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A Remark on the Applicability of the CNDO Calculation to the Chemical Reactivity Theory

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The usefulness of the CNDO calculation for the interpretation of the chemical and physical properties of organic molecules has been verified in numerous cases.[1] The extended Hückel MO method gave good results with respect to the calculation of the chemical reactivity index, the frontier electron density, of hydrogens in the E2 reaction of some halogenated hydrocarbons, in the base-catalyzed allylic rearrangement of some olefins, and in the halogenation of norbornane.[2-4] It has been reported, however, that the extended Hückel MO method sometimes fails to give satisfactory results when it is applied to a molecule containing polar bonds.[5] The discrepancy may partly be attributed to the unreasonable parametrizations due to the ambiguity of the physical meaning of the one-electron Hamiltonian operator in this method.[6] Hence, it may be expected that the CNDO method can be a convenient means for discussing the chemical reactivity of sizable molecules, since the electron populations are smoothed out by the self-consistent-field iteration procedure. The purpose of this note is to present the results of our CNDO calculation of the chemical reactivity of the hydrogens of some substituted and unsubstituted hydrocarbons. The method of calculation is CNDO/2, using the integrals given in the literature.[1]

Chemical Reactivity of Hydrogens toward Nucleophilic Abstraction. The frontier electron density of a hydrogen for nucleophilic reactions is defined by;[7]

$$f_r^{(N)} = 2(C_r^{(\mathrm{LU})})^2$$

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[1] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York (1970).

[2] a) K. Fukui and H. Fujimoto, *Tetrahedron Lett.*, **1965**, 4303. b) K. Fukui, H. Hao, and H. Fujimoto, This Bulletin, **42**, 348 (1969).

[3] H. Fujimoto, H. Oba, and K. Fukui, *Nippon Kagaku Zasshi*, **90**, 1005 (1969).

[4] H. Fujimoto and K. Fukui, *Tetrahedron Lett.*, **1966**, 5551.

[5] See, for instance, M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York (1969).

[6] K. Fukui and H. Fujimoto, This Bulletin, **40**, 2787 (1967).

[7] K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *J. Chem. Phys.*, **22**, 1433 (1954).

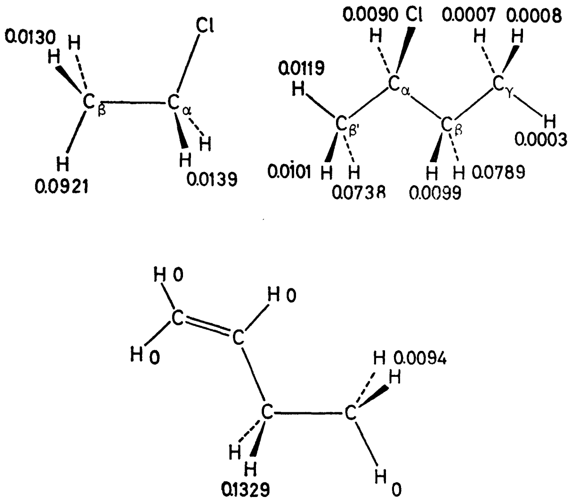

Fig. 1. Frontier electron densities of hydrogens toward nucleophilic abstraction.

where $C_r^{(LU)}$ is the coefficient of the hydrogen, 1s AO r, in the lowest unoccupied (LU) MO. Figure 1 shows that β-hydrogens of ethyl chloride and 2-chlorobutane which are located *trans* to chlorine are most reactive toward the attacking nucleophile, while, in the case of butene-2, the allylic hydrogens have the largest frontier electron density, which is in accordance with the experimental results.[8,9]

Chemical Reactivity of Hydrogens toward Homolytic Abstraction. The frontier electron density of a hydrogen for homolytic reactions is defined by;

$$f_r^{(R)} = (C_r^{(HO)})^2 + (C_r^{(LU)})^2$$

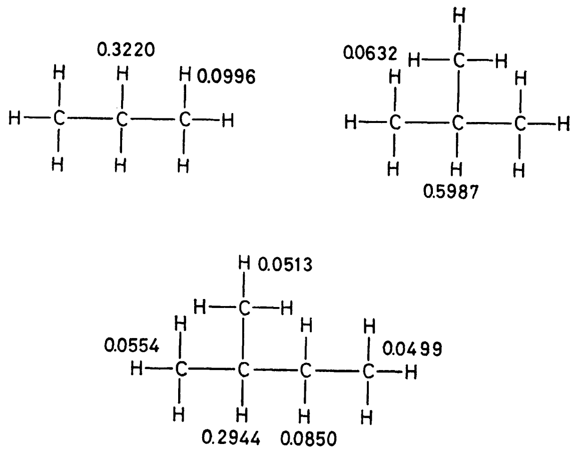

Fig. 2. Frontier electron densities of hydrogens toward homolytic abstraction.

where HO implies the highest occupied MO. Figure 2 shows the $f_r^{(R)}$ values of hydrogens in propane, isobutane, and isopentane. The values indicate the averages with respect to three hydrogens of primary carbons and two hydrogens of secondary carbons. The frontier electron densities decrease in this order:

tertiary > secondary > primary

showing a good agreement with the well-established experimental results.[10]

In some unfortunate cases, the MO levels calculated by the CNDO method may happen to be in an unrealistic order. The present results suggest, however, that the chemical reactivity index, the frontier electron density, obtained from the CNDO MO wave function can be a suitable measure for an intramolecular comparison of the chemical reactivities in a variety of organic compounds.

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[8] See, for instance, E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Reinhart and Winston, New York (1959) p. 472.

[9] a) A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *J. Amer. Chem. Soc.*, **84**, 3164 (1962). b) S. Bank, C. A. Rowe, Jr., and A. Schriesheim, *ibid.*, **85**, 2115 (1963).

[10] See Ref. 8, p. 695.