Correlation between Two Molecular Orbital Theories on Organic Reactions. II*. Radical Substitution

By Hiroaki BABA

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Introduction

It has been pointed out in the previous paper⁽¹⁾ (hereafter referred to as I) that in ionic substitutions the static measures of chemical reactivity are closely associated with the corresponding dynamic quantities. That is, they become equivalent to each other, if a certain condition is fulfilled. That condition refers to the coefficients of the powers appearing in the expansions of the secular determinants for the residual molecules appropriate to the substitutions concerned. In the present paper it will be shown that under the same conditions the two sets of quantities used as the measures of the reactivity in radical substitution become also mutually correlated. Further, it will be proved that in the same relation, Dewar's approximate values[2,3] of localization energy become

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* Read in part at the Symposium on π-Electron Problems held by the Chem. Soc. Japan, in October 1954.

[1] H. Baba, This Bulletin, **30**, 147 (1957).

[2] M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3355 (1952).

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

completely parallel with the accurate ones.

Change in Total Energy of π-Electrons with Variation of Resonance Integrals

Before entering into the subject of this article we shall briefly refer to the role of the free valence in radical substitution[4]. Consider an even AH, and let the positions adjacent to position r be denoted by t, t'……. Suppose that a radical reagent attacking at position r brings about the same amount of change, $\beta\delta$, in the resonance integrals β_{rt} $\beta_{rt'}$,……. Then the energy change will be expressed as a Taylor series:

$$\delta E=\sum_t{}' \frac{\partial E}{\partial \beta_{rt}}\delta\beta+\cdots\cdots, \tag{1}$$

where $\delta\beta$ is assumed to be small and positive. By the use of Eqs. (2), (3) and (6) of I, this may be rewritten as

$$\delta E=2N_r^0\delta\beta+\cdots\cdots=2(\sqrt{3}-F_r^0)\delta\beta+\cdots\cdots. \tag{2}$$

Eq. (2) shows that the samllest increase in energy will occur for the largest value of free valence F_r^0 or the smallest value of bond number N_r^0, and hence the most reactive position is the one with the highest free valence or the lowest bond number in the initial state of the molecule.

Now, for the purpose of relating the above-mentioned static quantities F_r^0 and N_r^0 to the dynamic one $L_R^{(r)}$, let it be assumed that the resonance integrals β_{rt}, $\beta_{rt'}$,…… change simultaneously from their initial value β to a certain value between β and 0. Further it is assumed that the other resonance integrals and coulomb integrals are all kept at their initial values. Then the total energy of π-electrons E_r, bond order p_{rt} and bond number N_r may be regarded as continuous functions of β_r, where $\beta\leqq\beta_r=\beta_{rt}=\beta_{rt'}=\cdots\cdots\leqq 0$. These functions will be denoted by $E_r(\beta_r)$, $p_{rt}(\beta_r)$ and $N_r(\beta_r)$, respectively. Then, instead of Eq. (1), the following expression will be otained as the energy change[5]:

$$\Delta E_r(\beta_r)=E_r(\beta_r)-E_0=\int_\beta^{\beta_r}\frac{dE_r(\beta_r)}{d\beta_r}d\beta_r$$
$$=\sum_t{}'\int_\beta^{\beta_r}\frac{\partial E_r}{\partial\beta_{rt}}d\beta_r. \tag{3}$$

Again this may be rewritten as

$$\Delta E_r(\beta_r)=\sum_t{}'\int_\beta^{\beta_r}2p_{rt}(\beta_r)d\beta_r$$
$$=\int_\beta^{\beta_r}2N_r(\beta_r)d\beta_r. \tag{4}$$

Thus the bond number N_r as a function of β_r has come to be important, so that some remarks on it will be given.

First, from the definition of N_r^0

$$N_r(\beta)=N_r^0. \tag{5}$$

Next, let us consider what happens to the value of $N_r(\beta_r)$ when β_r approaches to zero. Consider a system consisting of carbon atom r and odd AH obtained when atom r is excluded from the even AH in question, and suppose that in this system there is no interaction between atom r and the odd AH; then we may regard $\beta_r=\beta_{rt}=\beta_{rt'}$…… as zero.

An odd AH has always a non-bonding molecular orbital (NBMO), so that there exists a degenerate level of zero energy in the system. The NBMO of the odd AH will be expressed as

$$\phi_{\mathrm{zero}}^{(r)}=\sum_v b_{0v}\chi_v. \tag{6}$$

The coefficients b_{0v}'s can be easily calculated on account of the characteristic property of NBMO[6].

Now consider such a perturbation for this system under which β_r changes from zero to negative. The correct zeroth order MO's for this perturbation will be linear combinations of χ_r and $\phi_{\mathrm{zero}}^{(r)}$[7]:

$$\phi_{\mathrm{zero}}^{\pm}=\frac{1}{\sqrt{2}}(\chi_r\pm\phi_{\mathrm{zero}}^{(r)}). \tag{7}$$

It may be assumed without loss of generality that it is ϕ_{zero}^{+} which becomes a bonding orbital under the influence of the perturbation. Conversely, when β_r for the even AH tends to zero, one of the MO's will reduce to ϕ_{zero}^{+} and the others to the bonding orbitals of the odd AH. Therefore it follows from Eqs. (6) and (7) that

$$p_{rt}(0)\equiv\lim_{\beta_r\to 0}p_{rt}(\beta_r)=2\cdot\frac{1}{\sqrt{2}}\cdot\frac{1}{\sqrt{2}}b_{0t}=b_{0t}, \tag{8}$$

$$N_r(0)\equiv\lim_{\beta_r\to 0}N_r(\beta_r)=\sum_t{}' b_{0t}. \tag{9}$$

It should be noticed that $p_{rt}(\beta_r)$ and hence $N_r(\beta_r)$ do not vanish even if β_r tends to

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4) R. D. Brown, *Quart. Rev.*, **6**, 63 (1952).

5) F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).

6) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265, 275 (1950).

7) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341 (1952).

zero. On the basis of these considerations the relation between $2N_r$ and β_r may be represented schematically by the curve shown in Fig. 1.

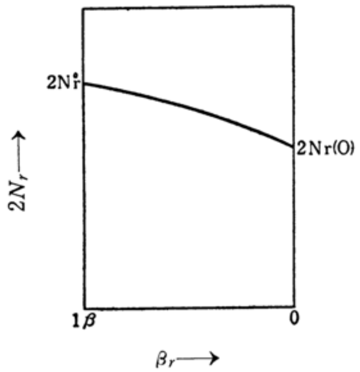

Fig. 1

According to the foregoing arguments, it follows at once that

$$\lim_{\beta_r\to 0} E_r(\beta_r) = E_R^{(r)} \tag{10}$$

and

$$\lim_{\beta_r\to 0} \varDelta E_r(\beta_r) = L_R^{(r)}. \tag{11}$$

On the other hand the approximate values of $L_R^{(r)}$, given by Dewar[2,3] based on the treatment of perturbation theory, are $-2\beta\sum_t{}' p_{rt}^0$ and $-2\beta\sum_t{}' b_{0t}$. If these values be designated as $L_R^{(r)\prime}$ and $L_R^{(r)\prime\prime}$, then we have

$$L_R^{(r)\prime} = -2N_r^0\beta, \tag{12}$$

$$L_R^{(r)\prime\prime} = -2N_r(0)\beta. \tag{13}$$

Now Eq. (4) shows that the value of $\varDelta E_r(\beta_r)$ is equal to the area under the curve of Fig. 1 between $\beta_r=\beta$ and $\beta_r=\beta_r$. Hence, $L_R^{(r)}$ is equal to the area under the curve between $\beta_r=\beta$ and $\beta_r=0$, while $L_R^{(r)\prime}$ is equal to the area of the reactangle whose adjacent sides are $-\beta$ and $2N_r^0$, and $L_R^{(r)\prime\prime}$ to that of the rectangle whose adjacent sides are $-\beta$ and $2N_r(0)$ (see Fig. 1).

As an example, the relation between N_r and β_r for benzene is shown in Fig. 2. In this example,

$$p_{rt}(0) = p_{rt'}(0) = \frac{1}{\sqrt{3}},$$

and

$$N_r(0) = \frac{2}{\sqrt{3}},$$

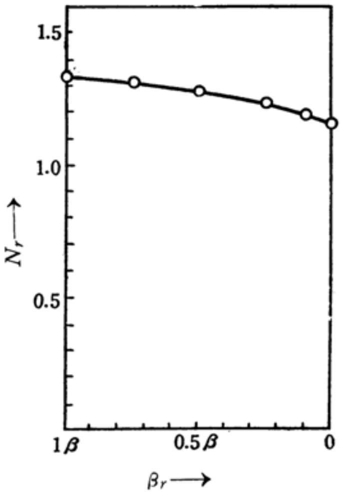

Fig. 2. $N_r(\beta_r)$ for benzene.

since the coefficients of the AO's in the NBMO of pentadienyl are calculated as shown in Fig. 3. It may be worthy of note that there exists the following relation among the magnitudes of N_r^0, $L_R^{(r)}$ and $N_r(0)$:

$$2N_r^0 > \frac{L_R^{(r)}}{-\beta} > 2N_r(0).$$

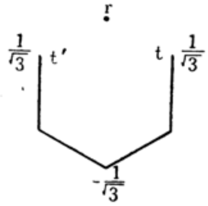

Fig. 3

This is easily seen from Fig. 2; in fact the calculated values of the three terms are 2.667, 2.536 and 2.309, respectively. The above relation means that $2N_r^0$ is the upper limit of $L_R^{(r)}/-\beta$, while $2N_r(0)$ is the lower one.

Correlation between the Static and Dynamic Quantities

Consider two positions r and s in an even AH. According to the integral expression given by Coulson and Longuet-Higgins[8] for π-bond order

$$p_{rt}(\beta_r) = (-1)^{r+t+1}\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{D_{r,t}}{D}\,dy. \tag{14}$$

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[8] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947); **A192**, 16 (1947).

When D is expanded with respect to the rth row,

$$D=\sum_{t}{}'(-1)^{r+t}\beta_r D_{r,t}-\varepsilon D_{r,r}. \tag{15}$$

Therefore it can be shown that

$$N_r(\beta_r)=\frac{-1}{\pi\beta_r}\int_{-\infty}^{\infty}\frac{D(iy)+iyD_{r,r}(iy)}{D(iy)}dy, \tag{16}$$

which reduces to

$$N_r(\beta_r)=\frac{-\beta_r}{\pi\beta^2}\times\int_{-\infty}^{\infty}\frac{D^0(iy)+iyD^0_{r,r}(iy)}{(\beta_r/\beta)^2D^0(iy)+\{(\beta_r/\beta)^2-1\}iyD^0_{r,r}(iy)}\times dy. \tag{17}$$

A similar expression may be obtained for $N_s(\beta_s)$. Now, if inequalities (41) and hence inequality (42) of I hold, then it follows

$$\frac{iyD^0_{r,r}(iy)}{(-1)^{n/2}}<\frac{iyD^0_{s,s}(iy)}{(-1)^{n/2}}<0 \quad (-\infty<y<\infty,\ y\neq 0). \tag{18}$$

Consequently, using Eq. (39) of I, it is easily verified that

$$N_r(\beta_r)<N_s(\beta_s) \text{ for } \beta\leqq\beta_r=\beta_s\leqq 0. \tag{19}^*$$

In particular cases where $\beta_r=\beta_s=\beta$ and $\beta_r=\beta_s=0$, we have

$$N^0_r<N^0_s, \tag{20}$$

and

$$N_r(0)<N_s(0), \tag{21}$$

respectively. These relations are explained by Fig. 4.

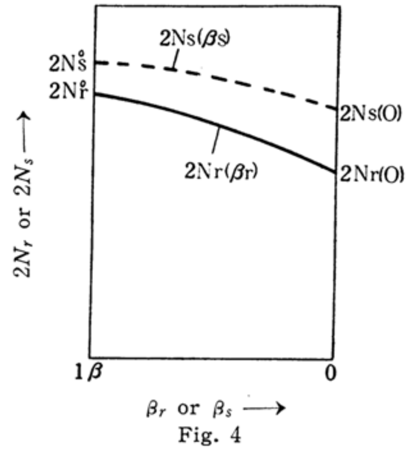

Fig. 4

Thus, the conclusions derived from inequalities (41) of I are summarized as follows:

1. The bond number N^0_r is smaller than N^0_s, and hence the free valence F^0_r is larger than F^0_s;
2. The localization energy $L^{(r)}_R$ is smaller than $L^{(s)}_R$;
3. Dewar's approximate values of localization energy $L^{(r)\prime}_R$ and $L^{(r)\prime\prime}_R$ are smaller than $L^{(s)\prime}_R$ and $L^{(s)\prime\prime}_R$, respectively;
4. The bond number $N_r(\beta_r)$ is smaller than $N_s(\beta_s)$ for $\beta\leqq\beta_r=\beta_s\leqq 0$;
5. The change in total energy of π-electrons $\varDelta E_r(\beta_r)$ is smaller than $\varDelta E_s(\beta_s)$ for $\beta<\beta_r=\beta_s\leqq 0$.

From (2) and (3) it follows that the two approximate values of $L^{(r)}_R$, i.e. $-2N^0_r\beta$ and $-2N_r(0)\beta$ will run parallel to the accurate one. Conclusion (5) is in accord with the concept of chemical non-crossing rule.

All the correlations stated above may be found for any pair of positions in those molecules shown in Table I of the previous paper except for positions 1 and 9 in phenanthrene, and 1 and 2 in diphenylene.

Lastly, it should be added that the method used in the present paper in dealing with the radical substitution is essentially the same as that used previously in treating the ionic substitutions. This situation may be understood by inspection of Table I where the correspondence among the used variables is recorded*.

TABLE I

Ionic substitutions		Radical substitution
Nucleophilic	Electrophilic	
$0\leqq\alpha_r<+\infty$	$-\infty<\alpha_r\leqq 0$	$\beta\leqq\beta_r\leqq 0$
$q_r(\alpha_r)$	$q_r(\alpha_r)$	$N_r(\beta_r)$
$\varDelta E_r(\alpha_r)$	$\varDelta E_r(\alpha_r)-2\alpha_r$	$\varDelta E_r(\beta_r)$

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[*] For $\beta_r=\beta_s=0$ it is assumed that $a^{(r)}_1>a^{(s)}_1$ in inequalities (41) of I. If $a^{(r)}_1=a^{(s)}_1$, then $\lim_{\beta_r\to 0}N_r(\beta_r)=\lim_{\beta_r\to 0}N_s(\beta_s)$.

[*] A quantity corresponding to the partial polarization energy $P_r(q_r)$ in ionic substitutions may be defined as

$$L_r(N_r)=\varDelta E_r(\beta_r(N_r))-2N_r\{\beta_r(N_r)-\beta\},$$

which might be called partial localization energy. $L_r(N_r)$ appears to be not so useful as $P_r(q_r)$. This is partly due to the fact that, so far as the π-bond order is calculated according to its usual definition, $N_r(\beta_r)$ does not reduce to zero when β_r tends to zero.

Conclusion

Both the argument of the present paper and that of the previous one have made clear that: When the condition of inequalities (41) of I hold for two positions in an even alternant hydrocarbon, the same conclusion follows for the relative reactivities of the positions both in ionic and radical substitutions, and it does not matter which quantity be employed as a measure of the reactivity from among self-polarizability, free valence and locarization energy (accurate or approximate). This condition of inequalities (41) is satisfied in many alternant hydrocarbons. Therefore, it is not peculiar that the two theories usually give the same prediction concerning the reactivity of this sort of molecules, notwithstanding the fact that there is a striking difference in fundamental assumptions involved in them.

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Research Institute of Applied Electricity
Hokkaido University, Sapporo