

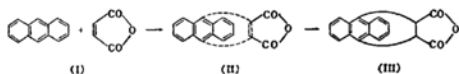
Theoretical Reactivity Index of Addition in the "Frontier Electron Theory"

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It is well known that many polycondensed aromatic hydrocarbons undergo addition such as that of the Diels-Alder type and oxidation with osmium tetroxide: the former is the addition of e.g. quinone or maleic anhydride to the reactive para position and the latter is the addition to the reactive ortho bond.

It is suggested that the frontier electron density and superdelocalizability which have been proved to be good indexes of substitution reaction in conjugated compounds¹⁻³⁾ will also be applicable to interpreting the reactivity in simultaneous addition reactions stated above, because the substitution and addition seem to be not so greatly different in nature from each other, at least until the activated complex is formed. In substitution reaction, the hydrogen atom of the attacking position and the reagent was considered to form a pseudoatom and the hyperconjugation energy due to the charge transfer between the pseudoatom and the orbital at the attacking position was assumed to make the reaction easy⁴⁾. The situation in the addition reaction can be considered to resemble the substitution reaction in the sense that the delocalization energy due to the charge transfer in the transition state play a dominant role in decreasing the activation energy of the reaction. The circumstances will be clearly seen in the following example: the addition of maleic anhydride to the para position of polycondensed aromatic hydrocarbon, e.g. anthracene is deemed to proceed by a one-step process as follows:



The charge transfer between the maleic anhydride and the substrate molecule through the orbitals at the ethylenic bond of the former and the para position of the latter will occur in the transition state (II), and the delocaliza-

tion energy due to the charge transfer is naturally considered a measure of easiness of addition reaction because the activation energy is decreased according as the increase of delocalization energy. In this connection, the frontier electron density and the superdelocalizability which could be derived from the delocalization energy are expected to be a good measure of the addition reaction.

In the present paper, the theoretical index for addition reaction in the frontier electron theory is derived and the index is compared with the rate of reactions hitherto carried out.

Theoretical Treatment

The secular equation of the π part of the transition complex which includes the orbitals of reagent and substrate π electron system is written as

$$D(\epsilon) = \begin{vmatrix} \alpha_h - \epsilon & 0 & 0 & \gamma & 0 & 0 & \cdots & 0 \\ 0 & \alpha_h - \epsilon & \gamma & 0 & 0 & 0 & \cdots & 0 \\ 0 & \gamma & a_{11} - \epsilon & a_{12} & a_{13} & a_{14} & \cdots & a_{1n} \\ \gamma & 0 & a_{21} & a_{22} - \epsilon & a_{23} & a_{24} & \cdots & a_{2n} \\ 0 & 0 & a_{31} & a_{32} & a_{33} - \epsilon & a_{34} & \cdots & a_{3n} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & a_{n1} & a_{n2} & \cdots & \cdots & \cdots & a_{nn} - \epsilon \end{vmatrix} \\ = (\alpha_h - \epsilon)^2 \Delta(\epsilon) - \gamma^2 [(\alpha_h - \epsilon) \{ \Delta_{rr}(\epsilon) + \Delta_{ss}(\epsilon) \}] + \gamma^4 \Delta_{rrss}(\epsilon) = 0 \quad (1)$$

where

$$\Delta(\epsilon) = \begin{vmatrix} a_{11} - \epsilon & a_{12} & a_{13} & \cdots & a_{1n} \\ a_{21} & a_{22} - \epsilon & a_{23} & \cdots & a_{2n} \\ a_{31} & a_{32} & a_{33} - \epsilon & \cdots & a_{3n} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ a_{n1} & a_{n2} & \cdots & \cdots & a_{nn} - \epsilon \end{vmatrix}$$

is the secular determinant for the substrate π -electron system and $\Delta_{rr}(\epsilon)$ and $\Delta_{ss}(\epsilon)$ are the minors of $\Delta(\epsilon)$ corresponding to the rr - and ss -elements, and a_{ii} and $a_{ij} (i \neq j)$ are the

1) K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952).

2) K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, *ibid.*, **22**, 1433 (1954).

3) K. Fukui, T. Yonezawa and C. Nagata, *ibid.*, **27**, 1247 (1957).

4) K. Fukui, T. Yonezawa and C. Nagata, *This Bulletin*, **27**, 423 (1954).

Coulomb and the resonance integrals, respectively. For simplicity, the values of these integrals are assumed to be the same as those in an isolated molecule. α_h and γ are the Coulomb integral of the reagent*, and the resonance integral between the reagent and the r th and the s th atom of the substrate molecule at which the reaction takes place, respectively.

When the conjugation between the substrate molecule and reagent is small, i. e., in the case of $0 < \gamma \leq 1$, the perturbed orbital energy of the complex are given by the following formula

$$\varepsilon_j' = \varepsilon_j + \delta\varepsilon_j\gamma^2 + 0(\gamma^4) + \dots \quad (2a)$$

$$\alpha_h' = \alpha_h + \delta\alpha_h\gamma^2 + 0(\gamma^4) + \dots \quad (2b)$$

The values of $\delta\varepsilon_j$ and $\delta\alpha_h$ are easily obtained by the perturbation treatment as

$$\delta\varepsilon_j = \frac{\Delta_{rr}(\varepsilon_j) + \Delta_{ss}(\varepsilon_j)}{(\alpha_h - \varepsilon_j)\Delta'(\varepsilon_j)}\gamma^2 + \dots \quad (3)$$

$$\delta\alpha_h = -\frac{\{\Delta_{rr}(\alpha_h) + \Delta_{ss}(\alpha_h)\}}{2\Delta(\alpha_h)} \pm \frac{\sqrt{\{\Delta_{rr}(\alpha_h) - \Delta_{ss}(\alpha_h)\}^2 + 4\{\Delta_{rs}(\alpha_h)\}^2}}{2\Delta(\alpha_h)} \quad (4)$$

ε_j' and α_h' are the roots of $D(\varepsilon)=0$ and they correspond to the energy of the molecular orbital of the unperturbed system $\Delta(\varepsilon)$ and the orbitals of the reagent, respectively. We assumed that $\Delta(\varepsilon)=0$ has no multiple roots here, but in the case in which $\Delta(\varepsilon)=0$ has double roots, the final result is not altered.

The delocalization energy \mathcal{R}_{r+s} is derived by treatment analogous to the case of substitution reaction³. It is given according as the type of reaction as follows:

for electrophilic reaction,

$$\begin{aligned} \mathcal{R}_{r+s} &\cong 2 \sum_{j=1}^m \frac{\Delta_{rr}(\varepsilon_j) + \Delta_{ss}(\varepsilon_j)}{(\alpha_h - \varepsilon_j)\Delta'(\varepsilon_j)}\gamma^2 \\ &= 2 \sum_{j=1}^m \frac{(C_r^j)^2 + (C_s^j)^2}{\varepsilon_j - \alpha_h}\gamma^2 \end{aligned} \quad (5)$$

for radical reaction**,

$$\begin{aligned} \mathcal{R}_{r+s} &\cong \left[- \sum_{j=1}^m \frac{\Delta_{rr}(\varepsilon_j) + \Delta_{ss}(\varepsilon_j)}{(\varepsilon_j - \alpha_h)\Delta'(\varepsilon_j)} \right. \\ &\quad \left. - \sum_{j=m+1}^n \frac{\Delta_{rr}(\varepsilon_j) + \Delta_{ss}(\varepsilon_j)}{(\alpha_h - \varepsilon_j)\Delta'(\varepsilon_j)} \right] \gamma^2 \end{aligned}$$

* In this treatment, the attacking reagent was assumed to be composed of two non-conjugating components. In other words, the reaction was considered to occur with two reagents. The one reagent attacks the r position and the other the s position simultaneously or stepwise. In the case of the addition of maleic anhydride to polycondensed aromatic hydrocarbons, the reagent as well as the substrate is a conjugated system, and the whole π electron system of maleic anhydride should be taken into consideration. In this case, however, the reaction was considered as an addition of two reagents to the substrate separately.

$$\begin{aligned} &= \left[\sum_{j=1}^m \frac{(C_r^j)^2 + (C_s^j)^2}{\varepsilon_j - \alpha_h} \right. \\ &\quad \left. + \sum_{j=m+1}^n \frac{(C_r^j)^2 + (C_s^j)^2}{-(\varepsilon_j - \alpha_h)} \right] \gamma^2 \end{aligned} \quad (6)$$

for nucleophilic reaction,

$$\begin{aligned} \mathcal{R}_{r+s} &\cong -2 \sum_{j=m+1}^n \frac{\Delta_{rr}(\varepsilon_j) + \Delta_{ss}(\varepsilon_j)}{(\alpha_h - \varepsilon_j)\Delta'(\varepsilon_j)}\gamma^2 \\ &= 2 \sum_{j=m+1}^n \frac{(C_r^j)^2 + (C_s^j)^2}{-(\varepsilon_j - \alpha_h)}\gamma^2 \end{aligned} \quad (7)$$

where C_r^j is the coefficient of the r th atomic orbital of j th molecular orbital of non-perturbed substrate molecule and the relation $-\Delta_{rr}(\varepsilon_j)/\Delta'(\varepsilon_j) = (C_r^j)^2$ was used in deriving the last terms of the right hand side of the above equations.

When the value of α_h is equal to α , the Coulomb integral of carbon atom in benzene, the coefficients of γ^2 in Eqs. 5, 6 and 7 are nothing but $(S_r + S_s)$ for electrophilic, radical and nucleophilic reactions, respectively. Therefore, the theoretical index for addition reaction at two positions r and s is the sum of the superdelocalizability at r and s positions. It is clearly seen in the expression in Eqs. 5, 6 and 7 that the contribution of the frontier orbital is the greatest, hence as in the case of the treatment of substitution reaction³, the one term approximation taking into consideration the frontier orbital alone, will be allowed.

It is noted that the present treatment gives the same result regardless whether one considers the reaction as a simultaneous or two-step one. This indiscernability is also seen in other treatments such as static and localization methods. Therefore, it is impossible to decide whether the reaction is one-step or not by comparing the theories and experimental results.

The theoretical index derived above is qualified as a good index for predicting the reactivity in simultaneous addition reaction as a result of comparison with the experiment. For instance, the data of the attacking positions in the Diels-Alder reaction are in agreement without an exception with the predicted most reactive position in a molecule (Table I). The relative rate of these compounds in the Diels-Alder reaction has not been measured in one

** For a radical reaction twice the second term (the energetically lower term) of Eq. 4 are omitted in deriving Eq. 6. It is because one may conclude that the term has no connection with the simultaneous addition reaction. That is to say, from the configuration interaction's point of view, it originates in the interaction between the initial configuration (initial state of reaction) and the configuration corresponding to one-electron transfer from a component of the reagent to another component. Not involving the charge transfer between the reagent and the substrate molecule but between the two components of reagents, this interaction seems to have no connection with the reaction.

TABLE I. SUM OF THE SUPERDELOCALIZABILITY AT PARA CARBON ATOMS IN SOME AROMATIC HYDROCARBONS (S_r+S_s) IN COMPARISON WITH EXPERIMENTS

Compound	Para position	S_r+S_s	Experiment; position of attack
Hexacene	6, 15	4.011	6, 15 ^{a)}
	5, 16	3.459	
	1, 4	2.355	
Pentacene	6, 13	3.589	6, 13 ^{a)}
	5, 14	3.269	
	1, 4	2.308	
Naphthacene	5, 12	3.010	5, 12 ^{a)}
	1, 4	2.243	
Anthracene	9, 10	2.627	9, 10 ^{b)}
	1, 4	2.147	
1, 2-Benzanthracene	9, 10	2.437	9, 10 ^{a,c)}
	5, 8	2.098	
	1', 4'	1.915	
1, 2, 3, 4-Dibenzanthracene	9, 10	2.303	9, 10 ^{a,d,h)}
	5, 8	2.056	
	1', 4'	1.853	
1, 2, 5, 6-Dibenzanthracene	9, 10	2.292	9, 10 ^{e)}
	1', 4'	1.919	
Naphthalene	1, 4	1.989	No addition ^{f)}
Phenanthrene	1, 4	1.918	No addition ^{g)}
Chrysene	1, 12	1.907	No addition ^{g)}
Benzene		1.667	No addition ^{f)}

a) E. Clar, *Ber.*, **64**, 2194 (1931); **65**, 503 (1932); **72**, 1817 (1939).

b) O. Diels, K. Alder and S. Beckmann, *Ann.*, **486**, 1191 (1931).

c) E. Clar, *Ber.*, **65**, 519 (1932).

d) E. Clar and L. Lombardi, *Ber.*, **65**, 1411 (1932).

e) J. W. Cook, *J. Chem. Soc.*, **1931**, 3273.

f) E. Clar, "Aromatische Kohlenwasserstoffe" p. 12 (1941).

g) R. N. Jones, C. J. Gogek and R. W. Sharpe, *Can. J. Res.*, **B26**, 719 (1948).

h) E. J. Moriconi, W. F. O'Conner and F. T. Wallenberger, *J. Am. Chem. Soc.*, **81**, 646 (1959).

and the same condition. However, considering the experimental data which have been so far reported (cf. references in Table I), one can conclude that the following order of reactivity might exist: hexacene > pentacene > naphthacene > anthracene > 1, 2-benzanthracene > 1, 2, 5, 6-dibenzanthracene > naphthalene, phenanthrene, benzene. This is in excellent accord with the order of magnitude of S_r+S_s of these compounds.

As is seen in Table II, the experimental position of attack of osmium tetroxide to the double bond of some polycondensed aromatic

TABLE II. SUM OF THE SUPERDELOCALIZABILITY AT TWO ADJACENT CARBON ATOMS IN SOME AROMATIC HYDROCARBONS (S_r+S_s) IN COMPARISON WITH EXPERIMENTS

Compound	Bond ($r-s$)	S_r+S_s	Experiment; position of attack
1, 2-Benzanthracene	3, 4	2.079	3, 4 ^{a)}
	5, 6	1.963	
	7, 8	1.953	
	3', 4'	1.849	
	1', 2'	1.832	
	6, 7	1.818	
1, 2, 5, 6-Dibenzanthracene	2', 3'	1.766	3, 4 ^{a,e)}
	3, 4	2.062	
	3', 4'	1.848	
	1', 2'	1.842	
Pyrene	2', 3'	1.771	1, 2 ^{b)}
	1, 2	2.052	
	3, 4	1.944	
Chrysene	1, 2	1.997	1, 2 ^{b)}
	3, 4	1.857	
	5, 6	1.852	
	4, 5	1.762	
Phenanthrene	9, 10	1.995	9, 10 ^{a,b,d)}
	1, 2	1.837	
	3, 4	1.832	
Anthracene	1, 2	1.995	1, 2, 3, 4 ^{a,c)}
	2, 3	1.843	
Naphthalene	1, 2	1.867	1, 2 ^{e)}
	2, 3	1.746	
Benzene		1.667	No addition ^{e)}

a) G. M. Badger, *J. Chem. Soc.*, **1949**, 456; Ref. 5.

b) J. W. Cook and R. Schoental, *ibid.*, **1948**, 170.

c) J. W. Cook and R. Schoental, *Nature*, **161**, 237 (1948).

d) N. L. Drake and T. R. Sweeney, *J. Org. Chem.*, **11**, 67 (1946).

e) E. J. Moriconi, W. F. O'Conner, W. J. Schmitt, G. W. Cogswell and B. P. Fürer, *J. Am. Chem. Soc.*, **82**, 3441 (1960).

hydrocarbons agree very well with the prediction by the theory. The reactive rate of reaction of these compounds is not determined completely; however, the experiment by Badger and Reed showed that 1, 2-benzanthracene reacts with osmium tetroxide faster than phenanthrene does⁵⁾. This fact is explained well by our calculated result.

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