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A Molecular Orbital Consideration on the Radical Reactivity of Quinones

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According to the simple LCAO MO method, were computed the localization energies of several quinones both at the positions of oxygen and of the nuclear carbon atoms. The methyl affinities of quinones determined by Szwarc *et al.* were found to be reasonably related to their oxygen localization energies, whereas they failed to parallel the localization energies at the most reactive nuclear carbon atoms. This might be in partial favor of a radical addition mechanism of quinones involving the oxygen atom. With the aid of Dewar's non-bonding molecular orbital method, the oxygen localization energies for a large number of possible quinones were computed, from which the corresponding methyl affinities were predicted.

INTRODUCTION

It is widely recognized that quinones are possessed of pronounced reactivity toward free radicals. On the basis of this nature, they have been employed as the inhibitor for many radical chain reactions, such as autoxidation of organic substances and radical polymerization of vinyl monomers. The minute mechanism of this inhibitory action of quinones, however, is still unsettled, though it is generally believed valid that the radicals are captured by quinones through the addition reaction between them. Some workers suggested the nuclear addition process, while others supposed that the attacking radicals might add to the oxygen atom of quinone molecules. Both of these opposite conclusions were drawn from the structures of the reaction products between radicals and quinones; the isolation of quinone di-ethers was taken as evidence for the addition of radicals on the oxygen atoms of quinones,[1~3] while the isolation of nuclear substituted quinones was considered to support the view that the attacking radicals would initially add to the nuclear carbon atoms of quinones.[4~6]

Recently, Szwarc *et al.*[7] have experimentally determined the relative rates of the methyl radical addition toward several kinds of conjugated compounds such as aromatic hydrocarbons, olefins, vinyl monomers and quinones, and have offered sets of values representing relative methyl affinity, r, of these compounds. As to aromatic hydrocarbons investigated by the above workers, Çoulson[8] has pointed out the value of $\log r/n$ is linearly correlated with both the localization energy, L, and free valence, f, for the most reactive carbon atoms of these compounds, where n refers to the number of the equivalent most reactive carbon atoms. With several vinyl monomers, a similar relation-

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ship between r and L has been found by the present authors.[9]

In the present paper, were computed the localization energies of several quinones both at the positions of oxygen and of the nuclear carbon atoms and compared with the methyl affinities of these compounds.[7b, d] As the result, it was found that, between the methyl affinity and the oxygen localization energy, there exists a similar relationship as stated above, while there is no correlation of this value of reactivity with the localization energy at the most reactive nuclear carbon atoms. This result might be in partial favor of an addition mechanism of quinones involving the oxygen atom.

METHOD OF COMPUTATION

It is to be expected in general that the activation energy of an addition reaction will be simply related to the over-all energy change accompanying the reaction; the larger the exothermicity of the bond-formation, the smaller will be the activation energy. The total energy change, ΔE, of this exothermic reaction may be written as

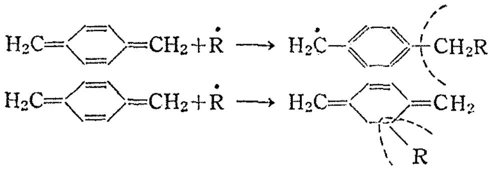
$$\Delta E = \Delta E_{\sigma} - \Delta E_{\pi}, \qquad (1)$$

where ΔE_{σ} is the change in σ-electronic energy associated with the σ-bond fromation and ΔE_{π} is the π-electronic energy decrement of the addition product with respect to the parent compound. Since every energy quantity in Equation (1) is positive in sign, ΔE will become larger with decreasing ΔE_{π} provided that ΔE_{σ} should remain nearly constant over a series of compounds. Thus, it may be possible to consider that the activation energy of the addition reaction will be parallel to the magnitude of ΔE_{π}.

In computation of ΔE_{π} for quinones, the simple MO method was applied to the π-electronic systems of the the parent quinones and of the addition products. The term ΔE_{π} obtained thus is equivalent to the localization energy of quinones at the position of methyl radical addition.

1. The First Approximation (Quinonedimethide Approximation)

The π-electronic energies of quinones and the resulting adducts were approximated by those of the dimethide analogues of quinones and those of the related aromatic hydrocarbons, respectively. The localization energy, ΔE_{π}, for the side chain addition reaction (2) was derived from the results calculated by Hush.[10] Similar addition (3) of quinones were obtained by solving the required secular equations.



(2)

(3)

R : attacking radical

2. The Second Approximation (Delocalized Carbonyl Bond Approximation)

The localization energies of quinones at the oxygen atom were computed assuming that the Coulomb integral for the oxygen and the resonance integral for the carbonyl π-bond are equal to $\alpha+2\beta$ and $\sqrt{2}\beta$, respectively,[10~12] where α is the Coulomb integral for a carbon atom in benzene and β is the resonance integral for a π-bond also in benzene.

RESULTS AND DISCUSSION

In Table 1 are collected the computation results of localization energies together with the data[7d] for the relative methyl affinities of quinones on the basis of $r=1$ for benzene. Inspection of the data represented in Table 1 shows that, in either approximation, the value for $\log r/n$* decreases from one quinone to another with the increasing magnitude of ΔE_π for the position of oxygen atom. This is graphically illustrated in Fig. 1, where it can be seen that a linear correlation holds between $\log r/n$ and ΔE_π in either of the two cases.**

On the other hand, no relation seems to exist between the methyl affinity and the ΔE_π for the most reactive nuclear carbon atom calculated according to the first approximation method. This might also be true in the case of the second approximation. Although, in the former approximation, there remain unestimated ΔE_π's for a large number of possible alternative positions in aro-

Table 1. Methyl affinities and localization energies[a] of quinones.

Quinone	r[7d]	$\log r/n$*	Position	ΔE_π 1st Approximation[b]	ΔE_π 2nd Approximation[c]
p-Benzoquinone	15,200	3.88	1′,4′	1.20	2.53
	± 300		2, 3, 4, 5	2.20	
1, 4-Naphthoquinone	4,900	3.39	1′,4′	1.31	2.64
	± 230		2, 3	2.17	
			5, 8	2.39	
			6, 7	2.46	
1, 2-Naphthoquinone	3,400	3.53	1′	1.37	—
	± 350		2′	1.30	2.58
			4	2.18	
9, 10-Phenanthraquinone	700	2.54	9′,10′	1.46	2.81
	± 20		1, 8	2.43	
			4, 5	2.42	
9, 10-Anthraquinone	—	—	9′,10′	1.45	2.80
			1, 4, 5, 8	2.38	
			2, 3, 6, 7	2.45	

[a] All the energies are given in units of $-\beta$.

[b] $\alpha_O=\alpha,\ \beta_{CO}=\beta$.

[c] $\alpha_O=\alpha+2\beta,\ \beta_{CO}=\sqrt{2}\,\beta$.

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* It should be noted here that n refers to the number of equivalent oxygen atoms.

** Owing to the asymmetric structure, 1, 2-naphthoquinone has two different oxygen localization energies : the value of ΔE_π plotted in Fig. 1 is the lower one, namely, -1.30β at the 2′-position.

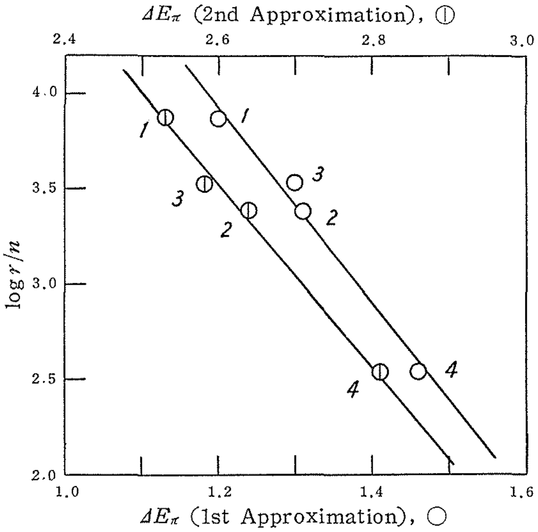


Fig. 1. Relationship between methyl affinities of quinones and their oxygen localization energies.

1. *p*-Benzoquinone	3. 1, 2-Naphthoquinone
2. 1, 4-Naphthoquinone	4. 9, 10-Phenanthraquinone

matic nuclei, none of these positions might be the most reactive. The situation is easily verified according to the algebraic analysis[13] of the expanded forms of the secular equations corresponding to the hydrocarbon analogues of the quinone adducts.

From the results stated above, ΔE_π for the oxygen atom of quinones seems to be a satisfactory measure for their radical affinity. Thus, it is suggested that an attacking radical might first add to the oxygen atom of quinones at least in the case of the four quinones treated here.

Provided that the resulting quinone radicals are enough stable not to react with any coexistent substances or that all the radical chains are terminated only by coupling or disproportionation between quinone radicals, the relative intensity and the mechanism of the inhibitory action of these quinones upon vinyl polymerization or autoxidation will be self-explanatory from the discussion made above.

The successive reactivity of the resulting quinone radicals is possibly discussed in terms of their own oxgen localization energy, $\Delta E_\pi'$. It is expected, however, that the quinone radical may initiate another sequence of chain reaction as Kice[14] has actually observed it with benzoquinone and chlorobenzoquinones. Hence $\Delta E_\pi'$ may not be simply related to the effectiveness of quinones as the inhibitor toward radical chain reactions.

As it has already been mentioned, both the quinonedimethide and the delocalized carbonyl bond approximations are equally well applied to relate the radical reactivity of quinones to their molecular structure. The former approximation is, however, more preferable to the other in the sense of the easiness in computation.

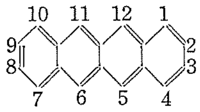
The most advantageous way to obtain the index for radical reactivity of quinones will be the one[10] employing Dewar's non-bonding molecular orbital theory.[15] According to this theory, the localization energy, ΔE_π^N, can be easily obtained as

$$\Delta E_\pi^N = -2|C_{ro}|\beta,$$

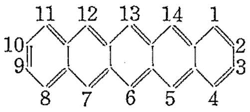
where ΔE_π^N is the localization energy for a side chain addition of a quinonedimethide and C_{ro} is the modulus of the atomic orbital coefficient of this molecular orbital for the hydrocarbon analogue of the quinone radical at the position of carbon atom bearing the reaction center.

We have computed ΔE_π^N for a large number of possible quinones and have predicted their relative methyl affinities, r, on the basis of the linear relationship between ΔE_ι^N and $\log r/n$ in four quinones, *i.e.*, *p*-benzoquinone, 1, 4-naphthoquinone, 1, 2-naphthoquinone and 9, 10-phenanthraquinone. The results are summarized in Table 2. For the purpose of checking up these predicted values, more experimental results are hoped to become available.

APPENDIX



Naphthacene



Pentacene

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Table 2. Prediction of methyl affinities of quinones.

No.	Quinone	Reactive position[a]	$\Delta E_{\pi}^{N b}$	$\log r/n^{*}$	r^{c}
1	*p*-Benzoquinone		0.756	$\bar{1}.70$	(1.00)
2	1, 5-Naphthoquinone	1,5	0.447	0.98	19.1
3	2, 6-Naphthoquinone	2,6	0.485	0.82	13.2
4	2, 3-Naphthoquinone	2,3	0.485	0.82	13.2
5	1, 7-Naphthoquinone	7	0.447	0.98	9.55
6	1, 4-Naphthoquinone	1,4	0.894	$\bar{1}.20$	(0.32)
7	1, 2-Naphthoquinone	2	0.894	$\bar{1}.35$	(0.225)
8	1, 8-Phenanthraquinone	1,8	0.272	1.69	98.0
9	3, 6-Phenanthraquinone	3,6	0.286	1.64	87.2
10	2, 7-Phenanthraquinone	2,7	0.295	1.61	81.4
11	2, 10-Phenanthraquinone	2	0.267	1.73	53.7
12	4, 10-Phenanthraquinone	4	0.267	1.73	53.7
13	1, 6-Phenanthraquinone	6	0.272	1.69	49.0
14	2, 5-Phenanthraquinone	2	0.280	1.66	45.7
15	1, 9-Phenanthraquinone	1	0.535	0.61	4.07
16	3, 9-Phenanthraquinone	3	0.535	0.61	4.07
17	2, 3-Phenanthraquinone	2	0.572	0.46	2.88
18	1, 2-Phenanthraquinone	2	0.816	$\bar{1}.45$	0.28
19	1, 4-Phenanthraquinone	4	0.816	$\bar{1}.45$	0.28
20	3, 4-Phenanthraquinone	3	0.840	$\bar{1}.35$	0.22
21	9, 10-Phenanthraquinone	9,10	1.069	$\bar{2}.36$	(0.046)
22	1, 5-Anthraquinone	1,5	0.309	1.55	71.0
23	2, 3-Anthraquinone	2,3	0.343	1.40	50.2
24	2, 6-Anthraquinone	2,6	0.343	1.40	50.2
25	1, 7-Anthraquinone	7	0.309	1.55	35.5
26	2, 9-Anthraquinone	2	0.535	0.61	4.07
27	4, 9-Anthraquinone	4	0.535	0.61	4.07
28	1, 4-Anthraquinone	1,4	0.926	$\bar{2}.99$	0.20
29	1, 2-Anthraquinone	2	0.926	$\bar{2}.99$	0.098
30	9, 10-Anthraquinone	9,10	1.069	$\bar{2}.36$	0.046
31	Naphthacene-1, 9-dione	9	0.231	1.86	72.5
32	Naphthacene-2, 11-dione	2	0.366	1.32	20.9
33	Naphthacene-4, 11-dione	4	0.366	1.32	20.9
34	Naphthacene-2, 12-dione	2	0.548	0.56	3.63
35	Naphthacene-4, 12-dione	4	0.548	0.56	3.63
36	Naphthacene-5, 11-dione	5,11	0.731	1.80	1.26
37	Naphthacene-1, 4-dione	1,4	0.924	$\bar{1}.00$	0.20
38	Naphthacene-1, 2-dione	2	0.924	$\bar{1}.00$	0.10
39	Naphthacene-5, 12-dione	5,12	1.095	$\bar{2}.30$	0.040
40	Pentacene-6, 13-dione	6,13	1.114	$\bar{2}.21$	0.032
41	*p*, *p'*-Diphenoquinone	*p*,*p'*	0.359	1.34	43.8
42	*p*, *p'*-Stylboquinone	*p*,*p'*	0.338	1.43	53.8

[a] The numbers indicate the positions of carbon atoms bearing oxygen atoms. The numberings are illustrated in Table 1 and Appendix.

[b] The energies are given in units of $-\beta$.

[c] On the basis of $r=1.00$ for *p*-benzoquinone as standard. Values in parentheses are the experimental data determined by Rembaum and Szwarc.[7d)]