"Frontier Electron Density" in Saturated Hydrocarbons

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Several simple quantum-mechanical methods have been proposed to discuss the physical properties of aliphatic compounds[1-3], but they were not always successful in interpreting quantum-chemically the chemical reactivity of these compounds.

In our previous papers treating aliphatic compounds, we calculated the ionization potential, the bond energy[4] and the reactivity in nucleophilic substitution[5] by using Yoshizumi's C–C skeleton method[6].

In the present paper, we have investigated the chemical reactivity of several aliphatic hydrocarbons in a metathetical reaction by using the simple LCAO MO method including all of the atomic orbitals which participate in forming C–C and C–H σ bonds in these compounds. The molecular orbital of aliphatic hydrocarbons, ϕ_j, may be represented by a linear combination of 1s orbitals of hydrogen atoms, ϕ_{Hl}, and sp^3 orbitals of carbon atoms, ϕ_{Cr}.

$$\phi_j=\sum_r C_{rj}\phi_{Cr}+\sum_l C_{lj}\phi_{Hl}$$

where C_{rj}, C_{lj} are the coefficients of the rth sp^3 orbital of carbon atom and the lth 1s orbital of hydrogen atom in the jth molecular orbital, respectively.

The resonance integrals between neighboring atomic orbitals are assumed

$$\int \phi_{C,n} H \phi_{H,n+1} d\tau = b\beta$$

1) R. D. Brown, *J. Chem. Soc.*, **1953**, 2615.
2) M. J. S. Dewar and R. Pettit, ibid., **1954**, 1625.
3) J. Lennard-Jones and G. G. Hall, *Disc. Faraday Soc.*, **53**, 127 (1957).
4) K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **33**, 1197 (1960).
5) K. Fukui, H. Kato and T. Yonezawa, ibid., **33**, 1202 (1960).
6) H. Yoshizumi, *Trans. Faraday Soc.*, **53**, 125 (1957).

the sp^3 orbital of carbon and the 1s orbital of hydrogen in a C–H σ bond:

$$\int \phi_{C,r} H \phi_{C,r+1} d\tau = \beta$$

between two sp^3 orbitals of two adjacent carbon atoms each:

$$\int \phi_{C,r} H \phi_{C,r+1} d\tau = m\beta$$

between two sp^3 orbitals belonging to one and the same carbon atom:

The Coulomb integrals are taken as

$$\int \phi_{Hl} H \phi_{Hl} d\tau = \alpha + a\beta$$

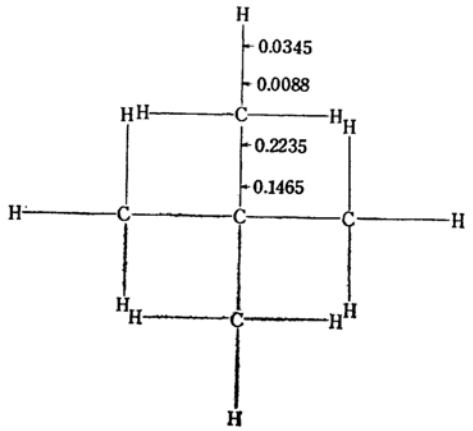
$$\int \phi_{C,r} H \phi_{C,r} d\tau = \alpha$$

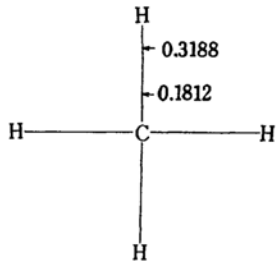
All overlap integrals are neglected.

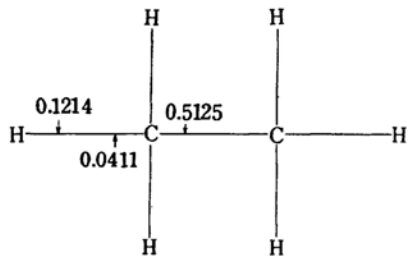
The values of m is taken as 0.34 determined by Yoshizumi, a is put equal to -0.2 referring the value of C–H bond moment ($C^{-\delta}$–$H^{+\delta}$, 0.4 D),* and b is put 1.1 which is the ratio of the overlap integral S_{C-H} to S_{C-C}[7].

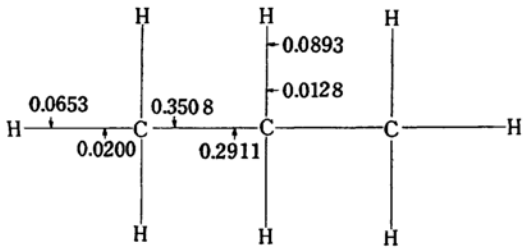
The calculated values of ionization potential and heat of formation of several compounds are listed in Table I, where the values of α and β are taken as -5.05 eV. and -8.8 eV., tentatively.

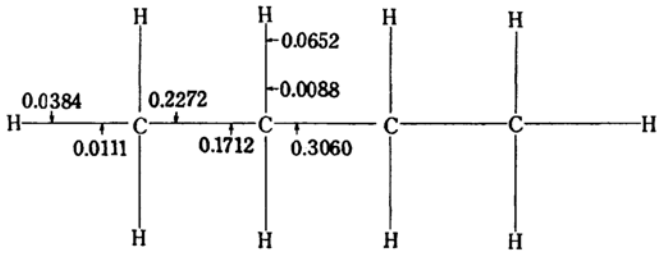
Since a good agreement between the calculated and experimental values is observed in this table, the numerical estimation of these parameters is considered to be reasonable.











7) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, 17, 1248 (1949).

* The value of a varies according as the hydrogen atom is primary, secondary or tertiary. In the present treatment a is taken as the same for simplicity's sake. Future improvement is expected with regard to this point.

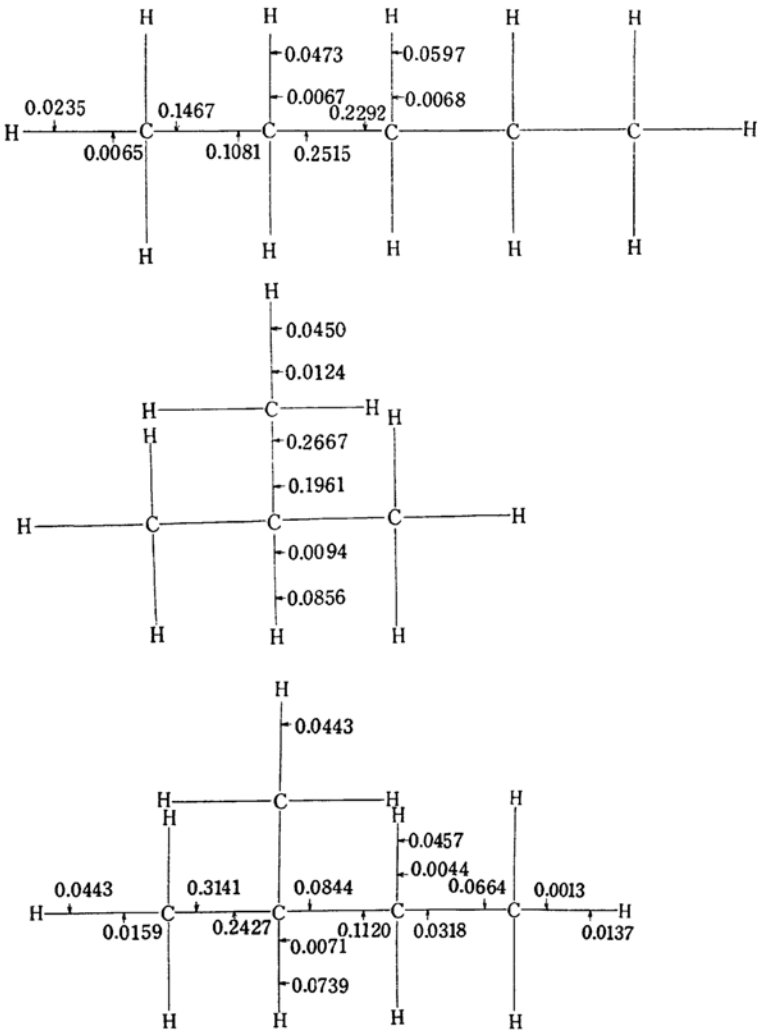


Fig. 1. The values of $f^{(R)}$ in several saturated hydrocarbons.

TABLE Ia. IONIZATION POTENTIAL

	Calcd. I. P.		Obs. I. P.[a]
	λ_{ho}	ε_{ho} eV.	eV.
CH_4 (1st)	0.8322	12.37	13.16
CH_4 (2nd)	1.6546	19.61	19.80
C_2H_6	0.7254	11.43	11.76
C_3H_8	0.7009	11.22	11.21
C_4H_{10}	0.6871	11.10	10.80

where λ_{ho} is the coefficient $\varepsilon_{ho}=\alpha+\lambda_{ho}\beta$, ε_{ho} is the highest occupied orbital energy.

The metathetical reaction of paraffins is expressed by the equation

$$R\text{-}H+\cdot X \rightarrow R\cdot + H\text{-}X$$

where R is an alkyl group and $\cdot X$ is an attacking radical.

We previously proposed the frontier electron

TABLE Ib. TOTAL ENERGY AND HEAT OF FORMATION

	Calcd.	Obs. heat of formation[b] kcal./mol.	Difference: Calcd. $-\beta$	Difference: Obs. kcal.
CH_4	$8\alpha+8.329\beta$	-17.9		
			6.334	-2.3
C_2H_6	$14\alpha+14.663\beta$	-20.2		
			6.337	-4.6
C_3H_8	$20\alpha+21.000\beta$	-24.8		
			6.368	-5.4
C_4H_{10}	$26\alpha+27.368\beta$	-30.2		

a) R. E. Hornig, *J. Chem. Phys.*, **16**, 105 (1948).
b) F. D. Rossini, K. S. Pitzer et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", Carnegie Press (1953).

density[8], $f^{(R)}$, as an excellent reactivity index for a radical reaction of conjugated systems. Now we can show that $f^{(R)}$ is found to be also available as the reactivity index of saturated compounds.* The calculated values of $f^{(R)}$ in several compounds are listed in Fig. 1. It is observed that the values of $f^{(R)}$ on hydrogen atoms in these compounds is parallel with the experimental results. That is to say, the activity of hydrogen-extraction in saturated hydrocarbons increases in the order *prim.* H $<$*sec.* H $<$*tert.* H[9].

Thus, the frontier electron density has been found to relate with the experimental chemical reactivity of aliphatic saturated molecules.

An application of this fact to explaining the reaction mechanism of oxidation or pyrolysis in aliphatic hydrocarbons seems to be possible.

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8) K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, ibid., **22**, 1432 (1954).

* According to the electronegativity of the attacking radical, $f^{(E)}$ or $f^{(N)}$ (frontier electron densities for electrophilic or nucleophilic attack) may be used in lieu of $f^{(R)}$. In the present case we are imagining e. g.·CH_3 for the attacking radical, whose energy level seems to lie between the highest occupied and the lowest vacant orbitals of R-H.

9) A. F. Trotman-Dickenson, *Quart. Revs.*, **7**, 198 (1953).