An MO-theoretical Interpretation of the Origin of the Orienting Effect in Aliphatic Systems

Hiroshi FUJIMOTO, Shinichi YAMABE, and Kenichi FUKUI
Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

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The importance of the charge-transfer interaction from the highest occupied (HO) molecular orbital (MO) of a donor to the lowest unoccupied (LU) MO of an acceptor molecule has been stressed on the basis of the numerical results of the calculation on a model of the S_N2 reaction of methyl chloride. The effect of a counter ion on the frontier orbitals has been discussed. For the E2 reaction of ethyl chloride, it has been discussed how the orienting effect of the leaving nucleophile is transmitted to the *trans*-β-hydrogen by means of the frontier electron density. The influence of the rotation about the C_α–C_β bond upon the reactivity of β-hydrogen has also been discussed.

In one of our previous papers, we have discussed the interaction energy between two reactant systems, A and B, partitioning it into four terms: the Coulomb, exchange, delocalization, and polarization interaction terms.[1] A succinct expression for each of these four terms has also been derived. On the basis of the three principles which govern the orientation and the spatial direction of chemical reactions, it has also been pointed out that the cooperation of the change in the molecular shape in the neighborhood of the reaction center with the charge-transfer interaction can be a driving force in a majority of chemical reactions.[2]

In this paper, we will present a further discussion of the physical meaning of the charge-transfer interaction and the orienting effect in the chemical reactions of aliphatic systems. To save space, the same notations as the previous paper[1] will be used, and no explanation will be repeated here.

The Delocalization Interaction

First of all, let us briefly mention the delocalization interaction terms in order to clarify the later discussion of the numerical computations. The delocalization interaction energy, D, is generally given by:

$$D = \sum_{i}^{occ}\sum_{l}^{uno} \frac{|H_{0,i\to l} - S_{0,i\to l}H_{0,0}|^2}{H_{i\to l,i\to l} - H_{0,0}} + \sum_{k}^{occ}\sum_{j}^{uno} \frac{|H_{0,k\to j} - S_{0,k\to j}H_{0,0}|^2}{H_{k\to j,k\to j} - H_{0,0}} \quad (1)$$

The denominator, $H_{i\to l,i\to l} - H_{0,0}$, can be expressed in terms of the ionization potential and the electron affinity:

$$H_{i\to l,i\to l} - H_{0,0} = I_{Ai}^{(B)} - E_{Bl}^{(A-i)} = I_{Ai}^{(B+l)} - E_{Bl}^{(A)} \quad (2)$$

in which:

I_{Ai}: the vertical ionization potential of the electron in the ith MO of the reactant A, and

E_{Bl}: the vertical electron affinity of the reactant B with respect to the lth MO.

$I_{Ai}^{(B+l)}$ is the value of I_{Ai} in the case of the approach of the system B with an additional electron occupying the lth originally unoccupied MO, and where $E_{Bl}^{(A-i)}$ is the value of E_{Bl} in the case of the approach of the system A, in which one electron occupying the ith MO is subtracted. The relations given in Eq. (2) can be easily visualized by means of a schematic diagram of the electron configurations without any formalism, as has been shown in one of our previous papers.[1]

The Delocalization Interaction and the Frontier Orbitals

Let us first consider the case in which two electronically neutral molecules interact with each other. The denominator of Eq. (1) is not simply expressed as $I_{Ai}-E_{Bl}$. The quantity $I_{Ai}^{(B)}$ represents the ionization potential of the ith MO of the reactant A under the influence of the reactant B. Since B is electronically neutral, $I_{Ai}^{(B)}$ may not differ very much from I_{Ai}. On the other hand, $E_{Bl}^{(A-i)}$ is the electron affinity of the lth MO of the reactant B in the cationic field of the reactant A, in which an electron in the ith MO is subtracted. Therefore, $E_{Bl}^{(A-i)}$ may be much greater than E_{Bl}. This implies that the denominator of Eq. (1) can be small enough in comparison with $I_{Ai}-E_{Bl}$.

Secondly, let us consider the case in which the reactant A is an anion and the reagent B is a neutral molecule. In this case, $E_{Bl}^{(A-i)}$ may be close to E_{Bl}, since the system A in which an electron in the ith MO is subtracted, is electronically neutral, while $I_{Ai}^{(B)}$ may be much smaller than those in neutral systems.

Lastly, let us consider the case where A is neutral and B is cationic. In this case, the $E_{Bl}^{(A)}$ may be greater than those in neutral systems, although $I_{Ai}^{(B+l)}$ may rather be close to I_{Ai}. Thus, we may come to the conclusion that the denominator of Eq. (1) is small enough when i denotes the HO MO of the donor, and l, the LU MO of the acceptor, among the various terms in D, in comparison with those simply expected from the $I_{Ai}-E_{Bl}$ of neutral molecules. In the interaction between an anion, A, and a cation, B, there may be cases in which $I_{Ai}^{(B)}-E_{Bl}^{(A-i)}$ is zero.

Even in not exactly degenerate case, the one-term approximation of D, such as Eqs. (4) and (5) in Ref. 2, may be valid for a majority of chemical interactions between the two reactant systems.

To exemplify these circumstances, we have carried out a numerical calculation on a model of the S_N2 reaction shown in Fig. 1. The MO's of the isolated species were obtained by means of an all-valence-shell ASMO SCF method which was similar to the one developed by Yonezawa *et al.*[3] The Coulomb electron repulsion integrals were estimated by point-charge approximation for intermolecular AO pairs. The

1) K. Fukui and H. Fujimoto, This Bulletin, **41**, 1989 (1968).
2) K. Fukui and H. Fujimoto, *ibid.*, **42**, 3393 (1969).

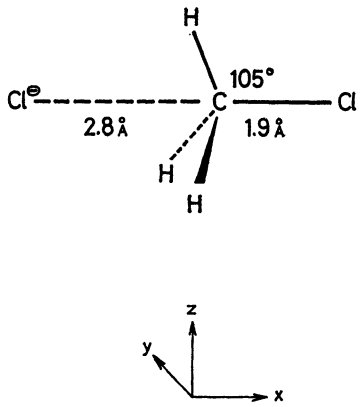


Fig. 1. The model of S_N2 reaction employed in this calculation.

integral, $\int t(1)(Z_\alpha e^2/r_{\alpha 1})t(1)\mathrm{d}v(1)$, was taken to be equal to $Z_\alpha e^2/R_{\alpha\gamma}$ if the AO t belongs to the γ ($\gamma \neq \alpha$) nucleus, while, when t belongs to α, it was estimated using the Slater AO's. The other multi-center integrals were all calculated by the use of the Mulliken approximation.[4] The results of the calculation on various $(H_{i\to l,i\to l}-H_{0,0})$ are given in Table 1. We can see that the terms corresponding to the charge-transfer configurations from the p_x, p_y, and p_z of the attacking chloride ion to the LU MO of methyl chloride are relatively small in comparison with the other terms. Three p orbitals in the attacking chloride ion are degenerate in the isolated state, while this degeneracy is removed in the event of interaction with methyl chloride.

Table 1. The values of $H_{i\to l,i\to l}-H_{0,0}$ (in eV) for the various charge-transfer configurations of $CH_3Cl\cdots Cl\ominus$ system

i	l			
	LU	LU+1	LU+2	LU+3
s	15.4819	27.9199	27.9199	33.2388
x	3.2279	16.3913	16.3913	22.7129
y	6.3149	17.5828	17.9707	24.9383
z	6.3149	17.9706	17.5828	24.9383

Orienting Effect

The numerator of Eq. (1) may be supposed to be proportional to the overlap integral between the wave function of a charge-transfer configuration and that of the zero configuration. Moreover, we have a relation:

$$S_{0,i\to l} \cong \sqrt{2}\, s_{il} \tag{3}$$

This implies that the ease of the mixing of the charge-transfer configuration from the ith occupied MO of the system A to the lth unoccupied MO of the system B is proportional to the overlapping of these specific MO's. Table 2 shows the values of s_{il} calculated with respect to the nuclear configuration shown in Fig. 1.

3) T. Yonezawa, K. Yamaguchi, and H. Kato, This Bulletin, **40**, 535 (1967).

4) R. S. Mulliken, *J. Chim. Phys.*, **46**, 497 (1949).

Table 2. The values of $|s_{il}|$ for the various charge-transfer configurations of $CH_3Cl\cdots Cl\ominus$ system

i	l			
	LU	LU+1	LU+2	LU+3
s	0.0434	0	0	0.0740
x	0.0608	0	0	0.0504
y	0	0.0346	0.0008	0
z	0	0.0008	0.0346	0

We can see that the p_y and p_z orbitals are orthogonal to the LU MO of methyl chloride, while p_x has the largest overlap with the LU MO. This is due to the symmetry of the LU MO of methyl chloride, which has its maximum extension in the direction of the x-axis. Here it should be noted that the attack of the chloride ion and the departure of the chlorine of methyl chloride take place in the direction parallel with the x-axis. As we have previously discussed,[2] the LU MO of methyl chloride has the largest partial electron population at the carbon atom and antibonding character in the region of the carbon-chlorine bond, supplying a cause of inversion in the event of a S_N2 reaction. Although the values of $(H_{i\to l,i\to l}-H_{0,0})$ for the $i=s$ of the chloride ion and the $l=$LU+3 of the methyl chloride are large, the overlap integral, s_{il}, corresponding to this charge-transfer configuration is quite large, also. However, according to the second principle in our previous paper,[2] the contribution of this configuration becomes less and less important as the nuclear configuration change takes place along with the chemical reaction. Moreover, the importance of the charge-transfer term from the HO MO of the donor to the LU MO of the acceptor is accentuated by the aid of the cationic species which are present in the environment of the electron-acceptor molecule and by the aid of the anionic species which exist in the neighbor of the electron-donor molecule. We have made a calculation of the system composed of methyl chloride and the lithium cation, as is shown in Fig. 2. The

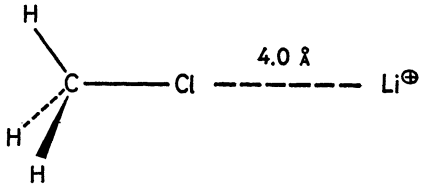


Fig. 2. The model employed for the calculation of the effect of a counter ion.

energy of the LU MO of methyl chloride is calculated to be 2.9570 eV, while that of the system shown in Fig. 2 is −4.5212 eV. In this case, the LU MO of the system comes to be almost degenerate with the HO MO of the chloride ion, which is calculated to be −3.4667 eV in our calculation. In real chemical MD of the chloride ion, which is calculated to be reactions, a reactant may hardly be exposed to the positive field of a bare nucleus. However, the one-term approximation of D, represented by Eqs. (4) and (5) in Ref. 2, might be valid in a majority of electron donor-acceptor interactions. Such an effect on MO's as to change their energy levels is an important role

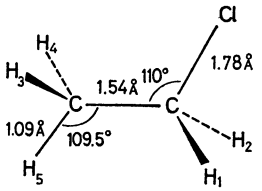
of counter ions, catalysts, solvents, and so on. This point will be discussed elsewhere.

Thus, we can conclude, as has already been discussed in our previous papers,[1,2] that the chemical reaction takes place at the position and in the direction where the overlapping of the HO MO of the electron-donor and the LU MO of the electron-acceptor is at its maximum; the present results support the conclusion fully.

Next, let us consider how the orienting effect of a nucleophile is transmitted to the *trans*-β-hydrogen, taking the case of the E2 reaction of ethyl chloride as an example. The partial valence-inactive population (C_r^2) and the partial valence-active population (v_r)[5] of β-hydrogen in the LU MO are given in Table 3.

Table 3. The partial valence-inactive and partial valence-active populations of hydrogens in LU of ethyl chloride

		Model I	Model II $F_{rs}\}=0$ $s_{rs}\}$ $r=Cl_{s,x,y,z}$ $s=H_3,H_4,H_5$	Model III $F_{rs}\}=0$ $s_{rs}\}$ $r=Cl_{s,x,y,z}$ H_1,H_2 $s=H_3,H_4,H_5$
$(C_r^{LU})^2$	3	0.0058	0.0058	0.0115
	5	0.0447	0.0453	0.0529
$v_r^{(LU)}$	3	−0.0027	−0.0030	−0.0065
	5	−0.0282	−0.0256	−0.0305



Model I is ethyl chloride, with the valence-angles and bond-lengths shown in the table, while Model II corresponds to the one in which the integrals between the chlorine and the 3, 4, and 5 hydrogens are put equal to zero in the secular equations and Model III is obtained by removing further the integrals between the 1 and 2 α-hydrogens and the 3, 4, and 5 β-hydrogens from Model II. We can see that the β-hydrogen *trans* to the chlorine has the largest frontier electron density ($(C_r^{(LU)})^2$) and anti-bonding character ($(v_r^{(LU)})^2$) among the three β-hydrogens in all of the three models presented in Table 3. This implies that the orienting effect of the nucleophile is transmitted to the *trans*-β-hydrogen mainly through the bonds having their maximum extension in the plane defined by chlorine, α,β-carbons, and *trans*-β-hydrogen.

Next, let us examine the change in the partial valence-inactive population and the partial valence-active population of hydrogens in the LU MO in the case of the rotation about the carbon α and carbon β bond axis. The results of the calculations on *n*-propyl chloride are shown in Table 4. It can be seen that the partial valence-inactive population of hydrogen in the LU MO is at its minimum when the plane involving the hydrogen and the α, β-carbons is perpendicular

Table 4. The partial valence-inactive and partial valence-active populations of hydrogens in LU of *n*-propyl chloride

$\theta°$	$(C_{H_1}^{LU})^2$	$v_{H_1}^{(LU)}$
0	0.0400	−0.0205
30	0.0261	−0.0132
60	0.0063	−0.0030
90	0.0003	−0.0003
120	0.0120	−0.0074
150	0.0330	−0.0200
180	0.0461	−0.0283

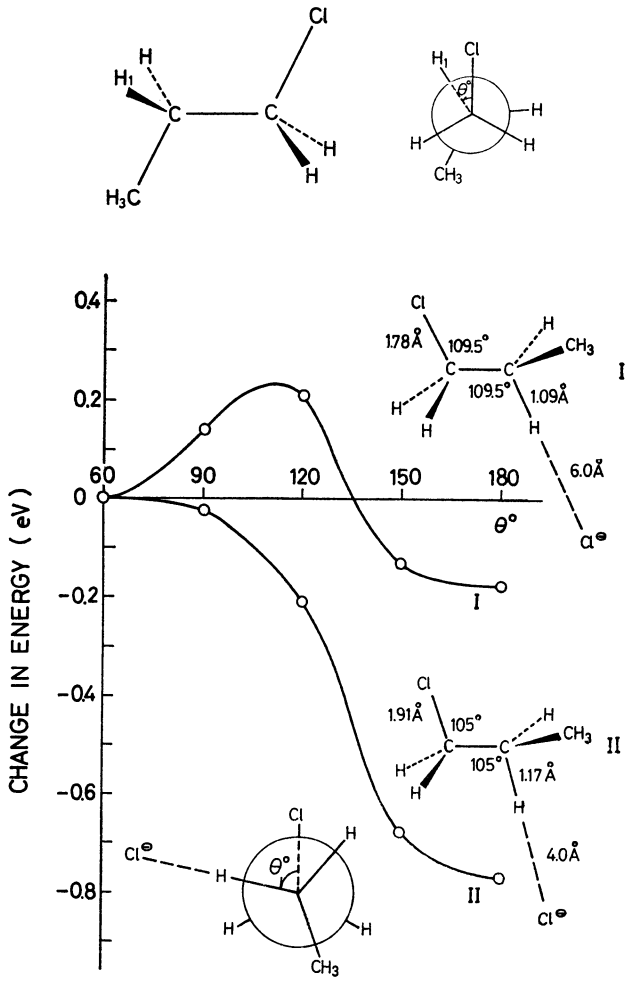


Fig. 3. The change in the energy of $CH_3CH_2CH_2Cl$----$Cl^{\ominus}$ system with the rotation about C_α—C_β axis.

to the one determined by the chlorine and the α, β-carbons, while it is at its maximum when the former is identified as the latter. When the methyl group is located *trans* to chlorine, the partial valence-inactive population of hydrogen in the LU MO is 0.0063. If the hydrogen comes to the *trans* position with respect to chlorine, the partial valence-inactive population increases to 0.0461. We have calculated the total energy of the system composed of *n*-propyl chloride and chloride ion in Fig. 3. The results shown in Fig. 3 have been obtained with reference to the approximation employed by Del Re and Parr in estimating

5) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).

the nuclear repulsion energy.[6] We can see that the *gauche* form ($\theta=180°$) with respect to methyl and chlorine has a lower total energy than the *trans* form ($\theta=60°$) separated by a relatively low rotation barrier. A distinct parallelism has been shown to exist between the experimentally-observed rate constant of the E2 reaction and $(C_r^{(LU)})^2$, an approximate form of D, for a variety of alkyl halides.[7] *n*-Propyl bromide is found to be more reactive than ethyl bromide.[8] This also seems to indicate that hydrogen in *n*-propyl chloride is liable to be abstracted at the *trans* position to chlorine. This is conceivable, since the partial valence-inactive population of *trans*-β-hydrogen of ethyl chloride in the *staggered* form is 0.0447. Similar considerations may hold for other alkyl chlorides.

The results in Table 4 show that the β-hydrogen at the *cis* position to chlorine in an *eclipsed* *n*-propyl chloride ($\theta=0°$) has a larger reactivity toward a nucleophile than the other β-hydrogen ($\theta=120°$). This implies that if a molecule is rigidly fixed to the *eclipsed* form, selective *cis* elimination may take place. This may be a principal reason for the preferential *cis-exo* elimination of hydrogen bromide in *exo*-2-bromonorbornane.[9] Such an orienting effect of the leaving nucleophile should always be kept in mind in discussing the chemical reactivity of hydrogens in cyclic systems.

We have discussed the important role of the charge-transfer between the frontier orbitals and the origin of the orienting effect in terms of the frontier electron density for several chemical reactions of aliphatic systems, demonstrating how the so-called "anti-coplanar" selectivity in E2 reactions could arise.

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6) G. Del Re and R. G. Parr, *Rev. Mod. Phys.*, **35**, 604 (1963).
7) K. Fukui, H. Hao, and H. Fujimoto, This Bulletin, **42**, 348 (1969).
8) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca (1969), p. 651.
9) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).