A Molecular Orbital Approach to the Electrophilicity of H and OH Radicals

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(Received April 28, 1978)

We tried to explain the electrophilicity of radical reagents such as H and OH radicals in the aromatic substitution reaction by using the molecular orbital theory. The delocalization energy of π electrons was decomposed into two parts: one is the energy due to the delocalization from a substrate to a reagent and another is that from a reagent to a substrate. The former was considered to be a measure of the electrophilicity and the latter of the nucleophilicity. The decomposition of the delocalization energy into two parts was carried out by modifying the relevant core resonance integrals as appropriate. The result indicated that the delocalization energy for the electrophilicity was much larger than that for the nucleophilicity for both radicals. Thus, H and OH radicals should be electrophilic in nature, in good agreement with the experimental facts. Finally, the origin of the electrophilicity was discussed in connection with the height of the relevant energy levels by following a perturbational approach.

Chemical reactivities of OH and H radicals have been extensively studied in connection with the radiobiological reaction mechanism.[1-6] In many studies of the reaction mechanisms of OH and H radicals, it has been shown that OH and H radicals are electrophilic in nature.[1,2] A beautiful proof for the electrophilicity of the OH radical was published by Anbar *et al.*:[2] they measured the relative rates of reaction of OH radicals with many benzene derivatives and substituted benzoate ion, and found that a plot of the reaction rate against Hammett's σ value is nearly linear, with $\rho=-0.41$, indicating the electrophilicity of the OH radical.

Molecular orbital studies of the reaction mechanism of the OH radical have also been carried out by many researchers.[10-12] In these studies, the electrophilicity of the OH radical was indicated by the electron transfer quantity from the substrate to the OH radical. This quantity, however, can only be used as a qualitative measure of the electrophilicity, since this quantity should be the difference of two electron transfer quantities, from substrate to OH radical and *vice versa.*

In the present paper, we used the unrestricted SCF method in the INDO approximation and calculated, separately, the stabilization energies due to the delocalization of electrons from radical reagent to substrate and those due to the delocalization of electrons from substrate to radical reagent. Obviously, the former can be considered to be a measure of the nucleophilicity of the radical reagent and the latter a measure of the electrophilicity. From the results obtained, OH and H radicals were found to have much more electrophilicity than nucleophilicity, in good agreement with the experimental data.[1,2]

Method of Calculations

First of all, we assumed that the transition state of the reaction between benzene and the radical reagent is the tetrahedral intermediate, as shown in Fig. 1. This model for the transition state has been used in many theories for the chemical reactivity, especially in the frontier electron theory of Fukui *et al.*[7,8] The geometry of the tetrahedral intermediate was tentatively assumed at follows: C–C bond=1.397 Å, C–H bond=1.084 Å, C–O bond=1.360 Å, O–H bond=0.967 Å, all bond angles except for those including the tetrahedral carbon =120°, bond angles including tetrahedral carbon=109°28′, ∠COH=107°18′, and the H atom of the OH group and the H atom of the CH bond are assumed to be in the trans form. Although the C–O and C–H bond lengths of the tetrahedral carbon atom in the transition state may be different from those used in the present article, it is difficult to determine the bond lengths in the transition state. However, the relative magnitude of the stabilization energies for delocalization of electrons from the substrate to the reagent and *vice versa* can probably be estimated by using the above-mentioned geometry.

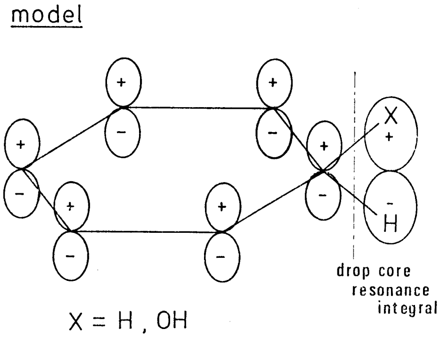


Fig. 1. The model for the tetrahedral intermediate. The orbital at the most right is the pseudo π orbital.

It has been well known that the chemical reactivity of aromatic substitution is mainly governed by the magnitude of the stabilization energy due to the delocalization of π electrons between benzene π orbitals and the pseudo π orbital which is formed from the attacking radical reagent and the remaining hydrogen atom.[7,8] In order to estimate the delocalization energy of π electrons, first, the total energy of the molecule was calculated by using the unrestricted SCF method with INDO approximation[9] after dropping all core resonance integrals between π atomic orbitals on the benzene moiety and the pseudo π orbital. This gives the total energy without the delocalization of π electrons. Next, the total energy of the molecule was calculated after partially including the core resonance integrals between π atomic orbitals and the pseudo π^* orbital, so as to include only the effect of the delocalization of π electrons from the substrate to the radical reagent, and not from the radical reagent to the substrate. The difference between these two total energies can be considered to be a measure of the electrophilicity of the radical reagent in question:

$$E_{\text{electrophilicity}} = E(\text{including the delocalization from the substrate to the radical reagent}) - E(\text{without the delocalization of } \pi \text{ electrons}), \tag{1}$$

where E is the total energy calculated under the restriction described in the parentheses. In a similar manner, we can obtain a measure of the nucleophilicity of the radical reagent by the following equation:

$$E_{\text{nucleophilicity}} = E(\text{including the delocalization from the radical reagent to the substrate}) - E(\text{without the delocalization of } \pi \text{ electrons}). \tag{2}$$

In calculating a measure of the electrophilicity as well as the nucleophilicity, the core resonance integrals between π atomic orbitals on the benzene moiety and the pseudo π orbital should be modified in order to include the delocalization of π electrons from the substrate to the radical reagent or *vice versa*. That is, for a measure of the electrophilicity, the core resonance integrals between atomic orbitals in question should be modified so that the core resonance integrals between the occupied π molecular orbitals on the benzene moiety and the vacant pseudo π^* molecular orbitals have the same value as those obtained by using the usual core resonance integrals between atomic orbitals, and the resonance integral between other molecular orbitals is always zero. Of course, the molecular orbitals which are used for calculating the core resonance integral have to be those obtained without the effect of the delocalization of π electrons, namely, by dropping the core resonance integrals between π and pseudo π atomic orbitals. The values of the core resonance integrals required can be calculated by the procedure described below.

Molecular orbitals obtained by dropping all the core resonance integrals between π atomic orbitals on benzene and pseudo π orbitals can be classified into two groups: one is those containing only π atomic orbitals on a benzene moiety and the other, the pseudo π orbitals as well as σ atomic orbitals of benzene. Thus, the molecular orbitals can be represented as follows:

$$\phi_{\pi i} = \sum_r C_{\pi i,r}\chi_r, \tag{3}$$

$$\phi_{\sigma j} = \sum_s C_{\sigma j,s}\chi_s, \tag{4}$$

where $\phi_{\pi i}$ denotes a molecular orbital containing only π atomic orbitals on the benzene ring, and $\phi_{\sigma j}$ denotes that containing pseudo π orbitals as well as σ atomic orbitals of benzene. From Eq. 3, an atomic orbital, χ_r, can be represented by a linear combination of molecular orbitals $\phi_{\pi i}$, as shown in the following. Equation 3 is multiplied by the coefficient $C_{\pi i.r_1}$ and the resulting equations are added for all i:

$$\begin{aligned}\sum_i C_{\pi i,r_1}\phi_{\pi i} &= \sum_r\sum_i C_{\pi i,r_1}C_{\pi i,r}\chi_r = \sum_r \chi_r \sum_i C_{\pi i,r_1}C_{\pi i,r} \\ &= \sum_r \chi_r \delta_{rr_1} = \chi_{r_1},\end{aligned} \tag{5}$$

where r_1 designates one of the π atomic orbitals $\{\chi_r\}$. Thus, we have

$$\chi_r = \sum_i C_{\pi i,r}\phi_{\pi i}. \tag{6}$$

Similarly,

$$\chi_s = \sum_j C_{\sigma j,s}\phi_{\sigma j}. \tag{7}$$

By using Eqs. 6 and 7, we can represent a core resonance integral between atomic orbitals χ_r and χ_s as the sum of core resonance integrals between molecular orbitals $\phi_{\pi i}$ and $\phi_{\sigma j}$:

$$\begin{aligned}I_{rs} &= \int \chi_r h^\circ \chi_s \mathrm{d}\tau = \sum_i\sum_j C_{\pi i,r}C_{\sigma j,s}\int \phi_{\pi i} h^\circ \phi_{\sigma j}\mathrm{d}\tau \\ &= \sum_i\sum_j C_{\pi i,r}C_{\sigma j,s}I_{ij},\end{aligned} \tag{8}$$

where I_{rs} and I_{ij} are the core resonance integral between the atomic orbitals χ_r and χ_s, and that between the molecular orbitals $\phi_{\pi i}$ and $\phi_{\sigma j}$, respectively, and h° means the one electron Hamiltonian. By modifying Eq. 8, we can obtain the value of the core resonance integral between atomic orbitals which gives the core resonance integrals between any specified molecular orbitals $\phi_{\pi i_1}$ and $\phi_{\sigma j_1}$ correctly and gives zero for the core resonance integrals between other molecular orbitals. That is,

$$I_{rs} = \sum_{(i_1-j_1)} C_{\pi i_1,r}C_{\sigma j_1,s}I_{i_1 j_1}, \tag{9}$$

where (i_1-j_1) means that the summation should cover only some specified molecular orbitals $\phi_{\pi i_1}$ and $\phi_{\sigma j_1}$. It is proved below that the core resonance integrals, I_{rs}, in Eq. 9 give the core resonance integrals between molecular orbitals $\phi_{\pi i_1}$ and $\phi_{\sigma j_1}$ correctly and give zero values for others. Consequently, when the vacant molecular orbitals localized in the radical moiety and the occupied molecular orbitals are chosen for i_1 and j_1, respectively, we can calculate the delocalization energy for the electrophilicity given by Eq. 1. The proof is as follows:

$$\begin{aligned}I_{ij} &= \sum_r\sum_s C_{\pi i,r}C_{\sigma j,s}\int \chi_r h^\circ \chi_s \mathrm{d}\tau = \sum_r\sum_s C_{\pi i,r}C_{\sigma j,s}I_{rs} \\ &= \sum_r\sum_s C_{\pi i,r}C_{\sigma j,s}\sum_{(i_1-j_1)} C_{\pi i_1,r}C_{\sigma j_1,s}I_{i_1 j_1} \\ &= \sum_{(i_1-j_1)} I_{i_1 j_1}\Big(\sum_r C_{\pi i,r}C_{\pi i_1,r}\Big)\Big(\sum_s C_{\sigma j,s}C_{\sigma j_1,s}\Big) \\ &= \sum_{(i_1-j_1)} I_{i_1 j_1}\delta_{ii_1}\delta_{jj_1}.\end{aligned} \tag{10}$$

Equation 10 indicates that I_{ij} is equal to the correct value only when $i=i_1$ and $j=j_1$ and is zero otherwise. Consequently, when molecular orbitals $\phi_{\pi i_1}$ cover all occupied orbitals, and $\phi_{\sigma j_1}$ cover all vacant pseudo π^* orbitals, the SCF calculations with the core resonance integrals of Eq. 9 should give a measure of the electrophilicity. On the other hand, when molecular orbitals $\phi_{\pi i_1}$ cover all vacant orbitals, and $\phi_{\sigma j_1}$ cover all occupied pseudo π orbitals, a measure of the nucleophilicity must be given.

The procedure of the calculations can be summarized as follows. (i) The total energy of the molecule in the transition state is calculated with the unrestricted SCF method in the INDO approximation after dropping all the core resonance integrals between the π atomic orbitals on the benzene moiety and the pseudo π orbital. (ii) By using the molecular orbitals obtained in step (i), the core resonance integrals between π atomic orbitals and pseudo π atomic orbitals are modified according to

Eq. 9 in order to take the electrophilic or the nucleophilic nature into account. (iii) The modified core resonance integrals are employed to calculate the total energy of the molecule in the transition state with the delocalization of π electrons, which corresponds to the electrophilic or the nucleophilic nature. (iv) A measure of the electrophilicity or the nucleophilicity of the radical reagent can be obtained by calculating the difference between energies obtained in steps (i) and (iii).

Results and Discussion

The electrophilicity of H and OH radicals was studied according to the procedure described. However, the procedures for H and OH radicals are slightly different owing to the symmetrical character of the pseudo π orbital; that is, in the case of the H radical, the pseudo π orbital is antisymmetric with respect to the reflection in the plane containing the benzene ring, but is lacking in the symmetry for the OH radical. Consequently, the results for H and OH radicals will be shown separately in the following.

H Radical. The unrestricted SCF method is applied to the tetrahedral intermediate of the benzene attacked by the H radical (see Fig. 1) in the INDO approximation. The obtained energy levels are as indicated in Fig. 2 when the delocalization of π electrons is prohibited. As is clearly shown in Fig. 2, the energy level of the pseudo π orbital for α-spin is much lower than that for β-spin owing to the effect of the spin polarization. The delocalization energy for the measure of the nucleophilicity of the H radical is obtained when the core resonance integrals are retained only between the pseudo π orbital and the vacant π^* molecular orbitals on the benzene moiety for α-spin, as shown by arrows in Fig. 2. On the other hand, the measure of the electrophilicity can be calculated by retaining the core resonance integrals between the pseudo π^* orbital and the occupied π molecular orbitals on the benzene moiety for β-spin.

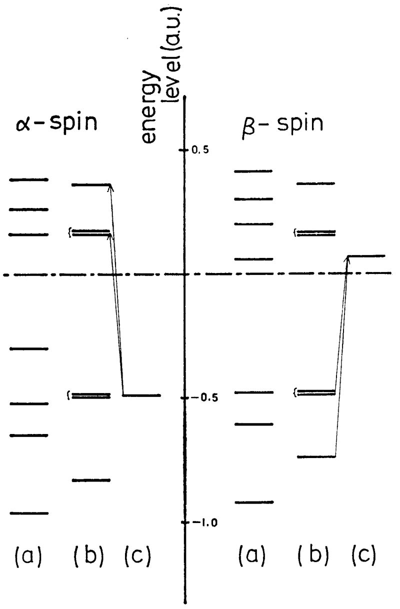


Fig. 2. Energy level diagrams of π molecular orbitals for the tetrahedral intermediate attacked by H radical. (a) The energy levels obtained by the usual UHF calculation. (b) The energy levels of benzene π molecular orbitals obtained by the UHF calculation after dropping core resonance integrals shown in Fig. 1. (c) The energy levels of pseudo π orbital obtained by the procedure in (b). The arrows in the figure indicate the direction of electron delocalization.

Table 1. Total energies of tetrahedral intermediate attacked by H radical with various types of delocalization effects

Interacting MO[a] (α-spin)	Interacting MO[a] (β-spin)	Total energy[b]	Delocalization energy[b]
all	all	−46.312	0.315
none	none	−45.998	0.0
pseudo π-all π^*	none	−46.060	0.063
none	all π-pseudo π^*	−46.161	0.164
pseudo π-all π^*	all π-pseudo π^*	−46.236	0.238
pseudo π-$\substack{\text{all }\pi^* \\ \text{all }\pi}$	none	−46.096	0.098
none	$\substack{\text{all }\pi \\ \text{all }\pi^*}$-pseudo π	−46.180	0.182

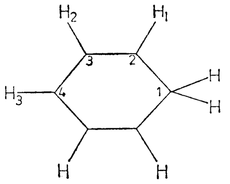
a) Interacting MO means molecular orbitals which retain the core resonance integrals between themselves.
b) In a.u.

The obtained results are listed in Table 1. The third line indicates the nucleophilicity and the fourth line the electrophilicity of the H radical. Obviously, the delocalization energy for the electrophilicity is much larger than that for the nucleophilicity. Consequently, it should be concluded that the H radical is electrophilic in nature for the radical reaction with benzene, in accordance with the experimental fact that the H radical behaves like an electrophilic reagent in the abstraction reaction[1)] (although this reaction is somewhat different from the model used in the present article). The fifth line of Table 1 includes the delocalization energy obtained by retaining core resonance integrals for the electrophilicity as well as the nucleophilicity. The delocalization energy in the fifth line is nearly equal to the sum of the delocalization energies in the third and the fourth lines, that is, the delocalizations of α-spin and β-spin electrons affect each other only slightly. The delocalization energy in the sixth line was obtained by including the core resonance integrals between the pseudo π orbital and all the π molecular orbitals on benzene moiety for α-spin, that is, the effect of the nucleophilicity as well as the redistribution of α-spin electrons were included in the value of the delocalization energy. Similarly, the delocalization energy in the seventh line includes the effect of the electrophilicity as well as the redistribution of the β-spin electrons. By comparing the values in the sixth and the seventh lines with those in the fourth and fifth lines, the redistribution effect is found not to be negligibly small, although the delocalization energy corresponding to the nucleophilicity and the electrophilicity are somewhat larger than those for the redistribution effect. In conclusion, for the H radical the delocalization energy for the electrophilicity was found to be the most important contribution to the total delocalization energy.

TABLE 2. CHARGE DISTRIBUTIONS OF TETRAHEDRAL INTERMEDIATE ATTACKED BY H RADICAL WITH VARIOUS TYPES OF DELOCALIZATION EFFECTS[a)]

Interacting MO[b)] (α-spin)	Interacting MO[b)] (β-spin)	H_1	H_2	H_3	C_1	C_2	C_3	C_4	H
all	all	−0.021	−0.027	−0.024	0.118	−0.007	0.032	0.008	−0.029
none	none	−0.024	−0.026	−0.024	0.039	0.018	0.024	0.024	−0.011
pseudo π-all π^*	none	−0.031	−0.030	−0.027	−0.035	0.007	0.029	0.012	0.049
none	all π-pseudo π^*	−0.012	−0.020	−0.019	0.193	0.040	0.015	0.046	−0.133
pseudo π-all π^*	all π-pseudo π^*	−0.012	−0.024	−0.022	0.112	0.027	0.021	0.032	−0.066
pseudo π-$\begin{smallmatrix}\text{all }\pi\\ \text{all }\pi^*\end{smallmatrix}$	none	−0.033	−0.035	−0.029	−0.002	−0.050	0.052	−0.036	0.099
none	$\begin{smallmatrix}\text{all }\pi\\ \text{all }\pi^*\end{smallmatrix}$-pseudo π^*	−0.012	−0.018	−0.018	0.158	0.069	0.001	0.076	−0.148

a) The numbering of the atom is as below: b) The meaning of "Interacting MO" is given in Table 1.



In Table 2, charge distributions of the tetrahedral intermediate were given for the various cases corresponding to the calculations in Table 1. It is obvious that the charges on the hydrogen atoms bonded to the tetrahedral carbon atom can help in determining the direction of the electron delocalization. The charge on the hydrogen atom in the third line is positive, in accordance with the fact that the calculations of the third line give a measure for the nucleophilicity. Similarly, the negative charge on the hydrogen in the fourth line corresponds with the calculations for the electrophilicity. The charges listed in the sixth and the seventh lines indicate that the inclusion of the redistribution effect makes the positive hydrogen more positive and the negative hydrogen more negative. As a result, the sum of the charges of the hydrogen atom in the sixth and seventh lines leads to a slightly negative charge, which corresponds to the value of the charge in the first line.

OH Radical. For the calculation of the electrophilicity of the OH radical, the tetrahedral intermediate of the benzene attacked by an OH radical (see Fig. 1) was subjected to the unrestricted SCF calculations in the INDO approximation. However, this intermediate has no symmetry for the reflection in the plane containing the benzene ring. In other words, the pseudo π and π^* orbitals don't localize in the parts of the H atom and OH group attached to the tetrahedral carbon atom, but these orbitals spread over the σ skeleton of the whole molecule. Because of the delocalizing character of the pseudo π and π^* orbitals, it becomes rather difficult to discriminate the pseudo π and π^* orbitals from other orbitals. In addition to this, the core resonance integrals between the $2p\pi$ atomic orbitals and the other 2s or 2p atomic orbitals of the same atom are apparently non-zero, using Eq. 9, since the values of $C_{\sigma j,s}$ for a pseudo π or π^* orbital are non-zero because of the spreading character of the pseudo π or π^* orbital.

In order to overcome these undesirable developments, the molecular orbitals $\psi_{\sigma j}$ given by Eq. 4 were transformed into the localized molecular orbitals according to the procedure of Edmiston and Ruedenberg.[13)] After this procedure, it becomes quite easy to pick up the pseudo π or π^* orbital. Furthermore, if the transformed orbital is localized completely, the core resonance integral between $2p\pi$ and 2s or $2p\sigma$ atomic orbitals, which is apparently non-zero if one uses canonical molecular orbitals, becomes completely zero if one uses localized molecular orbitals, since the value of $C_{\sigma j,s}$ in Eq. 9 vanishes. Usually, transformed orbitals don't localize completely, and hence the undesirable development cannot be completely excluded, but its contribution is expected to be significantly diminished. Therefore, the degree of localization given by Eq. 11 was calculated to check the validity of the calculations.

$$\text{Degree of localization} = \sum_{\substack{r\\(\mathrm{OH,H})}} C_{ir}^2, \tag{11}$$

where r in the summation covers all atomic orbitals on the OH group and H atom attached to the tetrahedral carbon atom.

TABLE 3. THE DEGREE OF LOCALIZATION OF CANONICAL AND LOCALIZED MOLECULAR ORBITALS[a)]

Molecular orbital[b)]	1	2	3	4	5
Canonical MO (α-spin)	0.782	0.533	0.506	0.464	0.411
Localized MO (α-spin)	0.980	0.962	0.908	0.786	0.767
Canonical MO (β-spin)	0.988	0.474	0.414		
Localized MO (β-spin)	0.956	0.766	0.519		

a) The degree of localization was calculated by using Eq. 11. b)The numbering of molecular orbitals is in the decreasing order of the degree of localization.

TABLE 4. TOTAL ENERGIES OF TETRAHEDRAL INTERMEDIATE ATTACKED BY OH RADICAL WITH VARIOUS TYPES OF DELOCALIZATION FEFECTS USING LOCALIZED MOLECULAR ORBITALS

Interacting MO[a] (α-spin)	Interacting MO[a] (β-spin)	Total energy[b]	Delocalization energy[b]
all	all	−63.879	0.428
none	none	−63.451	0.0
pseudo π-all π	none	−63.538	0.087
none	all π-pseudo π*	−63.623	0.171

a) The meaning of "interacting MO" is the same as that in Table 1. b) In a.u.

TABLE 5. TOTAL ENERGIES OF TETRAHEDRAL INTERMEDIATE ATTACKED BY OH RADICAL WITH VARIOUS TYPES OF DELOCALIZATION EFFECTS USING CANONICAL MOLECULAR ORBITALS

Interacting MO[a] (α-spin)	Interacting MO[a] (β-spin)	Total energy[b]	Delocalization energy[b]
all	all	−63.879	0.428
none	none	−63.451	0.0
pseudo π-all π	none	−63.517	0.066
none	pseudo π-all π*	−63.626	0.175

a) The meaning of "interacting MO" is the same as that in Table 1. b) In a.u.

The degree of the localization for some transformed molecular orbitals is listed in Table 3, and compared with that for the corresponding canonical molecular orbitals. Obviously, the degree of localization increases remarkably by the transformation of the molecular orbital. The measure of the electrophilicity of the OH radical was calculated in a similar manner to that of the H radical by using the transformed molecular orbitals. The results thus obtained are collected in Table 4. It is clearly indicated that the OH radical is quite electrophilic in nature, in agreement with the experimental data.[1,2] In order to investigate the effect of the localization of molecular orbitals, the same calculations were carried out by using canonical molecular orbitals. Table 5 contains the results which indicate the essential features of the electrophilicity of the OH radical. That is, by comparing Tables 4 and 5, the delocalization energy for the measure of the electrophilicity is much larger than that for the nucleophilicity, regardless of the degree of the localization. In other words, the conclusion that the OH radical is electrophilic in nature is valid independently of the degree of the localization for the molecular orbitals in question. In Table 6, charge distributions corresponding to the calculations of Table 4 are listed. This indicates that the electrophilicity of the OH radical is reflected in the negative charges of the H atom and OH group attached to the tetrahedral carbon atom. That is, when the conjugation of π electrons is completely prohibited between pseudo π or π* orbital and benzene π molecular orbitals, the charge on the tetrahedral group is somewhat negative (−0.110). When the effect of the nucleophilicity is taken into account, it becomes slightly positive (+0.003), and when the effect of the electrophilicity is taken into account, it becomes quite negative (−0.352). As a sum of these two effects, the considerable negative charge on the group results. This feature for OH radicals is quite similar to that for H radicals.

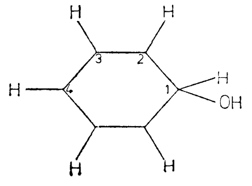
Concluding Remarks. In the present article, the electrophilicity of H and OH radicals was quantitatively evaluated by separating the delocalization energy in the nucleophilic and the electrophilic ones. The obtained result is in good agreement with the experimental fact that H and OH radicals are electrophilic in nature. In the present paragraph, we will discuss briefly the origin of the electrophilicity of H and OH radicals. Since the measure of the electrophilicity is a kind of delocalization energy, it should be very effective for the analysis of the electrophilicity of H and OH radicals to use the concept of the perturbation method.

In Figs. 2 and 3, the energy levels for zero-th order wave functions are given for H and OH radicals. As is well known, the delocalization energy is approximately proportional to the core resonance integral between pseudo π or π* orbital and benzene π molecular orbitals, and is inversely proportional to the energy difference between pseudo π and benzene unoccupied π* molecular orbitals or pseudo π* and benzene occupied π orbitals. The above-metioned reasoning is applicable only when the uncoupled approximation[14,15] in the SCF perturbation method is valid. The present approach has its

TABLE 6. CHARGE DISTRIBUTIONS OF TETRAHEDRAL INTERMEDIATE ATTACKED BY OH RADICAL WITH VARIOUS TYPES OF DELOCALIZATION EFFECTS USING LOCALIZED MOLECULAR ORBITALS

Interacting MO[b] (α-spin)	Interacting MO[b] (β-spin)	C_1	C_2	C_3	C_4	H	O	H(O)[c]	(H, OH)[d]
all	all	0.292	−0.042	0.034	0.011	−0.053	−0.317	0.164	−0.206
none	none	0.166	−0.016	0.028	0.020	−0.008	−0.289	0.187	−0.110
pseudo π-all π	none	0.103	−0.028	0.032	0.008	0.069	−0.264	0.198	0.003
none	all π-pseudo π*	0.309	0.007	0.019	0.045	−0.150	−0.361	0.159	−0.352

a) The numbering of the atom is as below:



b) The meaning of "Interacting MO" is the same as that in Table 4. c) The hydrogen atom in the group. d) The sum of the charges on the group of H and OH atoms.

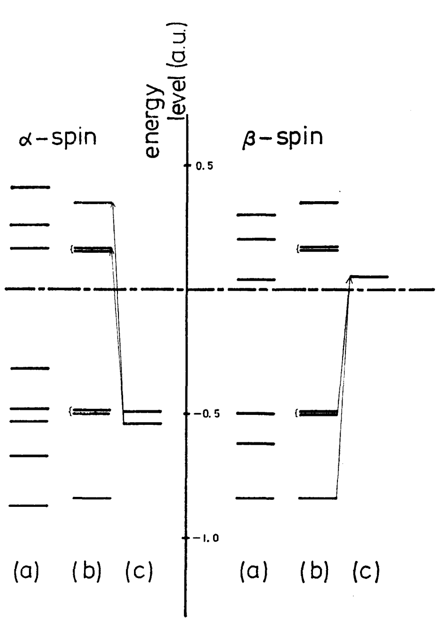


Fig. 3. Energy level diagrams of π molecular orbitals for the tetrahedral intermediate attacked by OH radical. The meaning of (a), (b), and (c) is the same as that in Fig. 2.

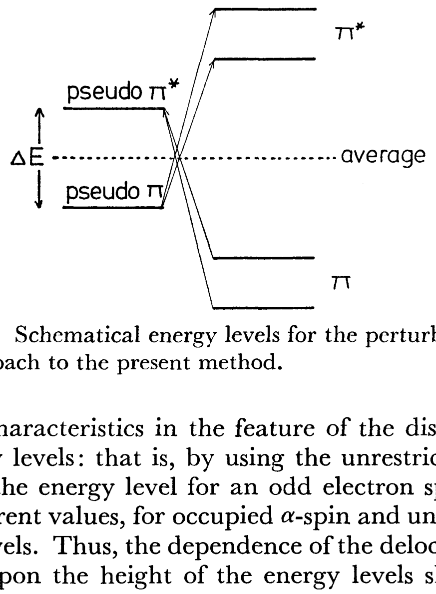


Fig. 4. Schematical energy levels for the perturbational approach to the present method.

special characteristics in the feature of the distribution of energy levels: that is, by using the unrestricted SCF method the energy level for an odd electron splits into two different values, for occupied α-spin and unoccupied β-spin levels. Thus, the dependence of the delocalization energy upon the height of the energy levels should be classified into two factors; one is the average height of the two split levels for an odd electron and the other is the magnitude of splitting of these two levels. This situation is schematically shown in Fig. 4. As is evident from this figure, the lower the average height of the two energy levels is, the more electrophilic the radical reagent is. On the other hand, a large magnitude of splitting of the two energy levels results in large values for the measures of both the electrophilicity and the nucleophilicity.[16] From the heights of the energy levels in Figs. 2 and 3, H and OH radicals can be inferred to be electrophilic in nature, although the quantitative evaluation of the delocalization energy is not accessible, owing to the contribution of the core resonance integral between pseudo π or π* orbital and benzene π molecular orbitals. In conclusion, the electrophilicity of the radical reagent may qualitatively be predicted by the average of the two energy levels of pseudo π and π* orbitals and the magnitude of their splitting. As to other radical reagents, analysis will soon be carried out in order to investigate whether the above-mentioned conclusion holds or not. Furthermore, the abstraction reaction of a hydrogen atom, as well as a halogen atom, by the reagent was subjected to an analysis similar to that in the present article and was published.[17]

The authors are very grateful to Prof. T. Masuda of Tokyo Metropolitan University for suggesting this problem and for stimulating discussion. We are also grateful to Dr. T. Minato for his considerable assistance with the computer program of localized molecular orbitals. The numerical calculations were carried out on the FACOM 230-75 at the Computer Center of Kyoto University. This research was supported in part by a Scientific Grant from the Ministry of Education.

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$$\Delta E = \sum_r\sum_s (P^{\alpha}_{rs}-P^{\beta}_{rs})(rr|ss)C^{\alpha}_{ir}C^{\alpha}_{is} \qquad (12)$$

where superscripts α and β denote α and β spins, respectively, and the number of α spin electrons is greater by one than that of β spin electrons.

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