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A THEORETICAL INTERPRETATION OF THE INTERACTION ENERGY IN BIMOLECULAR SUBSTITUTION REACTIONS

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In some of our previous papers,[1] the interaction energy between two reacting molecules has theoretically been discussed in terms of chemically graspable concepts. The energy is there divided into a few terms, including the usual electrostatic and exchange terms. The importance of the effect of electron delocalization between the reactants which originates from the mixing of charge-transfer configurations has been stressed. The purpose of this paper is to present some numerical results to compare the magnitude of each term, with reference to the bimolecular substitution of methyl chloride, which will presumably provide us with a simplest suitable example.

The interaction energy ΔW, the difference between the lowest total energy of the mutually-interacting system of two molecules and the sum of the initial stationary state energies of the two isolated molecules, is approximately given by the following equation, provided that the interaction is not yet very strong;

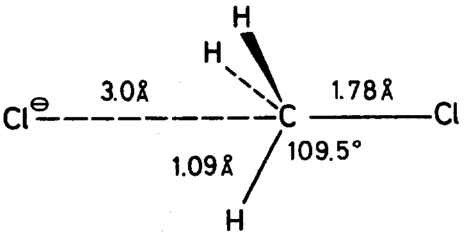
$$\Delta W = \varepsilon_Q + \varepsilon_K - D - \Pi$$

where ε_Q is the Coulomb interaction energy, ε_K is the exchange interaction energy, D is the delocalization interaction energy, and Π is the polarization interaction energy. The full presentation of these four terms can be found in our previous paper.[1a]

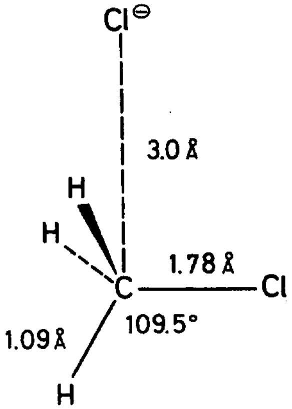
Here, we take, for the simplicity in calculation, a chloride ion as the attacking base. The molecular orbitals (MO) used have been obtained from an all-valence-shell-electron SCF method.[2] The ionization potentials of methyl chloride and chloride ion obtained by this calculation are 11.447 eV and 3.467 eV, respectively, showing a fairly good agreement with the observed values.[3] The results of calculations of the interaction energies are given in Table I with respect to two different models.

Table I. The Calculated Results of the Interaction Energies.

	Model I (eV)	Model II (eV)
ε_Q	-0.7876	-0.2594
ε_K	1.1641	1.5932
D	1.0525	0.3111
π	0.1762	0.1288



Model I



Model II

It is clear that Model I is more stable than Model II. Thus, we may say, although Models I and II are very arbitrarily set up, the course which leads to the inversion process is more favourable. The preference of the back-side attack of base to the carbon atom is highly attributable to the magnitude of *D*. The large difference in *D* with respect to Models I and II is related to the nodal property of the lowest unoccupied (LU) MO of methyl chloride which has the maximum extension at the back-side of the carbon atom in the direction along the C-Cl axis.

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REFERENCES and NOTES

1. (a) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Japan*, 41, 1989 (1968);
   (b) K. Fukui, *Fortsch. chem. Forsch.*, 15, 1 (1970).
2. Our method of SCF calculation, employed to obtain the MO's of each of the two reacting molecules in isolated state, is the same as the one which has been developed by Yonezawa et al. (See, for instance, H. Kato, H. Konishi and T. Yonezawa, *Bull. Chem. Soc. Japan*, 40, 1017 (1967).), except that off-diagonal core integrals, H_{rs} ($r \neq s$), are estimated by the use of the Wolfsberg-Helmholtz scheme (M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, 20, 837 (1952).) in our calculation.

   In calculating interaction energy, the following approximations were adopted: (i) the atomic repulsion integral $(tt|uu)$ is put equal to $e^2/R_{\alpha\beta}$ for the intermolecular separation, where the atomic orbital (AO) t belongs to the nucleus α of reactant A and AO u to the nucleus β of reactant B; (ii) the integrals $\int t(1)(-Z_\alpha e^2/r_{\alpha 1})t(1)dv(1)$ is taken equal to be $-Z_\alpha e^2/R_{\alpha\gamma}$ when the AO t belongs to the nucleus γ ($\gamma \neq \alpha$), while, when t

belongs to α, it is calculated theoretically using the Slater AO's; (iii) Other multi-center integrals are all estimated by the use of the Mulliken approximation (R. S. Mulliken, *J. chim. phys.*, 46, 497 (1949)).

3. (a) K. Watanabe, *J. Chem. Phys.*, 26, 542 (1957);

   (b) T. L. Bailey, *ibid.*, 28, 792 (1958).