its $H_3(H_4)$, $H_3(H_4)$ has more positive

Table II. Energetics.

R—  —SO ₂ CH ₂ CH ₂ Cl (R=CH ₃ O, CH ₃ , H, Cl)				
R	E (eV)	ϵ^{HO}	ϵ^{LU}	$\Delta\epsilon$
CH ₃ O	-1368.3345	-12.4276	-8.0425	4.3851
CH ₃	-1351.6843	-12.3382	-8.0276	4.3105
H	-1248.3345	-12.5847	-8.0320	4.5527
Cl	-1356.5623	-12.4148	-8.0240	4.3908

charge than $H_1(H_2)$. Therefore $H_3(H_4)$ are more reactive than $H_1(H_2)$ to be attacked by the base. Also, the formal charge of C_2 has more positive than C_1 .

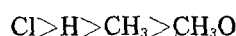
These results means that $C_2-H_3(C_2-H_4)$ bond are more polarity than $C_1-H_1(C_1-H_2)$ and covalent nature of the $C_2-H_3(C_2-H_4)$ linkage is relatively weaker than $C_1-H_1(C_1-H_2)$ bond and the others bond as shown Fig. 1. $H_3(H_4)$ atom are more easily broken than $H_1(H_2)$ and hydrogens of other bond in the nucleophilic attack.

Table III shows the atomic bond population of LU orbitals, $M_{C_2-H_3}^{LU}$, for C_2-H_3 and the valence-inactive AO population of LU levels is called a frontier electron density, $P_{H_3}^{LU}$, for nucleophilic and the experimental data of the rate constant of *p*-substituted phenyl- β -chloroethylsulfones in anhydrous acetonitrile using $Et_2NCH_2CH_2OH$, $EtN(CH_2CH_2OH)_2$ and $N(CH_2CH_2OH)_3$ at 50°C as the base^{19, 20)}.

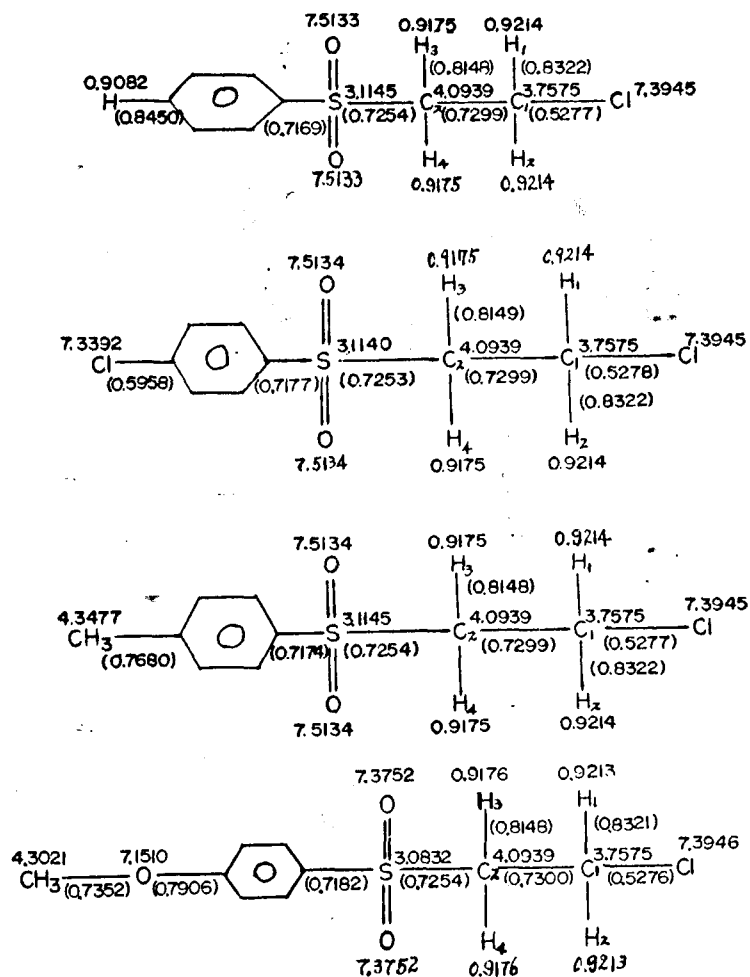
The value of $M_{C_2-H_3}^{LU}$ decreases from -0.00001 to -0.00251



Therefore, antibonding character increases in this order. Also, the valence inactive AO population of LU level increases from 0.00012 to 0.00458



According to Fukui et al., The greater is nucleophilic reactivity, the larger is the value of $P_{H_3}^{LU}$ ²⁷⁾.



The figures without parentheses indicate M_A

The figures with parentheses stand for M_{AB}

Fig. 1. Atom and Atom Bond Populations for *p*-substituted phenyl- β -chloroethylsulfones.
 (R=H, Cl, CH₃, CH₃O)

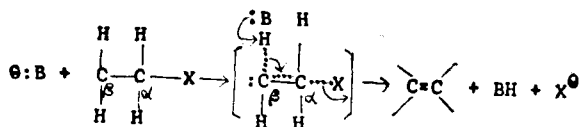
Table III. The Value of M_{C2-H3}^{LU} , P_{H3}^{LU} , and Experimental data of the E_2 reactivity
 $[KE_2 (M^{-1} sec^{-1})]^*$

X	M_{C2-H3}^{LU}	P_{H3}^{LU}	$Et_2NCH_2CH_2OH$	$EtN(CH_2CH_2OH)_2$	$N(CH_2CH_2OH)_3$
CH ₃ O	-0.00001	0.00012	$1.25 \pm 0.02 \times 10^{-2}$	$1.82 \pm 0.07 \times 10^{-3}$	$2.29 \pm 0.01 \times 10^{-4}$
CH ₃	-0.00006	0.00036	$1.82 \pm 0.03 \times 10^{-2}$	$2.65 \pm 0.01 \times 10^{-3}$	$3.86 \pm 0.02 \times 10^{-4}$
H	-0.00155	0.00288	$3.02 \pm 0.04 \times 10^{-2}$	$4.64 \pm 0.08 \times 10^{-3}$	$5.75 \pm 0.02 \times 10^{-4}$
Cl	-0.00251	0.00458	$8.95 \pm 0.15 \times 10^{-2}$	$1.26 \pm 0.04 \times 10^{-2}$	$1.71 \pm 0.05 \times 10^{-3}$

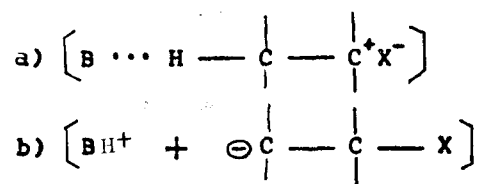
* The rates of the base-catalysed eliminations of a series of *p*-substituted phenyl- β -chloroethylsulfones have been determined in anhydrous acetonitrile using $Et_2NCH_2CH_2OH$, $EtN(CH_2CH_2OH)_2$ and $N(CH_2CH_2OH)_3$ as the bases.

The experimental data increase the same order as calculated values.

The mechanism of the base-promoted, bimolecular elimination (E_2) reactions has been experimentally studied in detail^{21, 22}. In this type of reaction, the attack of bases on the β -hydrogen atom and the departure of the nucleophile, x , from the α -carbon atom are thought to occur in concert with the double-bond formation between C_α - C_β bond;



The other β -eliminations are the two step mechanisms, $E_1(a)$ and $E_1cB(b)$ have formed transition state as following;



The various example of E_1 reactions are known, which the carbonium mechanism (E_1cB) is observed only in the extreme case where the β -carbon atom bears strongly electron attracting substituents^{21, 22}.

An alternative E_2 mechanism in which S_N2 and E_2 are "merged"^{23, 24} has been proposed, but it applies only to very special cases²⁵.

The E_2 type reactions of the p -substituted phenyl- β -chloroethylsulfones with a few tertiary amines are best suited to test the predictions derived in this work.

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