An NBMO Method for Saturated Compounds

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By the use of the extremely simple character of the nonbonding molecular orbital (NBMO) method, explanations have been offered of some physico-chemical properties of conjugated systems, for instance, the chemical reactivity, radical stability, and the basicity[1,2].

In the present paper, we will apply this method to σ electron systems. Consider, for example, a fission of a C–C or a C–H bond in a saturated hydrocarbon molecule (or vice versa, a recombination of the two corresponding radicals). It may be reasonable to assume in the first place that an "unpaired" sp^3 hybridized orbital of carbon* might appear just after the fission (or just before the recombination). Our previous papers[3,4] treated the saturated compounds by the simple LCAO MO method. This can also be applied to those compounds with an unpaired sp^3 hybridized orbital. In these compounds with an odd electron, the highest half-occupied orbital has an energy nearly equal to that of the Coulomb integral of an sp^3 hybridized orbital of a carbon atom (α). We will attempt to discuss the bond strength and the reactivity of the saturated compounds by using the characteristic regularity of the electron distribution in this half-occupied orbital. For the sake of simplicity, the compounds with an unpaired "σ" hybridized orbital are hereafter represented by the notation** R–, while the highest half-occupied molecular orbital is referred to as the "σ NBMO". The R– compounds treated in the present paper are CH_3–, C_2H_6–, *n*-C_3H_7–, *n*-C_4H_9–, *i*-C_3H_7–, *t*-C_4H_9– and so on. At the same time, the compounds which have an unpaired sp^2 hybridized orbital such as C_2H_3(vinyl)– and C_6H_5(phenyl)–, are also treated, together with those having an sp^3 unpaired orbital, since the procedure of calculation is common to both classes of compounds.

The Electronic Energy Levels and the Electron Distribution in R- Compounds

The calculations are carried out by the simple LCAO MO method, including all bonding atomic orbitals in the saturated compounds[3,4]. Hence, the calculated molecular orbital energies of the occupied orbitals of R– compounds are obtained in terms of $\lambda_i=\varepsilon_i-\alpha/\beta$, in which α is the Coulomb integral of sp^3 (or sp^2 in, e. g., the C_6H_5–) hybridized orbital of a carbon atom and β is the resonance integral between the sp^3 (or sp^2) orbitals of the adjacent carbon atoms. These values are listed in Fig. 1, together with those of the corresponding parent RH compounds. The calculated energies of σ NBMO (λ_N) and the electron distributions of the σ NBMO in these R– compounds are shown in Fig. 2.

The following conclusions can be derived from these results:

1) The energy value of σ NBMO in R– compounds is nearly equal to α. It may be observed in Fig. 1 that one σ-MO localized at the C–H bond in the parent RH compound disappears and that an NBMO appears in the R– compound. The energy difference between the corresponding occupied orbitals of the R– and RH compounds is very small.

2) The odd electron of the σ NBMO is largely located in the unpaired hybridized orbital, the odd electron density at this orbital being nearly equal to unity, while those of the other hybridized orbitals are alternately equal to zero and the value of the non-zero density rapidly decreases with the distance from the unpaired hybridized orbital. This implies that the R– compounds are very unstable and that the most reactive position is that of the unpaired hybridized orbital.

3) The odd electron density of the unpaired hybridized orbital in various R– compounds decreases in the order CH_3–> C_2H_5–> *n*-C_3H_7–> *n*-C_4H_9–> *i*-C_3H_7–> *i*-C_4H_9–> *t*-C_4H_9–. The density values are listed in Table I, along with the energy values of the σ NBMO.

According to the conclusions stated above, one can say that the energy of the σ NBMO is nearly equal to α, as it was in the π NBMO, whereas the mode of the odd electron distribution in the σ NBMO shows a remarkable

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* The unpaired hybridized orbital stands for the AO of the carbon atom, which does not participate into the C-C or C-H bonding.

[1] H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 283 (1950).

[2] M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3357 (1952).

[3] K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **34**, 442 (1961).

[4] K. Fukui, H. Kato and T. Yonezawa, ibid., **34**, 1111 (1961).

** R- should be discriminated from the species usually represented by R·, in which the reorganization of the odd electron may in general have already taken place.

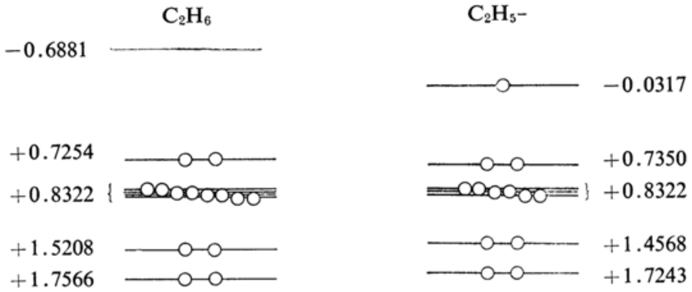

Fig. 1. The relation of energy levels of occupied orbitals between C_2H_6 and C_2H_5-.

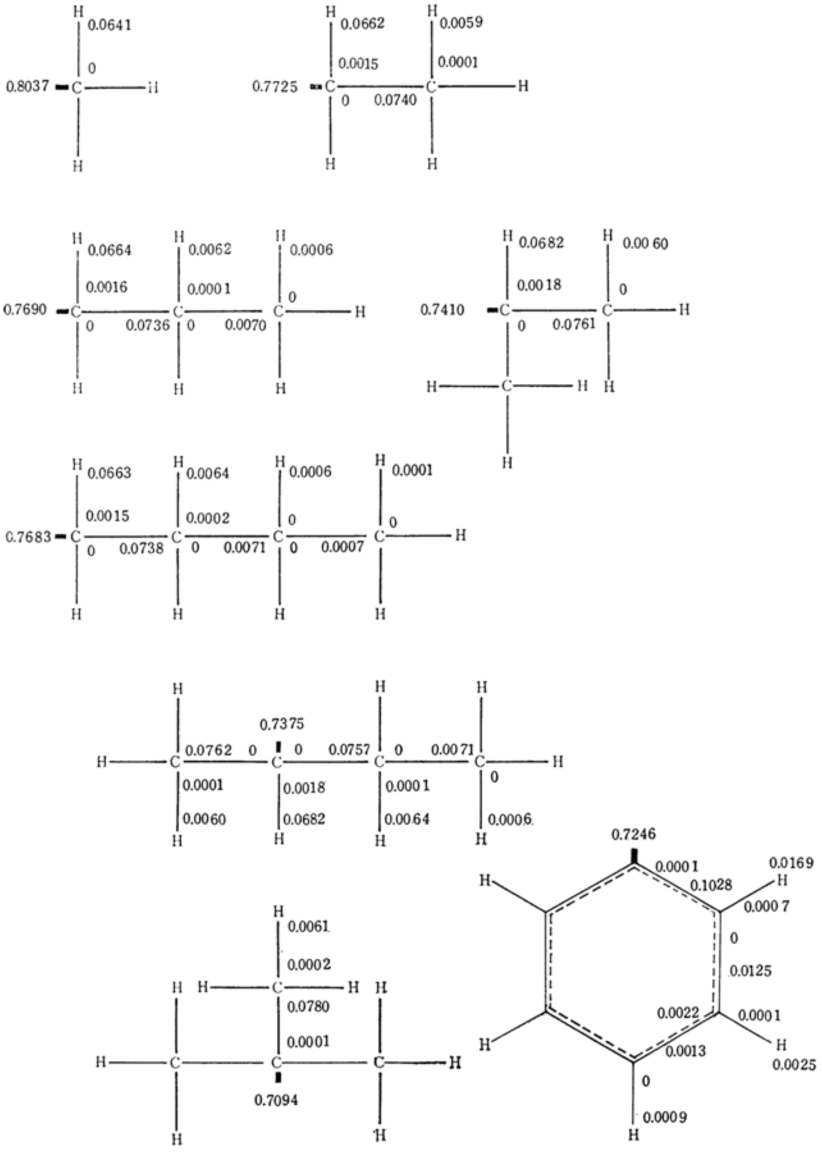

Fig. 2. The odd electron distributions in the σ NBMO of some R- compounds.

difference from that of the π NBMO; i. e., the former localizes and the latter does not (see appendix). In the following sections, it will be shown that the reactivity of alkyl compounds and the bond strength of C–C bonds in saturated compounds can be discussed by means of the extremely simple calculations based upon the properties of the σ NBMO.

The Reactivity Indecis Derived from the σ NBMO Method

In this section, some indecis for the chemical reactivity of saturated compounds are derived by means of the σ NBMO method. It may be worthwhile to recollect here that the activation energy of the reaction in the frontier electron theory has been discussed in terms of the stabilization energy at the transition state. Once the stabilization energy, ΔE, can be obtained, the activation energy, E, is written in the form:

$$E=C-\Delta E \tag{1}$$

in which C is a constant denoting the repulsive term due to the interaction between the reactant and the reagent[2,5]. For a definite type of reaction, it may be assumed that C is a constant and that E is determined only by the difference in the magnitude of ΔE.

In some types of reactions of saturated compounds, the stabilization of the σ-electronic energy, ΔE_σ, may easily be obtained by the σ NBMO method in the following way:

Abstraction Reaction.—The abstraction reaction in saturated compounds is represented by the following formula:

$$\mathrm{RX+Y\cdot \rightarrow [R{-}X\cdots Y] \rightarrow R\cdot + XY}$$

where RX is a saturated compound and Y· is an odd electron system. In this case, ΔE_σ is given by

$$\begin{aligned}\Delta E_\sigma = 2\Bigl(\sum_j^{\text{occ}}\sum_i^{\text{unocc}} - \sum_i^{\text{occ-N}}\sum_j^{\text{unocc}}\Bigr) &\times \frac{(C_r{}^j)^2(C_s{}^i)^2}{\lambda_j(\mathrm{RX})-\lambda_i(\mathrm{Y})} + \Bigl(\sum_j^{\text{occ}} - \sum_j^{\text{unocc}}\Bigr) \\ &\times \frac{(C_r{}^j)^2(C_s{}^{\mathrm{N}})^2}{\lambda_j(\mathrm{RX})-\lambda_{\mathrm{N}}(\mathrm{Y})} \\ &(\text{in units of } \gamma(-\beta))\end{aligned} \tag{2}$$

in which $C_r{}^j$ and $C_s{}^j$ are the coefficients of the r-th atomic orbital in the j-th molecular orbital of the RX molecule and of the s-th atomic orbital in the i-th molecular orbital of the reagent Y·; N denotes the half-occupied molecular orbital of Y; $\lambda_j(\mathrm{RX})$ is the energy of the j-th molecular orbital of the RX compound, and $\lambda_i(\mathrm{Y})$ is that of the i-th molecular orbital of Y: compound respectively. The unit is $\gamma(-\beta)$, which represents the absolute value of the resonance integral between the two NBMO's, X and Y. Since it may reasonably be considered that the radical Y· is converted to the Y− form in the transition state, λ_{N} is nearly equal to zero and the values of $(C_s{}^{\mathrm{N}})^2$ are larger than those of $(C_s{}^i)^2(\mathrm{N}\neq i)$. Thus, the first term in Eq. 2 can be ignored, since this should be much smaller than the second term. In this way, we obtain a simplified formula of ΔE_σ as

$$\Delta E_\sigma \cong D_r{}^{(\mathrm{R})}(C_s{}^{\mathrm{N}})^2 \tag{3}$$

in which $D_r{}^{(\mathrm{R})}$ is nothing but what we called "delocalizability", derived for the radical reaction of saturated compounds in our previous paper[4],*. That is, ΔE_σ is the reactivity index obtained by considering the interaction explicitly between the σ orbitals of the reactant molecule and the attacking radical.

Radical or Ionic Recombination Reaction.—A similar procedure is applicable when discussing the easiness of the reactions which are covered by the following general equation:

$$\mathrm{R+X \rightarrow [R\cdots X] \rightarrow RX}$$

In this equation, the type of reaction may be classified as follows according to the number of electrons occupying the σ NBMO of R and X:

1. One electron each exists in both the NBMO's, R and X ($\mathrm{R\cdot + X\cdot \rightarrow RX}$: radical recombination).
2. Two electrons in the NBMO of R, and none in the NBMO of X, or vice versa ($\mathrm{R^- + X^+ \rightarrow RX}$ or $\mathrm{R^+ + X^- \rightarrow RX}$: ionic recombination).

It may be considered that both R and X have one σ NBMO each in the transition state. If we can ignore the energy difference between the two σ NBMO's**, ΔE_σ can be obtained by the first order perturbation theory. Hence, ΔE_σ for all the cases stated above may be simply given as follows:

$$\Delta E_\sigma = 2|C_r{}^{\mathrm{N}}C_s{}^{\mathrm{N}}| \quad (\text{in unit of } \gamma(\text{-}\beta)) \tag{4}$$

In the series of reactions in which X does not change, the coefficient $C_s{}^{\mathrm{N}}$ is a constant, so ΔE_σ is proportional only to $|C_r{}^{\mathrm{N}}|$.

Radical or Ionic Dissociation Reaction.—Consider a dissociation reaction proceeding:

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5) T. Yonezawa, K. Hayashi, C. Nagata, S. Okamura and K. Fukui, *J. Polymer. Sci.*, **14**, 312 (1954).

* Delocalizability, $D_r{}^{(\mathrm{R})}$, for the radical reaction was defined by the following formula[4]:

$$D_r{}^{(\mathrm{R})} = \sum_j^{\text{occ}} \frac{(C_r{}^j)^2}{\lambda_j} + \sum_j^{\text{unocc}} \frac{(C_r{}^j)^2}{-\lambda_j}$$

** In general, the energies of the two -NBMO's of R and X are not exactly the same. Both of these levels, however, lie very close to α, so that it might be possible to ignore the difference.

$$RX \rightarrow [R\cdots X] \rightarrow R+X$$

In this case we also assume that both the R and X compounds have a σ NBMO each in the transition state. The magnitude of ΔE_σ is shown to be a measure of the activation energy. Namely, the activation energy, E, of the reaction is given by

$$E=\varepsilon(R\cdots X)-\varepsilon(RX) \qquad (5)$$

where $\varepsilon(R\cdots X)$ and $\varepsilon(RX)$ denote the total energy of R···X and RX respectively. Equation 5 may be written in another form as:

$$E=\{E(R\cdots X)-E(R+X)\} \\ -\{E(RX)-E(R+X)\} \qquad (6)$$

As was pointed out in the last section, the first term is put equal to $(C-\Delta E_\sigma)$. The term in the second parenthesis may become $(C-\Delta E'_\sigma)$ so long as one considers that the energy $E(RX)$ may be deemed an extreme of $E(R\cdots X)$ and that the stabilization due to the covalent interaction between R and X may be proportional to ΔE_σ, resulting from an incipient bond*. Therefore, the prime of ΔE_σ indicates that the resonance integral $(\gamma\beta)$ between R and X has a very large value. Let it be $\gamma'\beta$.

Based on these considerations, we can conclude that the activation energy of the dissociation reaction may be proportional to the difference between $\Delta E'_\sigma$ and ΔE_σ as

$$E=F_{rs}\simeq\Delta E'_\sigma-\Delta E_\sigma\simeq 2|C_r^N C_s^N| \\ (\text{in units of } |(\gamma'-\gamma)(-\beta)|) \qquad (7)$$

in which F_{rs} is σ new index representing the relative strength of the bond (rs).

In the present simplified treatment, the activation energy of the dissociation reaction does not vary according to whether it takes place in the radical or in the ionic mechanism. From this equation it is found that the larger the stabilization in the formation of the incipient bond between R and X, the less easily does the dissociation of the compound RX into R and X proceed.

Results and Discussion

Hydrogen Abstraction Reaction.—The reaction, $RH+R'\cdot \rightarrow R\cdot+R'H$, has also been discussed in our previous paper in terms of the reactivity indecis $f_r^{(R)}$ and $D_r^{(R)}$[3,4]. On that occasion we discussed the comparison of the reactivity of various RH's against a common $R'\cdot$ radical, so the energetical contribution of the attacking radicals was not taken into account. The new reactivity index, ΔE_σ, in Eq. 2, which has been derived by considering both the reactant molecule and the reagent with a σ NBMO in the transition state, enables us also to compare, e. g., the reactivity of RH against various alkyl-radicals. In Table II, the calculated values of ΔE_σ and $D_r^{(R)}$ for the hydrogen abstraction of saturated hydrocarbons are listed, together with values of the observed activation energy, E (kcal./mol.)[6]. In Fig. 3, the values of ΔE_σ are plotted against those of E. The linearity between the calculated and the observed values is seen; therefore, the value of $|C_r^N|$ in ΔE_σ for radical reactions may be said to reflect the reactivity of the alkyl radical.

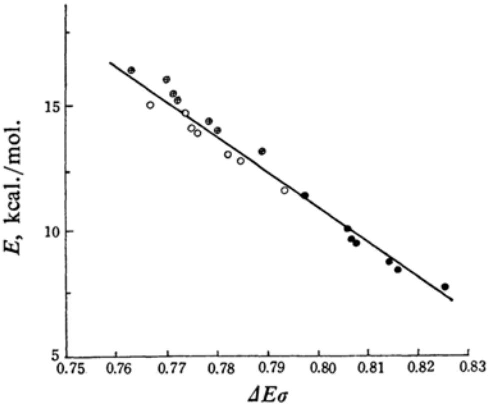

Fig. 3. The activation energy, E, of the reaction $RH+R'\cdot\rightarrow R\cdot+R'H$ vs. $\Delta E_\sigma=D_r^{(R)}(C_s^N)^2$.

Ionic Reaction.—The ionic dissociation reaction of saturated compounds is represented by the general formula $RX\rightarrow R^+ + X^-$, where X is, e. g., a halogen atom or a OH group. The quantity, F_{rs}, in Eq. 7 is adopted as the reactivity index of this type of reaction, assuming that the energy of the half-occupied orbital appearing in the X group in the transition state is nearly equal to α. Referring to the absolute value of the coefficient of the σ NBMO of various R– compounds, $|C_r^N|$, the order of easiness of dissociation of alkyl groups is predicted as follows:

$$CH_3<C_2H_5<n\text{-}C_3H_7<n\text{-}C_4H_8<i\text{-}C_3H_7 \\ <i\text{-}C_5H_{12}<t\text{-}C_4H_9$$

In Fig. 4, the values of the heat of the gasphase ionic dissociation of alkyl derivatives[7] are plotted against the $|C_r^N|$ values of the alkyl groups. Here, the upper oblique line corresponds to the dissociation reaction of ROH, the lower one, to that of RCl. In Fig. 5, the values of the heat of the reaction of the $RH\rightarrow R^+ + H^-$ type are plotted against

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* It may be allowed to consider that repulsion term in RX does not differ so much from that in R···X.

6) N. N. Tikhomirova and V. V. Voevodski, *Chem. Abstr.*, **45**, 9940 (1951).

7) A. Streitwiesser, *Chem. Revs.*, **56**, 571 (1956).

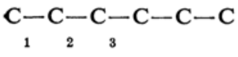
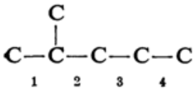
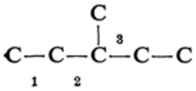
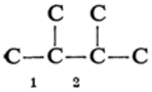
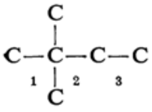
TABLE I. THE CALCULATED VALUES OF ODD ELECTRON DENSITY OF UNPAIRED HYBRIDIZED ORBITAL AND THOSE OF NBMO ENERGY OF SOME R- COMPOUNDS

Compound		$(C_r^{\mathrm{N}})^2$	λ_{N}
CH_3-	—	0.8037	−0.0415
C_2H_5-	Primary	0.7725	−0.0317
n-C_3H_7-	Primary	0.7690	−0.0308
n-C_4H_9-	Primary	0.7683	−0.0308
$(CH_3)CCH_2$-	Primary	0.7604	−0.0288
i-C_3H_7-	Secondary	0.7410	−0.0219
i-C_4H_9-	Secondary	0.7375	−0.0211
i-C_5H_{11}-	Secondary	0.7340	−0.0202
t-C_4H_9	Tertiary	0.7094	−0.0129
$(C_2H_5)(CH_3)_2C$-	Tertiary	0.7051	−0.0114

TABLE II. THE CALCULATED VALUES OF $D_r^{(\mathrm{R})}$ (H) and $\Delta E_\sigma = D_r^{(\mathrm{R})}(\mathrm{H}) \cdot (C_s^{\mathrm{N}})^2$ AND THE EXTRACTION REACTION OBSERVED VALUES OF ACTIVATION ENERGY, E (kcal./mol.), FOR HYDROGEN EXTRACTION REACTION OF SEVERAL SATURATED HYDROCARBONS

Compound		Attacking radical					
		$CH_3\cdot$		$C_2H_5\cdot$		*n*-$C_3H_7\cdot$	
	$D_r^{(\mathrm{R})}$	ΔE_σ	E	ΔE_σ	E	ΔE_σ	E
CH_3-H	0.9926	0.7978	11.5	0.7668	15.0	0.7633	16.6
C_2H_5-H	1.0029	0.8060	10.0	0.7747	14.8	0.7712	16.2
n-C_3H_7-H	1.0037	0.8067	9.5	0.7754	14.2	0.7718	15.5
n-C_4H_9-H	1.0040	0.8072	9.3	0.7758	13.9	0.7723	15.3
$(CH_3)_2CHCH_2$-H	1.0049	0.8076	—	0.7763	—	0.7728	—
$(CH_3)_2CH$-H	1.0135	0.8146	8.7	0.7829	13.3	0.7794	14.5
$CH_3CH_2(CH_3)CH$-H	1.0152	0.8167	8.2	0.7849	12.7	0.7813	14.1
$(CH_3)_3C$-H	1.0268	0.8254	7.7	0.7933	11.6	0.7898	13.4

TABLE III. THE CALCULATED VALUES OF C-C BOND STRENGTH AND *G*-VALUES OF RADIOLYSIS IN HEXANE ISOMERS

Hexane isomer	Bond	Calculated bond energy kcal./mol.	F_{rs}	Observed *G*-values
	1	82.4	1.572	0.2
	2	80.2	1.540	0.55
	3	80.2	1.538	0.45
	1	80.2	1.524	0.6
	2	78.1	1.510	1.6
	3	80.2	1.532	—
	4	82.4	1.560	—
	1	82.4	1.546	—
	2	78.1	1.496	1.2
	3	80.2	1.526	0.5
	1	80.2	1.534	0.2
	2	76.0	1.482	1.2
	1	78.1	1.514	0.8
	2	76.0	1.480	3.9
	3	82.4	1.566	—

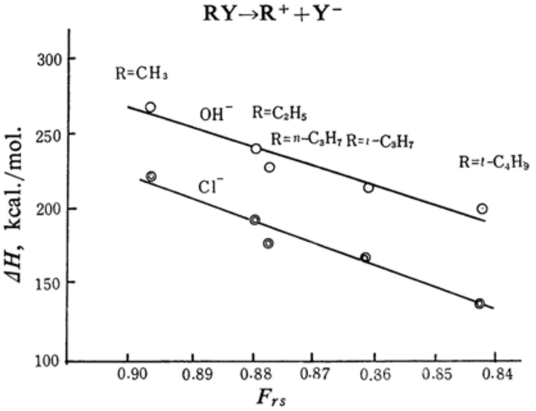


Fig. 4. The heat of reaction, ΔH, of gaseous ionic dissociation of alkyl compounds vs. $F_{rs}=\text{const}\times|C_r^N|$.

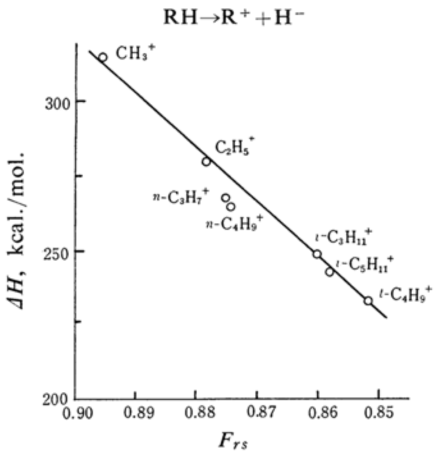


Fig. 5. The heat of reaction, ΔH, in the ionic dissociation of paraffins vs. $F_{rs}=\text{const}\times|C_r^N|$.

those of the $|C_r^N|$ values of various alkyl groups. The parallelism between the observed and the calculated values is obvious.

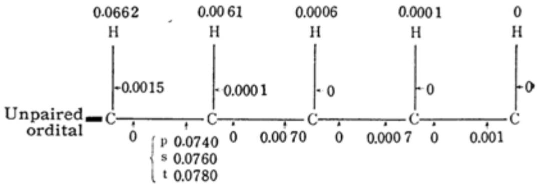
C–C Bond Fission.—How to obtain easily the strength of the C–C bond of a hydrocarbon molecule is a problem of interest not only from a theoretical but also from a practical point of view. The fission of a C–C bond is in general represented by

$$R\text{–}S \rightarrow R+S$$

in which R and S are alkyl groups. Using the σ NBMO method, we can easily obtain from Eq. 7 the activation energy of a C–C fission which we can adopt as a measure of the relative strength of the C–C bond. Namely,

$$F_{rs}=2|C_r^N C_s^N|$$

in which F_{rs} is the relative strength of the bond (rs) of the parent molecule. The calculated values of F_{rs} to each C–C bond in the isomeric hexanes are listed in Table III, together



(The notations p, s, and t stand for the cases where the carbon atom having the unpaired hybridized orbital is a primary, a secondary, and a tertiary carbon, respectively.)

Fig. 6. Diagram of approximate distribution of odd electron density of saturated hydrocarbons.

with the calculated bond energies[8] and the observed G-values obtained by radiolysis[9]. The parallelism between the calculated and the observed results is good. The calculated values of $|C_r^N|$ are obtained by means of the approximate values of odd electron distribution, as shown in Fig. 6, which is estimated by the regularity, as shown in Fig. 1. In Fig. 7, two calculated values[10] for the squalane molecule ($C_{30}H_{62}$) are given. The agreement between the calculated and the observed results[10] is almost entirely on satisfactory. From the two examples stated above, one can see that the F_{rs} index is a good and extremely simple index for the relative strength of a C–C bond.

The next problem is the catalytic cracking of hydrocarbons. Consider the decomposition of a carbonium ion represented by

$$R_1^+ \rightarrow R_2^+ + \text{olefin}$$

Several examples of this type of reaction are as follows:

1 $R\text{–}CH_2\text{–}CH_2^+ \rightarrow R^+ + C_2H_4$

2 $R\text{–}CH_2\text{–}CH^+\text{–}CH_3 \rightarrow R^+ + C_3H_6$

3 $R\text{–}CH\text{–}\underset{\displaystyle CH_3}{\underset{|}{C^+}}\text{–}CH_3 \rightarrow R^+ + i\text{-}C_4H_9$

In this case, the observed energy of the bond fission, ΔH (kcal./mol.)[11], is expected to be parallel to the value of F_{rs}, provided that one can assume the appearance of two σ NBMO's at the R_r–C_s bond in the transition state. In each series, 1, 2 and 3, of the reactions indicated above, the olefin molecule produced is the same, so the value of F_{rs} is proportional to the $|C_r^N|$ value of R only. In Fig. 8, the calculated $|C_r^N|$ values of R and the observed values of ΔH are given for the sake of comparison.

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[8] K. Fueki and K. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 985 (1956).

[9] H. A. Dewhurst, *J. Am. Chem. Soc.*, **80**, 5607 (1958).

[10] H. Yamazaki and S. Shida, *J. Chem. Phys.*, **33**, 950 (1960).

[11] T. Amamiya, "Sekiyu Kagaku", Sangyo Tosho, Tokyo (1959), p. 131.

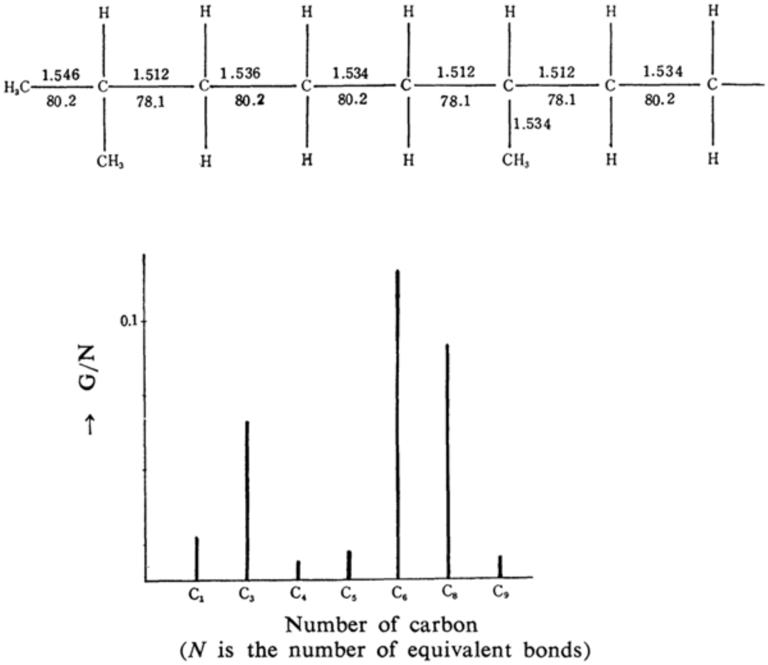

Fig. 7. The calculated values of F_{rs} and bond energy (kcal./mol.)[10], the observed G-values for irradiated squalane molecule.

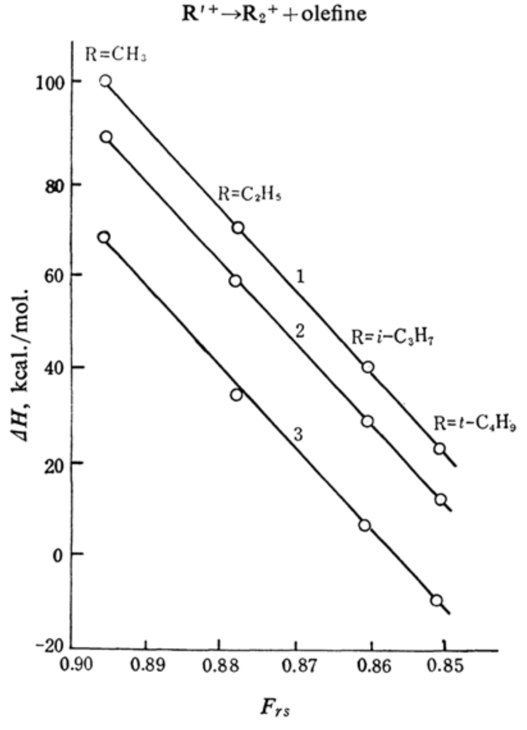

Fig. 8. The heat of reaction, ΔH, of C-C bond fission in alkyl cations vs. $F_{rs}=\mathrm{const}\times|C_r^{\mathrm{N}}|$ at the bond rs in R'^+ to be cloven.

1 $\mathrm{R\text{-}CH_2\text{-}CH_2^+ \rightarrow R^+ + C_2H_4}$
2 $\mathrm{R\text{-}CH_2\text{-}CH^+\text{-}CH_3 \rightarrow R^+ + C_3H_6}$
3 $\mathrm{R\text{-}CH_2\text{-}\underset{\overset{|}{CH_3}}{C^+}\text{-}CH_3 \rightarrow R^+ + C_4H_8}$

β-Fission Rule.—The C–C bond, β, to the charged carbon atom in an alkyl cation is often selectively cloven. This phenomenon is well known as the β-fission rule. This rule is satisfactorily explained by the relative bond strength of F_{rs}. That is, in the actual species of an alkyl ion or an alkyl radical, the hybridization of the carbon atom in question may be changed from sp^3 to sp^2. The odd electron distribution of some alkyl, i. e., $\overset{*}{\mathrm{C}}\mathrm{H_2}$–, $\overset{*}{\mathrm{C}}\mathrm{H_2CH_2}$– and $\overset{*}{\mathrm{C}}\mathrm{H_2CH_2CH_2}$–, are calculated by using the parameters of the sp^3 and sp^2 hybridized orbitals for the carbon atom designated by $*$[12]. The calculated results are shown in Fig. 9. For a long straight chain hydrocarbon, the $|C_s^{\mathrm{N}}|$ coefficient of the unpaired hybridized orbital in the σ NBMO of the radical R′ appearing as the result of the fission of the rs bond $|C_s^{\mathrm{N}}|$ (see the figure below) is almost independent of the position s. Hence, the relative C–C bond strength of these $*$ compounds is measured by the $|C_r^{\mathrm{N}}|$ values with respect to the C–C bond in question.

$$\underbrace{\overset{*}{\mathrm{C}}\mathrm{H_2\text{–}CH_2\cdots CH_2}}_{\mathrm{R}}\overset{r\quad s}{\text{——}}\underbrace{\mathrm{CH_2\cdots\cdots CH_3}}_{\mathrm{R'}}$$

These results are summarized in Fig. 10, where it is observed that the value of $|C_r^{\mathrm{N}}|$ is the smallest at the β bond to the carbon atom

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[12] K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, I. Imamura and C. Nagata, This Bulletin, 35, 38 (1962).

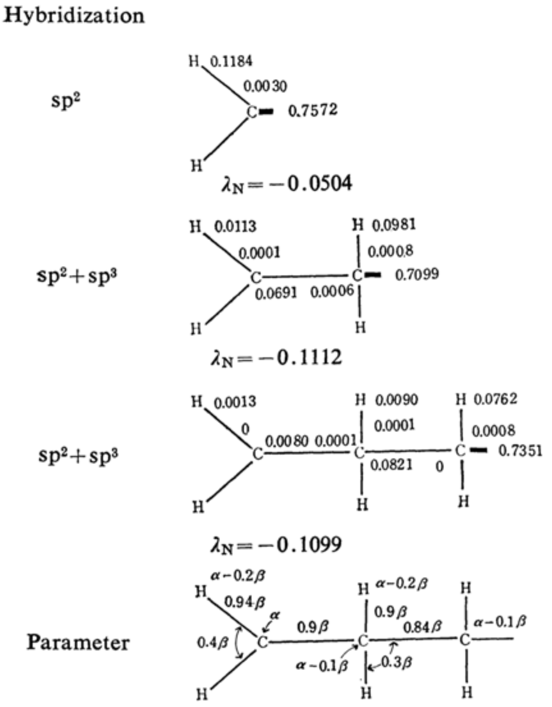

Fig. 9. The odd electron distribution of the σ NBMO in sp² or (sp²+sp³) systems and the values of parameter used.

designated by *. It is thus found that the β C–C bond becomes the weakest owing to the change in the hybridization of the * carbon atom.

This procedure will also be applied to treating the β fission problem of alkyl aromatics.

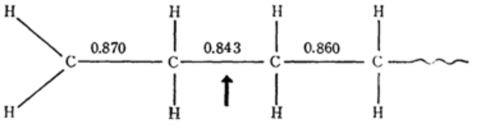

Fig. 10. The mode of β-C–C bond fission. The calculated values of F_{rs}=const×$|C_s^N|$ in (sp²+sp³) systems.

A part of the calculation has been carried out on a KDC-I digital computer at Kyoto University.

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Appendix

The tendency toward the degradation of the odd electron density becomes more apparent when R– compounds are treated by the C–C skeleton method[13,14]. That is to say, in this more simplified procedure the energy value of the σ NBMO is just equal to α[14], as it is in the NBMO of π electron systems, while in the case of straight chain R– compounds, the coefficients of the hybridized orbitals in the σ NBMO are alternately equal to zero, those of non-zero orbitals being given by $-ma$, $+m^2a$, $-m^3a$, $+m^4a$ and so forth, as is seen in Fig. 11. (m is the coefficient of the resonance integral between sp³ hybridized orbitals of the same carbon atom.) The odd electron distribution in the more complex R– compounds can be obtained by means of this simplified procedure. The results are given in Fig. 12. The odd electron densities at the unpaired hybridized orbital of primary, secondary and tertiary carbon atoms decrease in the order

$$(C_r^{\rm N})^2_{\rm prim} > (C_r^{\rm N})^2_{\rm sec} > (C_r^{\rm N})^2_{\rm tert}$$

which is in accordance with the results obtained in Section I.

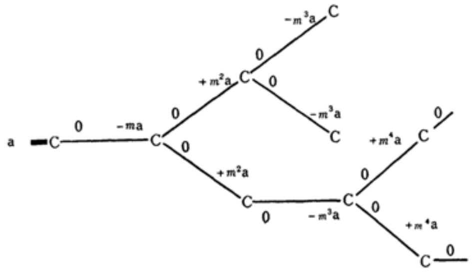

Fig. 11. The coefficients of sp³ hybridized orbitals in the σ NBMO of an R– compound obtained by the C–C skeleton method.

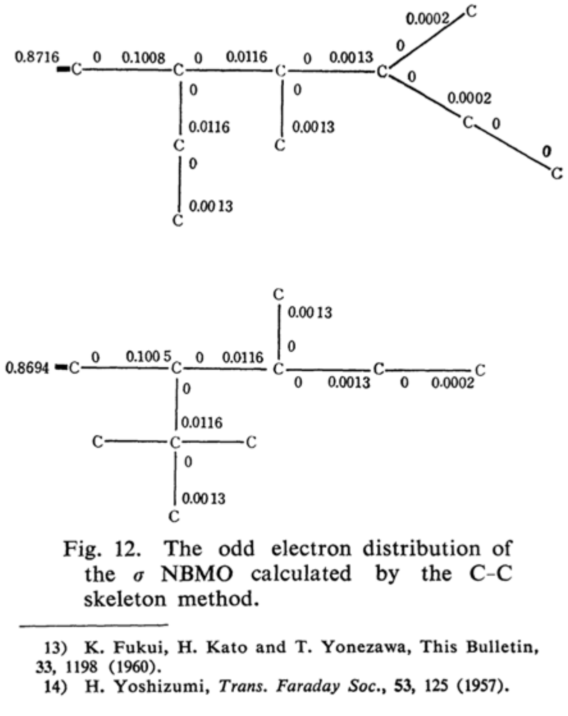

Fig. 12. The odd electron distribution of the σ NBMO calculated by the C–C skeleton method.

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13) K. Fukui, H. Kato and T. Yonezawa, This Bulletin, 33, 1198 (1960).

14) H. Yoshizumi, *Trans. Faraday Soc.*, 53, 125 (1957).