염화췌네틸의 친핵반응성에 대한 분자궤도론적 연구

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Molecular Orbital Studies on Nucleophilic Reactivities of Phenethyl Chlorides.

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요   약   1-염화 및 2-염화 췌네틸의 친핵성 반응에 대하여 분자 궤도론적 방법을 적용하여 상대적인 반응성을 연구하였다. EHT 계산에 의한 Population Analysis로 부터 할로겐 교환반응의 상대 속도를 설명할 수 있음을 밝혔으며 친핵성이 적은 Nucleophile의 경우 상대반응성이 바뀐다는 사실도 결합형성 과정이 중요하다는 것으로 이론적인 해석이 가능함을 밝혔다.

Abstract Nucleophilic reactivities of 1-and 2-phenethyl chlorides have been investigated MO-theoretically using the EHT method. It has been shown that results of population analysis are consistent with the experimental order of relative nucleophilic reactivities and furthermore the reversal of the reactivity order for the less reactive nucleophile, I⁻, could also be explained satisfactorily.

Introduction

The molecular orbital (MO) theory has been used successfully to account for chemical reactivities of both conjugated and saturated organic compounds. In particular Fukui and his collaborators[1] were able to predict reactivities of saturated carbon compounds using the extended Hückel theory (EHT) developed by Hoffmann.[2]

In this work we have carried out EHT calculations on 1-and 2-phenethyl chlorides to inevestigate theoretically the relative nucleophilic reactivities. The principal advantage of the EHT method lies in its computational simplicity compared with other more sophisticated sigma MO approximation. Typically an EHT calculation on a compound of about 40 valence atomic orbitals (VAO) takes less than 3 minutes of computer time with IBM 360/50 whereas a CNDO calculation[3] on the same would require more than 30 minutes.

In the EHT method, MO Ψ_j are constructed as a linear combination of Slater type atomic orbitals ϕ_i,

$$\Psi_j = \sum_{i=1}^{n} C_{ij}\phi_i \tag{1}$$

where n is the number of VAO. The Slater atomic orbital is in turn given as,

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$$\phi_i = Nr^{n-1} \exp(-rZ) Y_{lm}(\theta, \phi) \qquad (2)$$

where Z is the orbital exponent for the atom and other terms have their usual significances.[4] The summation in (1) is over all valence orbitals thought to be of importance, namely the $1s$ orbital for hydrogen, $2s$, $2px$, $2py$ and $2pz$ orbitals for the second row elements, and $3s$, $3px$, $3py$ and $3pz$ orbitals for the third row elements. The usual secular equation (3) is then solved with approximations

$$\sum_{i=1} [H_{ij} - ES_{ij}] C_{ij} = 0, \quad j = 1, 2, \cdots m. \qquad (3)$$

that the Coulomb integral H_{ii} is equal to the negative of valence state ionization potential (VSIP) and the off-diagonal matrix element H_{ij} is given by[5]

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij} \qquad (4)$$

The value of K is normally taken as 1.75.

Calculations

The computer program for EHT calculation was obtained from Quantum Chemistry Program Exchange, Indiana University, USA.

Input data in this program are the orbital exponents Z, VSIP, $-I$, of AO's and cartesian coordinates of atoms in the molecule. Z and $-I$ values used in this work are summarized in *Table* I. The cartesian coordinates were deter-

Table I The Orbital Exponents, Z and VSIP Used.

AO		$Z^{(a)}$	VSIP $(ev)^{(b)}$
H	1s	1.00	−13.60
C	2s	1.59	−21.01
	2p	1.59	−11.27
Cl	3s	2.20	−25.23
	3p	2.20	−13.34

(a) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(b) J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

mined by using interatomic distances and valence angles obtained from the literature.[6] Actual calculation was carried out with another program.[7] The Mulliken population analysis[9] has been carried out and the following MO quantities have been calculated.

Atomic Orbital Population,

$$N_r = 2 \sum_{j}^{occ} \sum_{s} C_r^j C_s^j S_{rs}$$

Gross Atomic Population,

$$M_A = \sum_r^A N_r$$

Atomic Orbital Bond Population,

$$N_{rs} = 4 \sum_{j}^{occ} C_r^j C_s^j S_{rs}$$

Atomic Bond Population,

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

Valence Inactive Atomic Orbital Population,

$$P_r = 2(C_r^j)^2$$

Valence Inactive Atomic Population,

$$P_A = \sum_r^A \sum_j^{occ} 2(C_r^j)^2$$

Formal Charge

$$Q_A = n_A - M_A$$

where C_r^j is the coefficient of AO r in the j-th MO, $\sum^A$ signifies the summation over all the AO's of atom A, and n_A is the number of electrons in atom A.

Results and Discussion

Results of calculations are summarized in *Tables* II and III, where numbering schemes for hydrogen and non-hydrogen atoms are also shown. ε's are orbital energies for the lowest unoccupied (LU) and hight occupied (HO) MO's.

The total energies of two compounds are different only by 1.2 Kcal; 1-phenethyl (1-PEC)

Table II Results for 1-Phenethyl Chloride (1-PEC)
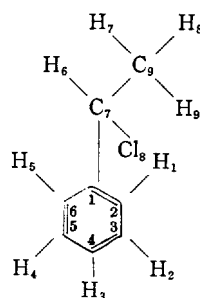
Total Energy $=-827.698$ ev.

$= -19094.973$ Kcal.

$\varepsilon^{LU} = -7.976$ ev.

$\varepsilon^{HO} = -12.171$ ev.

$\Delta\varepsilon = 4.195$ ev.

	Atomic Population					$\frac{1}{2}P_A$	Q_A
	Orbital				Gross		
	s	p_x	p_y	p_z			
H_1	0.8880				0.8880	0.5907	+0.1120
H_2	0.9100				0.9100	0.6067	+0.0900
H_3	0.9099				0.9099	0.6095	+0.0901
H_4	0.9098				0.9098	0.6095	+0.0902
H_5	0.9075				0.9075	0.6067	+0.0925
H_6	0.9083				0.9083	0.6247	+0.0917
H_7	0.8828				0.8828	0.5885	+0.1172
H_8	0.8691				0.8691	0.5771	+0.1309
H_9	0.8860				0.8860	0.5928	+0.1140
C_1	1.1513	0.9217	0.9212	0.9446	3.9378	2.7498	+0.0622
C_2	1.1647	0.9957	0.9592	1.0254	4.1451	2.8677	−0.1451
C_3	1.1610	0.9355	0.9912	0.9995	4.0872	2.7859	−0.0872
C_4	1.1612	0.9780	0.9505	1.0209	4.1106	2.8133	−0.1106
C_5	1.1610	0.9774	0.9505	0.9992	4.0881	2.7877	−0.0881
C_6	1.1623	0.9435	0.9916	1.0273	4.1247	2.8323	−0.1247
C_7	1.1367	0.9203	1.0012	0.6844	3.7426	2.4668	+0.2574
Cl_8	1.8384	1.9463	1.9820	1.5521	7.3189	7.1391	−0.3189
C_9	1.1595	1.0457	1.0814	1.0833	4.3698	2.9105	−0.3698

being more stable than 2-phenethyl (2-PEC). The ortho and para carbon atoms of the benzene ring have excess electron population over the meta position and these excess electrons are mainly placed on π orbitals. Thus according to this EHT calculation, the chloroethyl group is a weak electron donating substituent.

Chlorine atoms have a formal charge of −0.32 and the excess electon population on this atom are mostly valence inactive. This means that C-Cl bond has high polarity and covalent nature of the linkage is relatively weak. This is also shown in the M_{AB} values of C-Cl bonds which are given with other values of interest in Table IV. It can be seen from this Table that Mc-cl values are particularly low compared with other M_{AB} values. In comparing two similar reactions we are more or less obliged to assume that changes in solvation energy are the same, because of the complexity of solvent effects.

Table III Results for 2-Phenethyl Chloride (2-PEC)

Total Energy $= -827.646$ ev.

$\qquad = -19093.785$ Kcal.

$\epsilon^{LU} = -7.978$ ev.

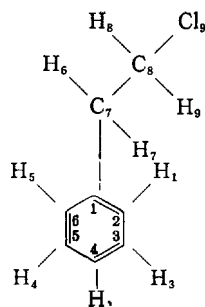$\epsilon^{HO} = -12.151$ ev.

$\Delta\epsilon = 4.173$ ev.

	Atomic Population					$\frac{1}{2}P_A$	Q_A
	Orbital				Gross		
	s	p_x	p_y	p_z			
H_1	0.8878				0.8878	0.5906	+0.1122
H_2	0.9101				0.9101	0.6097	+0.0899
H_3	0.9099				0.9099	0.6094	+0.0901
H_4	0.9098				0.9098	0.6095	+0.0902
H_5	0.9074				0.9074	0.6066	+0.0926
H_6	0.8911				0.8911	0.6080	+0.1089
H_7	0.8795				0.8795	0.5922	+0.1205
H_8	0.8989				0.8989	0.6052	+0.1011
H_9	0.8829				0.9929	0.5902	+0.1171
C_1	1.1524	0.9051	0.9173	0.9222	3.8970	2.6956	+0.1030
C_2	1.1651	0.9958	0.9605	1.0459	4.1674	2.8916	—0.1674
C_3	1.1610	0.9353	0.9912	0.9977	4.0852	2.7833	—0.0852
C_4	1.1612	0.9780	0.9505	1.0368	4.1266	2.8309	—0.1266
C_5	1.1610	0.9770	0.9503	0.9982	4.0866	2.7852	—0.0866
C_6	1.1625	0.9446	0.9916	1.0451	4.1438	2.8549	—0.1438
C_7	1.1508	0.9784	1.0186	1.0489	4.1966	2.8237	—0.1966
C_8	1.1498	0.7298	0.9432	1.0657	3.8884	2.5375	+0.1116
Cl_9	1.8376	1.6244	1.8680	1.9970	7.3270	7.1468	—0.3270

Therefore it has been stated[9] that electronic theories only predict the reacivity in a vacuum at absolute zero where $\Delta G^{\ne} = \Delta H^{\ne}$. The solvation effect of 1-PEC and 2-PEC may not differ significantly and this assumption is probably a safe one. The various molecular orbital approaches have been used in predicting reactivities and these can be classified into polarized state and activated state approximations.[9] There 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. In this work we will only be concerned with those reactivity parameters which are normally derived from the EHT analysis.

Table V shows the AO coefficients of C and Cl atoms which are broken in the nucleophilic attack. The LU levels are shown to be strong antibonding nature and this nature is stronger

Table IV Atomic Bond Population, M_{AB}

A—B	1-PEC	2-PEC
C_1—C_6	—	1.1152
C_2—C_3	—	1.0926
C_1—C_7	0.8244	0.8070
C_7—C_8	—	0.7355
C_8—Cl_9	—	0.5516
C_7—Cl_8	0.5541	—
C_7—C_9	0.7420	—
C_6—H_8	—	0.8427
C_9—H_7	0.8251	—

for 2-PEC. In the nucleophilic reaction it has been shown reasonable to assume that the nucleophile approaching interact with LU orbital and this orbital dictates the reactivity of substrate.[10] Thus in the activated state where the nucleophile is attached to the substrate C–Cl bond begins to break and this tendency is greater for 2-PEC than for 1-PEC. Bond breaking will therefore be easier for 2-PEC and rate of reaction faster accordingly. This relative reactivity prediction is supported by the atomic bond population of LU orbital for C–Cl, which are $M_{CCl}^{Lu}=-0.0014$ for 1-PEC and $M_{CCl}^{Lu}=-0.0104$ for 2-PEC. Here again antibonding nature is greater for 2-PEC.

The valence-inactive AO population of LU

level is called a frontier electron density, f_c^{LU} for nucleophilic reaction. The frontier electron densities are 0.0042 for 1-PEC ad 0.0326 for 2; PEC respectively.

According to Fukui et al, nucleophilic reactivity is greater, the larger the value of f^{LU}.[10] This means that 2-PEC will react faster than 1-PEC, again supporting the above predictions.

The MO quantities constidered so far in connection with reactivity are those for the activated state, i.e., for the state where attacking group has already formed partial bond and bond breaking is yet to progress in order to complete the reaction. At this stage bond breaking is more important in determining the reactivity.

However, if the bond formation has not progressed appreciably as in the polarized state where the systems, although interacting, are still recognizably distinct, the situation can be quite different. In this case, the slow approach of the nucleophile to the reaction center may be more important in determining the reactivity. This type of situation is encountered when the nucleophilicity of nucleophile is very small.

The formal charges of the carbon atom at the reaction center are +0.2547 for 1-PEC and +0.1116 for 2-PEC, respectively. Potential energy barrier for approaching nucleophile will be lower for the more positive reaction center.

Table V AO Coefficients

1-PEC				2-PEC			
		HO	LU			HO	LU
C_7	s	0.0179	0.0013	C_8	s	0.0044	−0.0017
	p_x	−0.0470	0.0204		p_x	0.0198	−0.0105
	p_y	−0.0141	0.0391		p_y	0.0821	−0.0029
	p_z	−0.0882	−0.0085		p_z	−0.0239	0.1275
Cl_8	s	−0.0250	−0.0028	Cl_9	s	0.0007	0.0194
	p_x	−0.1689	−0.0626		p_x	0.0723	0.0325
	p_y	0.1475	−0.1258		p_y	−0.0394	0.0158
	p_z	0.1281	0.0223		p_z	0.1236	−0.3234

Table VI   Rate Constants, $k_{55°}$, of Reactions in Acetone $RCl+X \to RX+Cl^-$

RCl	X^- ($k \times 10^4$)		
	Cl^-	Br^-	I^-
1-PEC	5.91	1.34	0.87
2-PEC	9.00	1.46	0.50

Thus bond formation will be easier in the case of 1-PEC than 2-PEC and rate will be faster accordingly. This is the reverse reactivity order to those obtained by activated state approximations above.

Halogen exchange reactions in acetone are typical $S_N 2$ reactions and best suited to test the predictions derived in this this work. The experimental data clearly distinguish the above possibilities and the predictions of opposite reactivity order are exactly borne out.

The exchange reaction rate constants in Table VI[11] shows that for the nucleophiles of relatively large nucleophilicity, Cl^- and Br^-, the reactivity order is $k2\text{-}PEC > k1\text{-}PEC$, while for the less reactive I^-, it is reversed to $k1\text{-}PEC > k2\text{-}PEC$.

This is in good accord with our MO theoretical predictions derived in this work.

In conclusion, the EHT analysis of nucleophilic reactivities of phenethyl chlorides can provide the correct prediction of relative reactivity and can even correctly predict the reversal of reactivity order for the less reactive nucleophile.

Acknowledgment

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