A Molecular Orbital Theory of Saturated Compounds. I. Ionization Potential and Bond Dissociation Energy

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(Received February 10, 1960)

Recently, several simple quantum-mechanical methods have been proposed to discuss physical properties of saturated compounds. That is to say, the bond energy and the heat of formation have been studied by Brown's bond orbital method[1] and by Dewar's perturbation treatment[2]. The ionization potential and the electron affinity have been investigated by the equivalent orbital method of Lennard-Jones and Hall, Franklin's united atom treatment[4], and Higuchi's UAO method[5].

In the present paper, the aliphatic and alicyclic compounds will essentially be treated by the use of the method previously presented by Yoshizumi[6], in which the skeleton consisting of carbon chain in an aliphatic molecule was exclusively taken into consideration. Thus, the ionization potential, heat of formation and bond energy of various saturated compounds are calculated according to this procedure, and the results obtained are in good agreement with experiments.

Theoretical

Yoshizumi applied the strategy which was usual for treating the π-electron system to attacking the σ electron system. Namely, in treating aliphatic molecules the sp^3-hybridized orbital of a carbon atom appeared in place of the $2p\pi$ atomic orbital in the treatment of conjugated molecules. He neglected the C–H bond of paraffin hydrocarbons for the sake of simplicity. Thus the molecular orbital was represented by a linear combination of sp^3 hydridized orbitals of carbon atoms, as follows:

$$\phi_j = \sum_j C_{rj}\phi_r \qquad (1)$$

where C_{rj} is the coefficient of the rth atomic sp^3 hybridized orbital of carbon, ϕ_r, in the jth molecular orbital, ψ_j. All the overlap integrals were neglected as in the simple LCAO MO theory in π-electron system. The resonance integrals in C–C bond and that between the orbitals attached to the same carbon atom were assumed as

$$\int \phi_i H \phi_{i+1} d\tau = \beta$$

and

$$\int \phi_i H \phi_{i+1} d\tau = m\beta$$

respectively, where m was a small quantity which was determined by Yoshizumi as $m^2 = 0.12$ referring to the value of dipole moment of halogen-substituted hydrocarbons. The resonance integrals between non-neighboring atomic orbitals were neglected. In Fig. 1, it will be seen that when the number of an orbital i is odd, the integral corresponds to that between two adjacent carbon atoms, and when i is even, the resonance integral between two atomic orbitals of one and the same carbon atom.

In Yoshizumi's paper only linear paraffins were treated. In treating the other saturated compounds, it is necessary to introduce some emprical parameters besides.

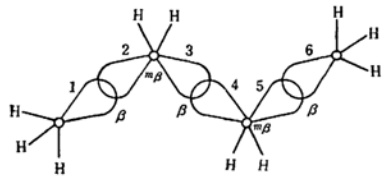

Fig. 1. Carbon sp^3 hybridized orbitals in *n*-butane.

Parameters

For tertiary and quaternary carbon atoms in branched chain hydrocarbons, the Coulomb integral is tentatively taken as $\alpha_C = \alpha - \delta\beta$ in common according to their electronegativity, where α is the Coulomb integral of sp^3 hybridized orbital of primary and secondary carbon atoms. The value of δ is determined as equal to 0.3 considering the value of ionization potential of *i*-butane.

For alkyl halides (R–X), the Coulomb integral, α_X, is taken as $\alpha + a\beta$ and the resonance integral, β_{C-X} as equal to $b\beta$, where b is determined by the formula $\frac{\beta_{C-X}}{\beta_{C-C}} = \frac{S_{C-X}}{S_{C-C}}$ (S is

1) R. D. Brown, *J. Chem. Soc.*, **1953**, 2615.
2) M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, **1954**, 1625.
3) J. Lennard-Jones and G. G. Hall, *Disc. Faraday Soc.*, **10**, 18 (1951); G. G. Hall, *Proc. Soc.*, **A213**, 102 (1952), *Trans. Faraday Soc.*, **49**, 113 (1953).
4) J. L. Franklin, *J. Chem. Phys.*, **22**, 1304 (1954).
5) J. Higuchi, *Summary of Electronic Structure Symposium*, 23 (1958).
6) H. Yoshizumi, *Trans. Faraday Soc.*, **53**, 125 (1957).

obtainable from Mulliken's table[7]*) and a is determined referring to the values of ionization potential of C–X bonding electron of methyl halides assigned by McDowell[8]. The values of a and b used in the present paper are listed in the following table.

X	a	b
F	0.91	0.51
Cl	0.56	0.65
Br	0.54	0.58
I	0.50	0.53

For alkyl alcohols, the Coulomb integral of alcoholic oxygen, α_{OH}, is taken as $\alpha+0.5\beta$ and the resonance integral, β_{C-OH}, as 0.5β, where β_{C-OH} is determined by using the formula stated above (the value of S_{C-OH} is put nearly equal to that of S_{C-O}). Since the value of the ionization potential of C–OH bonding electron of methyl alcohol has never been known, the value of α_{OH} is tentatively assumed as above.

Results and Discussion

a) Ionization Potential.—(1) It was pointed out[8,9] that in normal parraffins their first ionization could be attributed to the removal of one electron localized in C–C bonds. This was supported by the difference between observed C–H and C–C bond energies, and also by the result of Hall's calculation[3]. Namely, he elucidated the theory that in the highest occupied orbital of normal paraffins the electron density of C–C bond was larger than that of C–H bond. Therefore, the ionization potential may safely be considered to be equal to the negative of the highest occupied orbital energy obtained by solving the secular determinant. The calculated results are listed in Table I, and the plot of calculated energy values versus observed ionization potentials is shown in Fig. 2. From the linear relation between the calculated and the observed, the values of α and β are estimated as -5.850 eV. and -6.364 eV., respectively. With these values, the recalculated ionization potentials of paraffins are listed in the third column of Table I which are in good agreement with the observed, except in ethane.

TABLE I. CALCULATED ENERGIES OF THE HIGHEST OCCUPIED ORBITAL AND OBSERVED IONIZATION POTENTIALS OF NORMAL PARAFFINS

Compound	Calcd. energy[a] λ_{ho}	ε_{ho} eV.	Obsd. I. P.[9] eV.
Ethane	1.0000	12.21	11.76
Propane	0.8444	11.22	11.21
n-Butane	0.7752	10.77	10.80
n-Pentane	0.7388	10.55	10.55
n-Hexane	0.7170	10.41	10.43
n-Heptane	0.7034	10.33	10.35
n-Octane	0.6921	10.25	10.24
n-Decane	0.6820	10.19	10.19

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

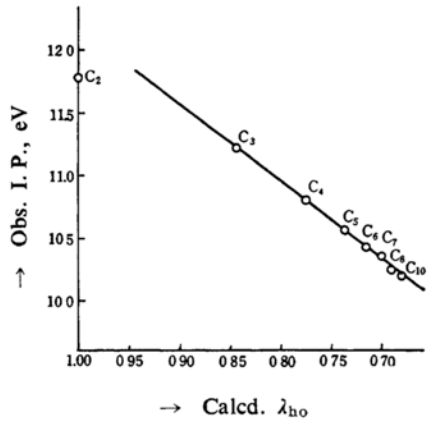

Fig. 2. Ionization potential of normal paraffins vs. λ_{ho}.

(2) In the calculation of cycloparaffins the steric configuration is left out of consideration, all the C–C–C angles being assumed equal to that of linear molecules. Therefore, no parameter is introduced anew. The results are listed in Table II, together with observed and Franklin's values[4] for the sake of comparison. It is seen that the smaller the deviation of an actual C–C–C angle from the normal one, the better agreement between the observed and the calculated results is found. This suggests that there is some room for improvement in future.

(3) For branched chain paraffins, the calculated values of ionization potentials are listed in the third column of Table III.

(4) It is considered that the first ionization potential of alkyl alcohols is due to removal of one of the lone pair electrons of the oxygen atom. The correlation of calculated values of the highest occupied orbital energies with observed ionization potentials is examined and an apparent linear relation between them is shown in Table IV, and it may result from the following cause. In general, the inductive effect of alkyl group may exert an influence

* The evaluation of the overlap integral, S_{C-X}, for bromine using the Slater orbital can not be carried out in the usual way. Therefore, the nearest integral power of r in Slater orbital is adopted in our calculation.

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

8) D. C. Frost and C. A. McDowell, *Proc. Roy. Soc.*, **A241**, 194 (1957).

9) R. E. Hornig, *J. Chem. Phys.*, **16**, 105 (1948).

TABLE II. CALCULATED ENERGIES OF THE HIGHEST OCCUPIED ORBITAL AND OBSERVED IONIZATION POTENTIALS OF CYCLOPARAFFINS

Compounds	Calcd. energy λ_{ho}	Calcd. energy ε_{ho} eV.	Calcd. I. P.[4] by Franklin eV.	Obsd. I. P. eV.	Deviation[b] from normal C-C-C angle
Cyclopropane	0.8806	11.45	11.76	10.23[4]	+24°44′
Methylcyclopropane	0.7050	10.34	10.98	9.88[4]	—
Cyclobutane	0.6600	10.05	10.21		+ 9°44′
Cyclopentane	0.7520	10.64	10.80	11.10[a]	+ 0°44′
Cyclohexane	0.6600	10.05	10.21	10.40[4]	− 5°16′

a) J. Hissel, *Bull. Soc. Roy. Sci. Liege*, **21**, 4576 (1952).
b) L. F. Fieser and M. Fieser, "Textbook of Organic Chemistry", D. C. Heath Co., Boston (1950).

TABLE III. CALCULATED ENERGIES OF THE HIGHEST OCCUPIED ORBITAL AND OBSERVED IONIZATION POTENTIALS OF BRANCHED PARAFFINS

Compounds	Calcd. energy λ_{ho}	Calcd. energy ε_{ho} eV.	Obsd. I. P. eV.
Methylpropane	(0.6995)	(10.30)	10.40[a]
Tetramethylmethane	0.6995	10.30	10.30[b]
Ethylpropane	0.6469	9.96	10.19[c]
2,2-Dimethylbutane	0.6378	9.93	9.90[c]
3-Methylpentane	0.6222	9.81	9.81[c]

a) D. P. Stevenson, *J. Am. Chem. Soc.*, **64**, 2766 (1942).
b) D. P. Stevenson, *Disc. Faraday Soc.*, **10**, 35 (1951).
c) M. B. Koffel, *J. Chem. Phys.*, **17**, 44 (1948).

TABLE IV. CALCULATED ENERGIES OF THE HIGHEST OCCUPIED ORBITAL AND TOTAL ELECTRON DENSITIES AT OXYGEN AND OBSERVED IONIZATION POTENTIALS OF ALKYL ALCOHOLS

Compounds	Calcd. energy λ_{ho}	Calcd. total dens. at oxy.	Obsd. I. P. eV.
Methyl alcohol	(0.8090)	1.4472	10.95[a]
Ethyl alcohol	0.7589	1.4618	10.60[a]
Propyl alcohol	0.7350	1.4643	10.46[a]
Butyl alcohol	0.7180	1.4712	10.30[b]
i-Propyl alcohol	0.6807	1.4784	10.27[b]

a) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).
b) Reference 10).

on the electronegativity of oxygen lone pairs[10]. Therefore, the parallelism may be more directly understood by comparing the observed ionization potential with the magnitude of total σ electron density the oxygen atom which is also given in the same table.

10) I. Omura, H. Baba and K. Higashi, This Bulletin, **28**, 147 (1955).

b) Total Electronic Energy and Bond Dissociation Energy.—The calculated total electronic energies are compared with observed values of heat of formation of several normal paraffins. The results indicate a good parallelism between them. For each increase of one CH_2-group the increment in the calculated energy lies between $2\alpha+2.057\beta$ and $2\alpha+2.059\beta$, while the observed difference in energy is in the range $-4.6\sim-5.2$ kcal./mol.[1] as shown in Table V. For cycloparaffins, the calculated total electronic energies are compared with observed heats of combustion and both the values per CH_2 are listed in Table VI*. Thus we can conclude that a simple additivity rule may approximately hold in normal paraffins and cycloparaffins.

In order to calculate the bond dissociation energy, we assume that it can be obtained by the following formula**.

$$D(R_1-R_2)=\{E(R_1\cdot)+E(R_2\cdot)\}-E(R_1-R_2) \quad (2)$$

where $D(R_1-R_2)$ denotes the dissociation energy of the bond between R_1 and R_2 in the compound R_1-R_2, E is the total electronic energy, and R_1 and R_2 are two alkyl groups. For simplicity, the energy of an odd electron in alkyl radical, which is localized on one carbon atom, is assumed equal to α. The results are listed in Table VII, where the numbers in parentheses are the observed values of bond energy and the numbers below them are the calculated values of bond energy in units of $(-\beta)$. In lower paraffins, the values obtained by Eq. (2) are shown to be a good measure for bond energy value. In hexane, a slight disagreement is observed. No internuclear repulsion is involved in the present treatment, and hence this discrepancy may, at

* The failure seen in the case of cyclobutane may probably be attributed to the approximation adopted in which steric circumstances are entirely disregarded.

** In the calculation of energy of alkyl radicals, the effect of hyperconjugation of alkyl group is left out of account.

TABLE V. CALCULATED TOTAL ELECTRONIC ENERGIES AND OBSERVED HEATS OF FORMATION OF NORMAL PARAFFINS

Compounds	Calcd. total energy	Obsd. heat of formation[a] kcal./mol.	Difference Calcd.	Difference Obsd. kcal./mol.
Ethane	$4\alpha+2.000\beta$	−20.2		
			$2\alpha+2.057\beta$	−4.6
Propane	$6\alpha+4.057\beta$	−24.8		
			$2\alpha+2.058\beta$	−5.0
n-Butane	$8\alpha+6.115\beta$	−29.8		
			$2\alpha+2.058\beta$	−5.2
n-Pentane	$10\alpha+8.157\beta$	−35.0		
			$2\alpha+2.058\beta$	−5.0
n-Hexane	$12\alpha+10.231\beta$	−40.0		
			$2\alpha+2.059\beta$	—
n-Heptane	$14\alpha+12.290\beta$	—		

a) F. D. Rossini et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", Carnegie Press, Pittsburgh (1953).

TABLE VI. CALCULATED TOTAL ELECTRONIC ENERGIES AND OBSERVED HEATS OF COMBUSTION OF CYCLOPARAFFINS

Compounds	Calcd. energy Total	Calcd. energy per CH_2	Obsd. heat of combustion[a] Total kcal./mol.	Obsd. heat of combustion[a] per CH_2 kcal./mol.
Cyclopropane	$6\alpha+6.203\beta$	$2\alpha+2.067\beta$	505.5	168.5
Cyclobutane	$8\alpha+8.225\beta$	$2\alpha+2.056\beta$	662.5	165.5
Cyclopentane	$10\alpha+10.293\beta$	$2\alpha+2.059\beta$	797	159
Cyclohexane	$12\alpha+12.348\beta$	$2\alpha+2.058\beta$	939	157

a) Reference b) in Table II.

TABLE VII. DISSOCIATION ENERGIES OF C–C BONDS

R_1 \ R_2	Methyl	Ethyl	Propyl	Butyl
Methyl	(82) 2.000	(82) 2.057	(79) 2.058	(78) 2.058
Ethyl	—	(82) 2.115	(79) 2.116	(78) 2.116
Propyl	—	—	(76) 2.117	—

Ethane $C\overset{(82)}{\underset{2.000}{}}C$

Propane $C\overset{(82)}{\underset{2.057}{}}C-C$

n-Butane $C\overset{(78)}{\underset{2.058}{}}C\overset{(82)}{\underset{2.115}{}}C-C$

n-Pentane $C\overset{(78)}{\underset{2.058}{}}C\overset{(79)}{\underset{2.116}{}}C-C\cdots C$

n-Hexane $C\overset{?}{\underset{2.058}{}}C\overset{(78)}{\underset{2.116}{}}C\overset{(76)}{\underset{2.117}{}}C-C\cdots C$

TABLE VIII. CALCULATED AND OBSERVED BOND DISSOCIATION ENERGIES OF ETHYL HALIDES

X in C_2H_5X	C–X bond diss. energy Calcd. $(-\beta)$	C–X bond diss. energy Obsd.[a] (kcal./mol.)
F	2.690	107.0
Cl	2.049	66.5
Br	1.896	54·0
I	1.749	45.5

a) Reference b) in Table II.

least partly, be ascribed to such a rough approximation adopted. Further improvement should be made on this point.

With regard to ethyl halides, the bond dissociation energies of C–X bond are obtained and compared with experimental values in Table VIII. Compounds are arranged in decreasing order of bond energies. It is seen that the result coincides well with experiments.

Summary

The ionization potential and the bond dissociation energy of saturated compounds are calculated by Yoshizumi's C–C bond skeleton method. With regard to ionization potentials, the calculated results are parallel to the observed values. In particular, for normal paraffins the parallelism is almost complete. For total electronic energies, the calculated results indicate a simple additivity rule in normal and cycloparaffins, and for bond dissociation energies an approximate agreement is obtained between the calculated and the observed values.

In spite of the rough approximation involved in the present treatment, it may be said that the results obtained are rather satisfactory.

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