A New Quantum-mechanical Reactivity Index for Saturated Compounds

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(Received January 24, 1961)

In our previous paper[1], the frontier electron density[2] was shown to become a good intramolecular index of the reactivity in a metathetical reaction of saturated compounds.

In the present paper, we treat several lower paraffins and halomethanes by using the same method as that used in the previous treatment[1], and attempt to derive a new intermolecular index of the reactivity, which is hereafter referred to as the delocalizability, D_r. This index is similar to the superdelocalizability[3] of conjugated molecules. It is found that the magnitude of D_r in these compounds has an intimate correlation with the value of activation energy observed in metathetical reactions.

Electronic Structure of *n*-Paraffins and Methyl Fluoride

The calculated values of orbital energies and electron distributions in methane, ethane, propane, *n*-butane and methyl fluoride are listed in Table I.

With regard to *n*-paraffins, we can point out the following characteristics:

(1) The bonding electrons tend to localize in the particular bonds in each molecular orbital. For example, the electrons in the highest occupied and the lowest vacant orbitals in these compounds except methane, have a general trend to localize in the central C-C bonds as shown in Fig. 1*.

(2) The electron distributions of occupied and unoccupied orbitals are almost symmetrical with respect to the energy equal to α (see below) as is seen in Fig. 1.

(3) The distances of levels of molecular orbital energy in these compounds are much larger than those of conjugated molecules. The excitation energy of the N-V transition in a simple LCAO MO sense is, therefore, estimated to be 9~10 eV. referring the presumed value

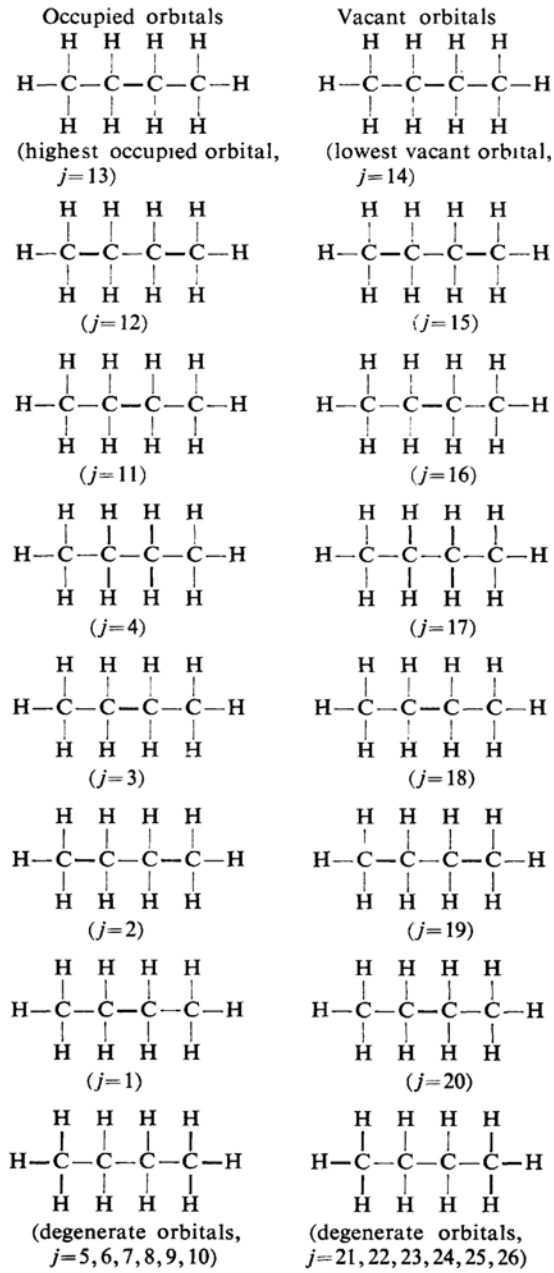
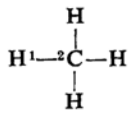


Fig. 1. The electron distributions of *n*-butane.
(Thick lines denote the most densely populated bonds of bonding electrons.)

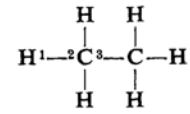
1) K. Fukui, H. Kato and T. Yonezawa, This Bulletin, 34, 442 (1961).
2) See e. g. K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, *J. Chem. Phys.*, 22, 1432 (1954).
3) K. Fukui, T. Yonezawa and C. Nagata, This Bulletin, 27, 423 (1954).
* This result suggests that in lower *n*-paraffins their first ionization can be attributed to the removal of one electron localized in C-C bonds.

TABLE I. THE ORBITAL ENERGIES AND ELECTRON DISTRIBUTIONS IN SEVERAL SATURATED COMPOUNDS



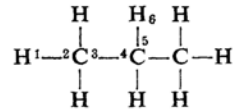
Orbital energy		Electron distribution	
j	ε_j	$(C^j_{H1})^2$	$(C^j_{C2})^2$
6,7,8	$\alpha-1.3722\beta$*	0.1171	0.1329
5	$\alpha-0.8478\beta$	0.1856	0.0644
2,3,4	$\alpha+0.8322\beta$*	0.1329	0.1171
1	$\alpha+1.6678\beta$	0.0644	0.1856

* threefold degenerate



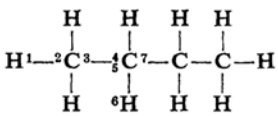
Orbital energy		Electron distribution		
j	ε_j	$(C^j_{H1})^2$	$(C^j_{C2})^2$	$(C^j_{C3})^2$
11,12,13,14	$\alpha-1.3722\beta$*	0.0781	0.0886	0
10	$\alpha-1.3527\beta$	0.0323	0.0355	0.2966
9	$\alpha-1.0019\beta$	0.1057	0.0561	0.0145
8	$\alpha-0.6881\beta$	0.0878	0.0173	0.1847
7	$\alpha+0.7254\beta$	0.0336	0.0238	0.3278
3,4,5,6	$\alpha+0.8322\beta$*	0.0886	0.0781	0
2	$\alpha+1.5208\beta$	0.0465	0.1139	0.0187
1	$\alpha+1.7566\beta$	0.0274	0.0867	0.1575

* fourfold degenerate



Orbital energy		Electron distribution					
j	ε_j	$(C^j_{H1})^2$	$(C^j_{C2})^2$	$(C^j_{C3})^2$	$(C^j_{C4})^2$	$(C^j_{C5})^2$	$(C^j_{H6})^2$
16,17,18,19,20	$\alpha-1.3722\beta$*	0.062	0.071	0	0	0.053	0.047
15	$\alpha-1.3576\beta$	0.011	0.012	0.105	0.106	0.115	0.104
14	$\alpha-1.3482\beta$	0.021	0.023	0.183	0.186	0	0
13	$\alpha-1.0614\beta$	0.058	0.036	0.035	0	0.070	0.113
12	$\alpha-0.8535\beta$	0.090	0.032	0.028	0.105	0	0
11	$\alpha-0.6169\beta$	0.045	0.006	0.144	0.100	0.013	0.089
10	$\alpha+0.6997\beta$	0.020	0.014	0.207	0.191	0	0
9	$\alpha+0.7548\beta$	0.013	0.009	0.117	0.128	0.081	0.108
4,5,6,7,8	$\alpha+0.8322\beta$*	0.071	0.062	0	0	0.047	0.053
3	$\alpha+1.4502\beta$	0.026	0.058	0.001	0.043	0.142	0.063
2	$\alpha+1.6419\beta$	0.035	0.099	0.079	0.020	0	0
1	$\alpha+1.7919\beta$	0.014	0.045	0.100	0.121	0.078	0.024

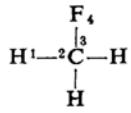
* fivefold degenerate



Orbital energy		Electron distribution						
j	ε_j	$(C^j_{H1})^2$	$(C^j_{C2})^2$	$(C^j_{C3})^2$	$(C^j_{C4})^2$	$(C^j_{C5})^2$	$(C^j_{H6})^2$	$(C^j_{C7})^2$
21,22,23,24,25,26	$\alpha-1.3722\beta$*	0.052	0.059	0	0	0.044	0.039	0
20	$\alpha-1.3612\beta$	0.005	0.006	0.047	0.048	0.074	0.066	0.092
19	$\alpha-1.3546\beta$	0.014	0.016	0.133	0.134	0.037	0.034	0
18	$\alpha-1.3436\beta$	0.012	0.013	0.104	0.101	0.005	0.005	0.200
17	$\alpha-1.0870\beta$	0.035	0.022	0.032	0.002	0.057	0.087	0.007
16	$\alpha-0.9473\beta$	0.070	0.032	0	0.032	0.012	0.027	0.083
15	$\alpha-0.7567\beta$	0.064	0.016	0.077	0.116	0.006	0.023	0.009
14	$\alpha-0.5822\beta$	0.026	0.003	0.099	0.058	0.008	0.063	0.114
13	$\alpha+0.6971\beta$	0.012	0.008	0.128	0.113	0.001	0.002	0.192
12	$\alpha+0.7339\beta$	0.016	0.011	0.151	0.155	0.024	0.033	0
11	$\alpha+0.7627\beta$	0.005	0.004	0.047	0.053	0.055	0.072	0.119
5,6,7,8,9,10	$\alpha+0.8322\beta$*	0.059	0.052	0	0	0.039	0.044	0
4	$\alpha+1.4135\beta$	0.014	0.031	0	0.037	0.107	0.050	0.014
3	$\alpha+1.5585\beta$	0.029	0.074	0.024	0.002	0.036	0.014	0.065
2	$\alpha+1.7073\beta$	0.023	0.070	0.094	0.064	0.022	0.007	0.004
1	$\alpha+1.8098\beta$	0.008	0.026	0.063	0.084	0.057	0.017	0.103

* sixfold degenerate

TABLE I (Continued)



Orbital energy		Electron distribution			
j	ε_j	$(C^j_{H1})^2$	$(C^j_{C2})^2$	$(C^j_{C3})^2$	$(C^j_{F4})^2$
7,8	$\alpha-1.3722\beta$*	0.1561	0.1773	0	0
6	$\alpha-1.0729\beta$	0.1756	0.1112	0.1291	0.0083
5	$\alpha-0.2183\beta$	0.0656	0	0.6691	0.1338
3,4	$\alpha+0.8322\beta$*	0.1773	0.1561	0	0
2	$\alpha+1.0527\beta$	0.0188	0.0244	0.0724	0.7962
1	$\alpha+1.6184\beta$	0.0723	0.1978	0.1285	0.0618

* doubly degenerate

of $-\beta$ (6~7 eV.). This excitation energy is consistent with the spectroscopic data[4].

The characteristics of orbital energies and of the electron distribution stated above agree with the properties observed experimentally in saturated compounds and also with calculated results obtained by Lennard-Jones and Hall's equivalent orbital method[5].

In the doubly degenerate highest occupied orbitals of methyl fluoride, the bonding electrons localize dominantly in the methyl group. In the next highest occupied orbital, an exceedingly large density is observed on the fluorine atom in accordance with the facts pointed out by Frost and McDowell[6], who measured the ionization potentials of methyl halides.

The Coulomb and resonance integrals used in the present paper are summarized in the following table.

$\alpha_H=\alpha-0.2\beta$	$\beta_{cc}=0.34\beta$*
$\alpha_F=\alpha+0.9\beta$	$\beta_{CH}=1.1\beta$
$\alpha_{Cl}=\alpha+0.5\beta$	$\beta_{CF}=0.5\beta$
$\alpha_{Br}=\alpha+0.45\beta$	$\beta_{CCl}=0.65\beta$
$\alpha_I=\alpha+0.40\alpha$	$\beta_{CBr}=0.58\beta$
$\alpha_C=\alpha$	$\beta_{CI}=0.53\beta$

* β_{cc} refers to the resonance integral between two sp^3 orbitals attached to one and the same carbon atom.

A New Reactivity Index for Radical Reactions of Saturated Compounds, $D_r^{(R)}$

The radical reactions of alkyl compounds are covered by the general equation

$$R\text{-}X+Y\cdot \rightarrow [R\cdots X\cdots Y] \rightarrow R\cdot + X\text{-}Y \qquad (1)$$

where R is an alkyl group, X is the group to be extracted and Y is an attacking radical or atom. The bracket in the equation refers to the transition state.

The secular determinant for the activated complex, [R-X···Y], is written

$$\Delta_\sigma = \begin{vmatrix} \alpha_Y-\varepsilon & \gamma\beta & 0 & 0 & 0 & 0 & 0 \\ \gamma\beta & \alpha_X-\varepsilon & \beta_{CX} & 0 & 0 & 0 & 0 \\ 0 & \beta_{CX} & \alpha_C-\varepsilon & \beta_{CH} & \beta_{cc} & & \\ 0 & 0 & \beta_{CH} & \alpha_H-\varepsilon & 0 & & \\ 0 & 0 & \beta_{cc} & 0 & \alpha_C-\varepsilon & & \\ 0 & \multicolumn{6}{l}{\text{(The secular equation for the R-X molecule)}} \end{vmatrix}$$

where α_A refers to the Coulomb integrals of atom A, β_{AB} is the resonance integral between bonding orbitals of atom A and B, and γ is a parameter for the resonance integral of the X-Y incipient bond in the transition state.

By using the perturbation theory, we can derive a new reactivity index, named D_r, for metathetical radical reactions in saturated compounds, in place of the superdelocalizability (S_r) in our previous paper[3].

$$D_r^{(R)}=\sum_j^{occ}\frac{(C_r^j)^2}{\varepsilon_j-\alpha}\beta+\sum_j^{unocc}\frac{(C^j_r)^2}{\alpha-\varepsilon_j}\beta \qquad (3)$$

where C_r^j is the coefficient of the rth atomic orbital in the jth molecular orbital, ε_j is the jth molecular orbital energy, α is the Coulomb integral of a sp^3 orbital in a carbon atom, and β is the resonance integral between two sp^3 orbitals in a C-C bond.

In the derivation of Eq. 3, we assume that α_X is equal to α, and the values of α and β in the activated complex are the same as those of the isolated molecule.

It may be worthy of notice that $D_r^{(R)}$ represents the stabilization energy due to σ type interaction in a radical reaction, while $S_r^{(R)}$ denotes the stabilization energy which

4) P. G. Wilkinson and H. L. Jhonston, *J. Chem. Phys.*, **18**, 190 (1950); W. P. Potts, ibid., **20**, 809 (1952).
5) J. Lennard-Jones and G. G. Hall, *Disc. Faraday Soc.*, **10**, 18 (1951); *Trans. Faraday Soc.*, **47**, 581 (1952); K. Fueki and K. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **81**, 212 (1960).
6) D. C. Frost and C. A. McDowell, *Proc. Roy. Soc.*, **A241**, 194 (1957).

TABLE II (a). THE CALCULATED VALUES OF $D_r^{(R)}$ AND OBSERVED ACTIVATION ENERGIES IN SEVERAL *n*-PARAFFINS

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

Compound R-H		$D_r^{(R)}(H)$	E(kcal./mol.)[8]		
			$CH_3\cdot$	$CH_3CH_2\cdot$	$CH_3CH_2CH_2\cdot$
CH_3-H		0.9926	11.5	15.0	16.5
CH_3CH_2-H	(prim-H)	1.0029	10.0	14.8	16.2
$CH_3CH_2CH_2$-H	(prim-H)	1.0032	9.5	14.2	15.5
$CH_3CH_2CH_2CH_2$-H	(prim-H)	1.0043	9.3	13.9	15.3
$(CH_3)_2CHCH_2$-H	(prim-H)	1.0049	—	—	—
$(CH_3)_2CH$-H	(sec-H)	1.015	8.7	13.3	14.5
$CH_3CH_2CH(CH_3)$-H	(sec-H)	1.016	8.2	12.7	14.1
$(CH_3)_3C$-H	(tert-H)	1.027	7.7	11.6	13.4

TABLE II (b). THE AVERAGE VALUES OF $D_r^{(R)}$ (H) AND RATE CONSTANTS CHARACTERISTICS OF VARIOUS TYPES OF HYDROGEN ATOM IN ALKANES

Type of hydrogen atom	$D_r^{(R)}(H)$	$k_C \times 10^{-6}$ at 182°C (mol^{-1} cc. sec^{-1}*[7])
H in methane	0.993	—
Primary H	1.003	0.3
Secondary H	1.016	2.1
Tertiary H	1.027	15

* k_C means the rate constant divided by the number of H atoms of the same kind.

arises from the hyperconjugation taking place between a reagent and a conjugated molecule.

Results and Discussions

In our previous paper[1], the magnitudes of the frontier electron densities at hydrogen atoms in several saturated hydrocarbons ran parallel with the experimental reactivities[7] of hydrogen atoms in metathetical reactions. The frontier electron density for radical attack was shown to be a good intramolecular index of reactivity. This index, however, does not indicate the correct order of reactivity in different molecules. Therefore, we adopt $D_r^{(R)}$ which is useful not only as an intramolecular index but also as an intermolecular index. The calculated values of $D_r^{(R)}$ in several saturated compounds are listed together with the observed values of activation energy[8,9] in various metathetical reactions in Tables II and III.

TABLE III. THE VALUES OF $D_r^{(R)}(H)$ AND ACTIVATION ENERGIES OF HALOMETHANES IN METATHETICAL REACTIONS

(a) $CH_nCl_{4-n} + CH_3\cdot \rightarrow CH_{n-1}Cl_{4-n}\cdot + CH_4$

Compound	$D^{(R)}(H)$	E(kcal./mol.)[9]
$CHCl_3$	2.181	5.8
CH_2Cl_2	1.237	7.2
CH_3Cl	1.058	9.4

(b) $CH_nF_{4-n} + CH_3\cdot \rightarrow CH_{n-1}F_{4-n}\cdot + CH_4$

Compound	$D_r^{(R)}(H)$	E(kcal./mol.)[9]
CH_3F	1.181	8.7
CH_2F_2	1.235	6.2

(c) $CH_nX_{4-n} + Br\cdot \rightarrow CH_{n-1}X_{4-n}\cdot + HBr$

Compound	$D_r^{(R)}(H)$	E(kcal./mol.)[9]
CH_4	0.993	17.8
CH_3Br	1.071	15.6
$CHCl_3$	2.181	10.0

Hydrogen Extraction Reaction.—In the case of reaction $RH + R'\cdot \rightarrow R\cdot + R'H$, results of calculation and experiments are cited in Table II (a) and (b), where R and R′ are two different alkyl groups. The values of $D_r^{(R)}$ at hydrogen atoms in several lower paraffins indicate a tendency that the larger the molecule RH is, the smaller is the magnitude of activation energy, this being in accord with experiments[8]. Furthermore, these values of $D_r^{(R)}$ agree with the activities of various kinds of hydrogen atoms estimated by Trotman-Dickenson[7] as shown in Table II (b).

In Table III (a), (b) and (c), the calculated values of $D_r^{(R)}$ at hydrogen atoms in various halomethanes are listed together with the observed activation energies[9]. In Table III (a), the radical reactions between methyl radical and chlorine-substituted methanes are indicated. The greater the number of chlorine atoms in methane is, the smaller is the activation energy, and also the magnitude of $D_r^{(R)}$ at hydrogen atoms increases with the number of chlorine atoms. The results on fluorine-substituted methanes are shown in Table III (b), and

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

8) N. N. Tikhomirova and V. V. Voevodskı, *Chem. Abstr.*, 45, 9940 (1951).

9) E. W. R. Steacie, "Atomic and Free Radical Reactions", Reinhold Co., New York. (1946); ibid., Second Ed. Vol. II (1954).

the case where a bromine atom attacks methane derivatives is indicated in Table III (c). Also in the last two cases, although experimental data are few, a parallelism between the values of $D_r^{(R)}$ and the activation energies[9] is clearly observed.

Halogen Abstraction Reaction.—In Table IV (a), (b) and (c) are illustrated both the calculated values of $D_r^{(R)}$ at the halogen atom

TABLE IV. THE VALUES OF $D_r^{(R)}(X)$ AND ACTIVATION ENERGIES IN HALOMETHANES IN METATHETICAL REACTIONS

(a) $CH_3X+H\cdot \rightarrow CH_3\cdot+HX$

CH_3X	$D_r^{(R)}(X)$	E(kcal./mol.)[9]
CH_3I	1.851	5
CH_3Br	1.669	—
CH_3Cl	1.496	7∼9
CH_3F	1.415	9

(b) $CH_nCl_{4-n}+H\cdot \rightarrow CH_nCl_{3-n}\cdot+HCl$

Compound	$D_r^{(R)}(Cl)$	E(kcal./mol.)[9]
CH_3Cl	1.496	7∼9
CH_2Cl_2	1.756	6
$CHCl_3$	3.200	4.3
CCl_4	3.829	3.5

(c) $CH_nBr_{4-n}+Na\cdot \rightarrow CH_nBr_{3-n}\cdot+NaBr$

Compound	$D_r^{(R)}(Br)$	E(kcal./mol.)[9]
CH_3Br	1.669	5.9
CH_2Br_2	2.045	2.6
$CHBr_3$	4.889	0.3

in various halomethanes and the observed values of activation energy in the halogen extraction reactions[9]. In Table IV (a), a good agreement is observed between the values of $D_r^{(R)}$ and the activation energies of various monosubstituted halomethanes. In Table IV (b), the values of $D_r^{(R)}$ at chlorine atoms in various chlorine-substituted methanes and the activation energies in the hydrogen-atom reactions are indicated. In Table IV (c), the values of $D_r^{(R)}$ at bromine atoms in several bromomethanes are compared with the activation energies in the sodium-atom reaction.

In spite of the fact that this is the first attempt of the quantum-mechanical investigation of the reactivity of saturated compounds, the agreement of the theory with experience is almost satisfactory, and hence the new quantum-mechanical quantity $D_r^{(R)}$ can be a useful index for predicting the reactivity of saturated compounds, equally with S_r in conjugated molecules. There remain, however, some points to be checked in future. These are summarized as follows:

(1) We assume that α_x is equal to α to derive D_r. Meanwhile, a slight change in activation energy is experimentally observed according to the species of attacking reagents. Hence, if the values of α_x would be modified according to the change of the attacking reagent, this effect can be interpreted in the present procedure.

(2) In the present treatment, we do not take into account the stabilization energy due to the resonance in an attacking alkyl radical or the radical formed. It has been made clear that this resonance energy has a remarkable influence on the magnitude of the activation energy[10]. In this connection, the present treatment should be modified so as to involve the contribution of this kind of resonance to the activation energy.

(3) A disagreement between the values of $D_r^{(R)}$ in methyl halides and the experimental activation energies is observed. This is probaly because the energies of the vacant orbitals of some methyl halides are nearly equal to α. Thus, the values of the $D_r^{(R)}$ become extremely large. If carefully selected values of parameters for halogen atoms should be adopted, these disagreements may be avoidable.

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10) M. G. Evans, *Disc. Faraday Soc.*, **10**, 1 (1951); C. A. Coulson, ibid., **2**, 9 (1947).