The Electronic Structures and Antioxidizing Activities of Substituted Phenols

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The autooxidation of several organic substance-for instance, petroleum hydrocarbons, rubber and oil-has long been studied by many authors and has been well recognized as a radical chain reaction. Such antioxidants as substituted phenols and anilines work as chain-breaking inhibitors of the peroxy radical:

$$RO_2\cdot + IH \rightarrow ROOH + I\cdot \qquad (1)$$

while the radical I· from the inhibitor is less reactive and can initiate a new chain reaction only with difficulty, as was first discovered by Bolland and ten Haave[1].

From the theoretical point of view, Fueno et al.[2] studied, in the simple LCAO MO approximation of π electronic systems, the relation between the highest occupied π electronic level and the oxidation potential of various hydroxy derivatives of aromatic hydrocarbons, and also the relation between the highest occupied level or the stabilization energy of the transition complex and the antioxidizing efficiency.

In the present paper the antioxidizing activity of substituted phenols is discussed in connection with their σ electronic structure as well as with their π electronic structure.

The π Electronic Structure and Antioxidizing Activity of Substituted Phenols

According to Boozer, Hammond et al.[3-5], the overall inhibition reaction, Eq. 1, does not necessarily mean that the rate determining step of the inhibition is the hydrogen abstraction reaction, for *N*-methylaniline-*N-d* and diphenylamine-*N-d* showed the same efficiency as the undeuterated compounds. They therefore proposed the following mechanism:

$$\left.\begin{array}{l} RO_2\cdot + IH \rightarrow [RO_2\cdot \leftarrow IH] \\ \qquad \text{(rate-determining)} \\ RO_2\cdot + [RO_2\cdot \leftarrow IH] \rightarrow \\ \qquad \text{inactive product} \end{array}\right\} \qquad (2)$$

$[RO_2\cdot \leftarrow HI]$ is a molecular complex between the inhibitor and the radical, and the first complex-formation step is rate-determining. On the nature or structure of the complex no decisive fact seems to have been revealed.

In this section π molecular orbital calculations will be given, and the complex will be discussed. The parameters of the Coulomb and the resonance integrals are as follows: $\alpha_O=\alpha+0.51\beta$, $\beta_{O-C'}=0.57\beta$, $\alpha_{C'}=\alpha+0.05\beta$[6]; $\alpha_{CH_3}=\alpha+3\beta$, $\beta_{C''-CH_3}=0.7\beta$, $\alpha_{C''}=\alpha-0.1\beta$; and $\alpha_{C(\text{adj. to } t\text{-butyl})}=\alpha-0.2\beta$.

The *t*-butyl group is taken as a purely inductive group, while the methyl group as partly inductive and partly hyperconjugative, hyperconjugation being treated by the well-known one-atom model[7].

The Highest Occupied π Level.—It has often been thought that, no matter what the structure of a molecular complex, the ionization potential of the electron donor and the electron affinity of the acceptor decide the ease of complex formation[8-10]. Some comparisons[11] of the oxidation potential and the antioxidizing efficiency (induction period) have supported this probability. In the molecular orbital sense, the ionization potential is the absolute value of the energy of the highest occupied π orbital. We compared the calculated energy of the highest occupied π level with the relative value of the molecular antioxidizing potency of the 2, 4, 6-substituted phenols measured by Rossenwald et al.[12], as is shown in the third and the

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1) J. L. Bolland and P. ten Haave, *Trans. Faraday Soc.*, 2, 252 (1947).

2) T. Fueno, T. Ree and H. Eyring, *J. Phys. Chem.*, **63**, 1940 (1959).

3) C. E. Boozer and G. S. Hammond, *J. Am. Chem. Soc.*, **76**, 3861 (1954).

4) C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, ibid., **77**, 3233 (1955).

5) G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, ibid., **77**, 3238 (1955).

6) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952).

7) A. Streitwieser, Jr. and P. M. Nair, "Conference of Hyperconjugation", Pergamon Press, London (1959).

8) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

9) K. Fukui, A. Imamura, T. Yonezawa and C. Nagata, This Bulletin, **34**, 1076 (1961).

10) K. Fukui, A. Imamura, T. Yonezawa and C. Nagata, ibid., **35**, 33 (1962).

11) C. D. Lowry, G. Egloff, J. C. Morrell and C. G. Dryer, *Ind. Eng. Chem.*, **25**, 804 (1933).

12) R. H. Rossenwald, J. R. Hoatson and J. A. Chenicek, ibid., **42**, 162 (1950).

TABLE I. ANTIOXIDIZING POTENCY AND π MOLECULAR ORBITAL INDEXES OF 2,4,6-SUBSTITUTED PHENOLS

Class	Substituents[a] at position			Relative molecular potency P	Energy of the highest occupied level[b] λ_{ho}	Stabilization energy of the model in Fig. 1 ΔE_1[c]	Stabilization energy of the model in Fig. 2 $S_O^{(R)}$[d]	Total π electron density on oxygen q_O
	2	4	6					
A	*t*-Bu	Me	*t*-Bu	76.0	0.343	—	2.257	1.9155
	t-Bu	*t*-Bu	*t*-Bu	39.5	0.351	—	2.234	1.9145
B	*t*-Bu	Me	Me	100.0	0.337	3.384	2.281	1.9162
	t-Bu	*t*-Bu	Me	42.5	0.344	3.378	2.258	1.9151
	t-Bu	Me	H	37.5	0.357	3.270	2.190	1.9094
	t-Bu	*t*-Bu	H	33.0	0.365	3.262	2.168	1.9083
	t-Bu	H	H	10.5	0.383	3.235	2.109	1.9018
C	Me	Me	Me	57.0	0.331	—	2.305	1.9169
	Me	Me	H	20.5	0.350	—	2.209	1.9100
	Me	*t*-Bu	Me	18.5	0.338	—	2.282	1.9159
	Me	H	Me	15.0	0.355	—	2.215	1.9095
	Me	*t*-Bu	H	14.5	0.358	—	2.190	1.9089
	H	Me	H	4.0	0.372	—	2.125	1.9039
	H	*t*-Bu	H	3.5	0.380	—	2.106	1.9027
	Me	H	H	3.0	0.375	—	2.130	1.9024
	H	H	H	1.5	0.398	—	2.049	1.8960

a) Me and *t*-Bu stand for methyl and *t*-butyl groups, respectively.

b) λ_{ho} is the coefficient of the energy of the highest occupied level:

$$\varepsilon_{ho}=\alpha+\lambda_{ho}\beta$$

c) In unit of $\gamma^2\beta$

d) In unit of $\gamma^2\beta$

fourth columns of Table I. In the table, the methyl and/or *t*-butyl substituted phenols are divided into three classes—one consisting of 2, 2-di-*t*-butyl phenols (class A), another of 2-*t*-butyl phenols (class B), and the third consisting of phenols with no *t*-butyl group at the 2 and 6 positions (class C). A parallelism between the potency and the energy of the highest occupied π level is observed within each class of compounds, suggesting that the smaller ionization potential will result in an easier formation of the complex and, therefore, in a larger potency. Fueno et al.[2] also compared the highest occupied level and antioxidizing efficiency of some hydroxy derivatives of aromatic hydrocarbons, but they interpreted a similar parallelism in a little different sense. Assuming that the efficiency is fully controlled by the dissociation reaction, $\mathrm{ROH}\rightarrow\mathrm{RO}\cdot+\cdot\mathrm{H}$, and dividing the heat of dissociation into the constant σ electronic contribution and the variable π electronic contribution, $\Delta H_\pi(\mathrm{RO{-}H})$, they found that, in a simple approximation, $\Delta H_\pi(\mathrm{RO{-}H})$ is nothing but the energy of the highest occupied level. In this connection, the σ electronic structure and the antioxidizing efficiency will be discussed in the next section. Pederson's ionic model[13] also seems to be certified by this parallelism:

$$\mathrm{RO_2\cdot}+\mathrm{IH}\rightarrow\mathrm{RO_2^-}+\mathrm{IH^+}\qquad(3)$$

but a complete one-electron transfer would be more difficult than a partial electron transfer, which is accomplished in the molecular complex.

The Delocalization Energy of the Complex.—In a more concrete model of the complex proposed by Russel[14,15] and by Walling and Mayahi[16], it is assumed that the peroxy radical will probably approach the inhibitor from the direction perpendicular to the aromatic ring in order to interact with the π electrons on it. If this is true, the delocalization calculation of the molecular complexes[9,10] will be appropriate. Assuming that the radical stays on the axis which stands from the center of the benzene ring and which is perpendicular to the ring and that it interacts with the six π atomic orbitals on it to the same extent (cf. the assumed model of the complex shown in Fig. 1), we obtain the following stabilization energy, ΔE_1, of this model by the perturbation treatment:

$$\Delta E_1=\Big(\sum_i^{\mathrm{occ}}-\sum_i^{\mathrm{unocc}}\Big)\frac{(\sum_r C_{ir})^2}{\lambda_i}\gamma^2\beta\qquad(4)$$

where $\gamma\beta$ is the resonance integral between the half-occupied orbital of peroxide and a π AO

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[13] C. J. Pederson, *Ind. Eng. Chem.*, **48**, 1881 (1956).

[14] G. A. Russel, *J. Am. Chem. Soc.*, **79**, 2977 (1957); **80**, 4987, 4997, 5002 (1958).

[15] G. A. Russel, *Tetrahedron*, **8**. 101 (1960).

[16] C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

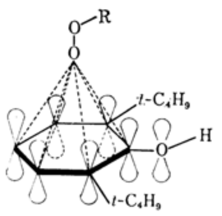


Fig. 1

on the ring, and $\sum_r$ should cover all the AO's on the benzene ring of the compound. The results shown in the fifth column of Table I seem to allow this possibility, too. The charge is transferred from the inhibitor to the peroxy radical in this model.

Another model of the complex would be such as is illustrated in Fig. 2, in which the peroxy radical approaches the phenol oxygen so as to interact with the pπ orbital on it. If the peroxy radical is assumed to have one atomic orbital and one electron available to conjugation with the inhibitor, the stabilization energy of the interaction by the second order perturbation treatment is nothing but the superdelocalizability of the oxygen for the radical reaction, $S_O^{(R)}$ [*, 17]:

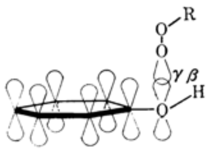


Fig. 2

$$S_O^{(R)}=(\sum_i^{\text{occ}}-\sum_i^{\text{unocc}})\frac{(C_{iO})^2}{\lambda_i} \qquad (5)$$

Setting this model, Fueno et al.[2] found a good linear relationship between the logarithm of relative antioxidizing efficiency proposed by Bolland and ten Haave[1] and the superdelocalizability for several unsubstituted phenols**.

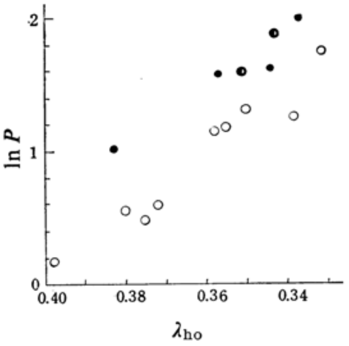
We calculated the superdelocalizability, $S_O^{(R)}$, for this series of compounds, obtaining a good parallelism with the potency in each class, as is shown in the sixth column of Table I. Thus, the model in Fig. 2 may be one of the possible structures of the complex in Eq. 2.

Some inhibitor radicals produced by the reaction, Eq. 1 or 2, may sometimes initiate a new chain reaction as follows[19,20]:

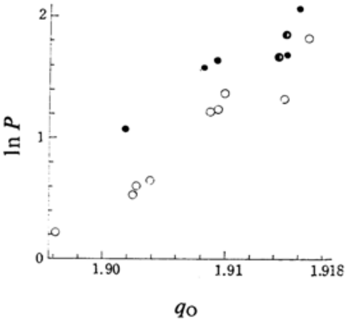
$$I\cdot + RH \rightarrow IH + R\cdot \qquad (6)$$

or

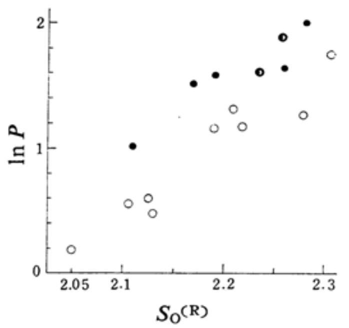
$$IO_2\cdot + RH \rightarrow IOOH + R\cdot \qquad (7)$$



a) The highest occupied level



b) Total π electron density on oxygen atom



c) Superdelocalizability on oxygen atom for radical attack

Fig. 3. Linear relationship between logarithm of antioxidizing potency and reactivity indexes.
(◐, group A ; ●, group B ; ○, group C)

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

[*] As the interacting orbital is not the pseudo-π orbital but the half-occupied orbital of the peroxy radical, the quantity should be rather named "delocalizability" instead of "superdelocalizability".

[**] In their paper the formula for the transferred charge includes a part of the fourth-order terms mixed with the following correct second order term[18]:

$$\Delta q(\text{second order})=(\sum_i^{\text{occ}}-\sum_i^{\text{unocc}})\frac{(C_{iO})^2}{(\lambda_i)^2}\gamma^2$$

[18] K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **27**, 1247 (1957).

[19] A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, **1956**, 2215; **1957**, 2415.

[20] W. A. Waters and C. Wickham-Jones, ibid., **1951**, 812.

Ingold[21] has recently proposed to classify the inhibitors into two groups: one, "strong" inhibitors which react very rapidly with the peroxy radical to break the chain reaction, and the other, "efficient" inhibitors each of whose phenoxy radical produced by the reaction (Eq. 1 or 2) is stable enough not to initiate any new chain reaction. Sterically hindered inhibitors are "efficient" inhibitors, for their phenoxy radical is protected from the reactions to follow.

It would be interesting here to discuss the difference in potency among the classes. In Fig. 3 are plotted the calculated indexes against the logarithm of potency. With regard to each index the plots of class A and of class B fall on one line, while those of class C fall on another line. Compounds of classes A and B are both restricted with the bulky *t*-butyl group. The linear relationship found in both these two classes seems to suggest that the restriction would be enough by one *t*-butyl substitution. Judging from the models, the calculated indexes seem to represent only the "strength" of the inhibitors; therefore, the difference, which is estimated from Fig. 3 to be of the order of $\Delta \log P=0.4$, should probably be attributed to the difference in the "efficiency".

The Total π Electron Density on the Oxygen Atom. — The total π electron density on the oxygen atom, q_O, has also been calculated; as given in the last column of Table I and in Fig. 3b, it is found to possess a good parallelism with the antioxidizing potency. Since, in a radical reaction such as the attack of the peroxy radical, the total π electron density can no longer be the reactivity index, this parallelism would have to be interpreted as indicating that the electron density may affect some other quantity which in turn, has a direct influence upon the reaction. In the next section the total electron density will be taken as affecting the σ electronic structure of the O–H bond.

The σ Electronic Structure and Antioxidizing Activity of Phenols

In this section σ molecular orbital calculations on phenol will first be presented, and then the antioxidizing activity will be discussed in connection with the σ electronic structure.

LCAO MO calculations of the σ electronic structure of conjugated molecules have been carried out with respect to hydrocarbons[22], halides[23] and aldehydes[24], while the parameters of the Coulomb and the resonance integrals of hydrogen and carbon atoms had been determined already[22]. The parameters for phenolic oxygen have been determined to be as follows*: the Coulomb integral of oxygen is settled to be $\alpha_\sigma+0.3\beta_\sigma$ in accord with that of aldehyde oxygen, β_{O-O} (one center)$=0.29\beta_\sigma$ from the σ MO treatment of alcohols and peroxides[25], $\beta_{C-O}=0.6\beta_\sigma$, in accord with the small overlap integral $S(C_{sp^2}-O_p,\ 1.43\text{Å})=0.37$, in comparison with $S(C_{sp^2}-C_{sp^2},\ 1.34\text{Å})=0.77$ and $\beta_{OH}=0.7\beta_\sigma$, also with reference to $S(O_p-H_s,\ 0.96\text{Å})=0.35$. To make the results more reliable, a calculation with another parameter, $\beta_{OH}=1.1\beta_\sigma$, has also been made.

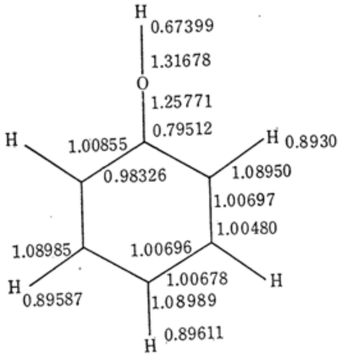

Fig. 4. Total σ electron density of phenol ($\alpha_O=\alpha_\sigma+0.3\beta_\sigma$, $\beta_{OH}=0.7\beta_\sigma$).

Figure 4 gives the calculated total σ electron density of phenol, where we can see a clear inductive effect of the oxygen atom. The small σ electron density and, accordingly, the large net positive charge on phenolic hydrogen seem to correspond to its strong acidity. In Table II are gathered the reactivity indexes—delocalizabilities, $D_H^{(N)}$, $D_H^{(E)}$ and $D_H^{(R)}$, for nucleophilic, electrophilic and radical abstractions of phenolic and para hydrogens, corresponding to the model in Fig. 5. The definition of D_H is as follows[29]:

$$D_H=\sum_i^{\text{all}}(\nu_i-k)\frac{(C_{iH}^{\sigma})^2}{\lambda_i^{\sigma}} \tag{8}$$

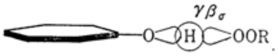

Fig. 5

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[21] K. U. Ingold, *Chem. Revs.*, **61**, 563 (1961).

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

[23] K. Morokuma, K. Fukui, T. Yonezawa and H. Kato, ibid., **36**, 47 (1963).

[24] K. Fukui, K. Morokuma, H. Kato and T. Yonezawa, ibid., **36**, 217 (1963).

[25] K. Fukui and H. Kato, to be published.

* α_σ and β_σ are the standard Coulomb and the standard resonance integrals of carbon sp² orbitals[22].

TABLE II. DEPENDENCY OF σ DELOCALIZABILITY OF HYDROGEN ON PARAMETER

β_{OH}		$0.7\beta_\sigma$		$1.1\beta_\sigma$	
Position of hydrogen		para	phenolic	para	phenolic
Total σ electron density q_H^σ		0.8961	0.6740	0.8961	0.7852
Delocalizabilities[a]	$D_H^{(E)}$	1.2058	0.9529	1.2058	0.7271
	$D_H^{(R)}$	1.1967	1.4949	1.1968	0.9618
	$D_H^{(N)}$	1.1876	2.0369	1.1877	1.1964

a) In unit of $\gamma^2\beta_\sigma$

TABLE III. CHANGE OF σ REACTIVITY INDEXES OF HYDROGEN ABSTRACTION

α_O		$\alpha_\sigma+0.3\beta_\sigma$		$\alpha_\sigma+0.25\beta_\sigma$	
Delocalizability[a]		$D_H^{(R)}$	$D_H^{(R)}(0.3)$	$D_H^{(R)}$	$D_H^{(R)}(0.3)$
Positions	phenolic	1.4949	1.5955	1.4952	1.6992
	ortho	1.2112	1.5050	1.2098	1.5084
	meta	1.1982	1.5041	1.2120	1.5046
	para	1.1967	1.5067	1.1966	1.5069

a) In unit of $\gamma^2\beta_\sigma$

where ν_i is the number of electrons on the ith σ MO, λ_i^σ is the coefficient of the energy, ε_i^σ, of the ith σ MO, $\varepsilon_i^\sigma=\alpha_\sigma+\lambda_i^\sigma\beta_\sigma$ and $k=$ 0, 1, 2, according to electrophilic, radical, nucleophilic reactions respectively, and the energy of the reagent X is assumed to be equal to α_σ. If we assume that the change in the reactivity index will be proportional to the square of β_{OH}, as in Fig. 6, $(\beta_{OH})^2$ must be smaller than $0.9(\beta_\sigma)^2$ in order to agree with the experimental findings that phenolic hydrogen is more liable than p-hydrogen to radical abstraction reactions. Our choice, $\beta_{OH}=0.7\beta_\sigma$, is supported by this finding.

Now we are going to discuss the relation between the σ electronic structure and antioxidizing activity. Experimentally, either no isotope effect or only a small one on activities have been observed between substituted phenols and their O-deuterated species[21] more than between aromatic amines and their N-deuterated derivatives[3-5]. Therefore, the molecular complex formation has been considered to be rate-determining. However, there are also some reports which have reported some isotope effects[26,27]. Furthermore, if the earlier stage of the hydrogen abstruction reaction is the transition state of antioxidation, there would naturally be little isotope effect. It would be worth while to study the possibility of such a mechanism. The delocalizability would be capable of being a measure of this mechanism, since this index is derived from a model in Fig. 5 composed of a molecule and a reagent weakly interacting with each other, upon perturbation treatment.

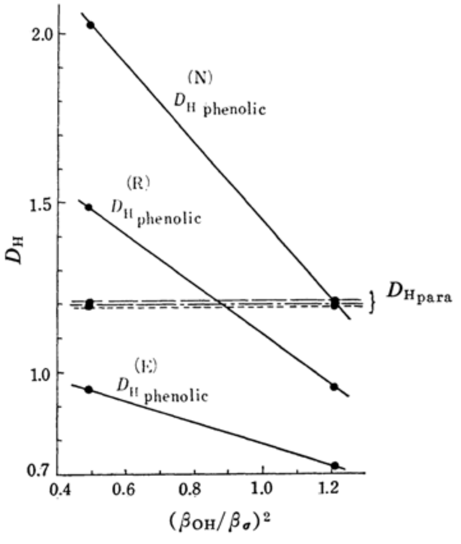

Fig. 6. Crossing of delocalizability of phenolic and para hydrogens.

For an attack of the peroxy radical, a quantity named $D_H^{(R)}(0.3)$ would be more appropriate than $D_H^{(R)}$;

$$D_H^{(R)}(0.3)=\left(\sum_i^{\text{occ}}-\sum_i^{\text{unocc}}\right)\frac{(C_{iH}^\sigma)^2}{\lambda_i^\sigma-0.3} \tag{9}$$

This index fits the model in Fig. 5 if the Coulomb integral of the orbital X is equal not to α_σ (in the case of $D_H^{(R)}$) but to $\alpha_\sigma+0.3\beta_\sigma$, the Coulomb integral of the oxygen atom. As is shown in Table III, the high reactivity of phenolic oxygen is indicated also by $D_H^{(R)}$ (0.3). Although all ring hydrogens have almost the same reactivities, the relative reactivity of each position seems to show a slight

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[26] J. R. Shelton and E. T. McDonel, *J. Polymer Sci.*, 32, 75 (1958).

[27] J. R. Shelton, E. T. McDonel and J. C. Crano, ibid., 42, 289 (1960).

difference according to the index, $D_{\mathrm{H}}^{(\mathrm{R})}$ or $D_{\mathrm{H}}^{(\mathrm{R})}$ (0.3).

The parallelism between the total π electron density on oxygen and the antioxidizing activity, which we demonstrated in the previous section, might be interpreted as follows: the total π electron density on the oxygen atom, increased by methyl and *t*-butyl substitutions, will necessarily decrease the electronegativity of the oxygen and make the Coulomb integral of the σ orbitals on oxygen more positive. This change in the Coulomb integral then causes the changes in the σ electronic structure of phenol, especially at the O–H bond. Tentatively putting the Coulomb integral of the oxygen σ orbital as equal to $\alpha_\sigma + 0.25\beta_\sigma$, instead of its normal value $\alpha_\sigma + 0.3\beta_\sigma$, we obtain the values of the indexes $D_{\mathrm{H}}^{(\mathrm{R})}$ and $D_{\mathrm{H}}^{(\mathrm{R})}$ (0.3) shown in Table III. As one can clearly see in the table, for an ordinary radical attack, in which $D_{\mathrm{H}}^{(\mathrm{R})}$ would be the index, the reactivity of phenolic hydrogen would hardly be influenced by the change in the total π electron density of oxygen, while for an electronegative radical (such as the peroxy radical) attack, in which $D_{\mathrm{H}}^{(\mathrm{R})}(0.3)$ would be the index, the reactivity is much elevated by an increased π electron density on oxygen.

In order to discuss the change in reactivity, the difference in the calculated total π electron density in Table I should be translated into the difference in $D_{\mathrm{H}}^{(\mathrm{R})}(0.3)$. The change in the Coulomb integral $\varDelta\alpha$ caused by the change in the electron density, $\varDelta q$, on the atom is often estimated by the equation:

$$\varDelta\alpha = \omega\varDelta q \tag{10}$$

where ω is a proportionality constant and would have a value ranging from $0.2\beta_\sigma \sim 2\beta_\sigma$*. The difference in the total π electron density between the largest and the smallest (phenol) ones in Table I, 0.02, would make the change in the Coulomb integral $\varDelta\alpha = 0.004\beta_\sigma \sim 0.04\beta_\sigma$. Since the change in $D_{\mathrm{H}}^{(\mathrm{R})}$ (0.3) would be proportional to the change in the Coulomb integral, the difference in $D_{\mathrm{H}}^{(\mathrm{R})}$ (0.3), 0.1037, for $\varDelta\alpha_{\mathrm{O}} = 0.05\beta_\sigma$ (in Table III) would make $\varDelta D_{\mathrm{H}}^{(\mathrm{R})}(0.3) = 0.0083 \sim 0.0830$ between the most reactive and the least reactive compounds. These magnitudes of the difference seem to be almost sufficient to explain the experimental differences in antioxidizing activity.

Summary

We have tested several models and their molecular orbital indexes of the rate-determining step of antioxidization by substituted phenols. Some molecular complex models have been found to be rational, though the problem of which of them is actually the true mechanism of the chain-breaking inhibition of autooxidation cannot yet be settled. Another possibility, that the earlier stage of the hydrogen abstraction reaction may be the rate-determining step, cannot yet be abandoned.

The numerical calculations have been carried out on the KDC-I digital computer of Kyoto University.

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* ω is the difference in the Coulomb integral between the two states, one of which has one more electron than the other. The difference, which is interpreted as being that between the ionization potential and the electron affinity of oxygen in its valence state, would be about 15 eV.[28] As the unit $\beta\sigma$ is estimated to be ca. -7 eV.[23], ω would be ca. $2\beta\sigma$. On the other hand, the ω value, which is often used in π electronic calculations is $0.5\beta\pi \sim 2\beta\pi$, and, referring to the ratio $\beta\pi/\beta\sigma \sim 1/3$[23], $\omega = 0.2\beta\sigma \sim 0.7\beta\sigma$ seems to be rational.

[28] H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

[29] K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **34**, 1111 (1961).