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Electron Transfer in Pre-reaction *p*-Quinonemethide--9,10-Dihydroxyanthracene Dianion System

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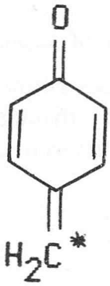
The dependence of the electronic structure of *p*-quinonemethide-9,10-dihydroxyanthracene dianion system on interplane distance and mutual orientation of the reactants was analyzed on the basis of CNDO/S3 calculations. Mutual perturbation of donor's and acceptor's electronic systems during parallel approaching of the reactants does not change qualitative conclusions about their reactivity based on the analysis of the electronic structure of individual molecules. The low energy of charge transfer transition indicates a high probability of electron transfer to be the first stage of the thermal chemical reaction.

INTRODUCTION

In a previous publication[1] we have analyzed a mechanism of the reaction between *p*-quinonemethide (*1*) and phenolate-anion (*2*), taking into account the possibility of electron transfer (ET) in the course of the reactants approaching each other. In that case ET has been shown to be an unlikely event in the absence of photoexcitation. This conclusion seems to hold also for a number of substituted *p*-quinonemethides and monophenols. However, this situation may change drastically in case of polyphenols, 9,10-dihydroxyanthracene dianion (*3*) being a typical and maybe most essential example.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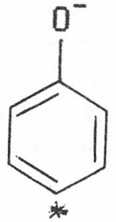
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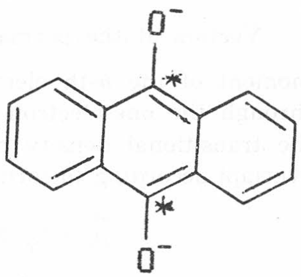
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The energy of the highest occupied molecular orbital (HOMO) in phenolic series is very sensitive to conjugation, as well as to the number of ionized hydroxy groups (for example, *2*: —5.1, 9-hydroxyanthracene anion: —4.7, 9,10-dihydroxyanthracene monoanion: —4.5, *3*: —0.9 eV[2]). It is to be expected that dianion *3* may have some characteristic features in its reaction with *p*-quinonemethides because of the extremely high HOMO energy, which differentiates it from the usual phenolic anions.

Dianion *3* is an important component of the mixture of reduced forms of anthraquinone being formed in aqueous alkaline solution during catalytic pulping of wood.[3,4] These reduced forms, with the corresponding anion-radical present also in a significant amount,[5] provide the so-called reducing stage of a catalytic cycle. At this stage, an interaction between the catalyst and *p*-quinonemethidic structural units of lignin macromolecule leads to the desirable cleavage of lignin.[4,7] High efficiency of anthraquinone catalysis was attributed to the great difference between HOMO energy of dianion *3* (and, very probable, of the corresponding anion-radical) and of ionized monophenols also present in pulping liquor.[2] In the former case, the orbitally controlled reaction, such as phenol — *p*-quinonemethide interaction, seems to be much faster. But all conclusions based on orbital energies of isolated reactants may seem doubtful because of their mutual influence when the reactants approach each other in the course of chemical reaction. Considering all the points mentioned above, we have theoretically closely examined the dependence of electronic structure of the system *1 . . . 3* on the mutual orientation and distance between the reactants.

RESULTS

CNDO/S3 calculations[8,9] have been performed for the system *p*-quinonemethide — 9,10-dihydroxyanthracene dianion (*1 . . . 3*) with different mutual orientation and interplane distances of the reactants (see Figure, compare[1]). The geometry parameters of *1* were the same as in ref. 10. The bond lengths used for *3* were: C—C 140, C—O$^-$ 136, and C—H 110 pm; all valent angles were taken to be equal to 120° (compare[11,12]). Wave functions and excited state energies were calculated considering 144 singly excited configurations. These correspond to singlet-singlet electron excitations from one out of twelve highest occupied levels to one out of twelve lowest unoccupied levels.

Vectors of the permanent dipole moment ($\vec{\mu}_o$, $\vec{\mu}_o'$ and $\vec{\mu}_o''$) and of dipole moment of the *n*-th electron transition ($\vec{\mu}_{on}$, $\vec{\mu}_{on}'$ and $\vec{\mu}_{on}''$) were determined through the one-electron density matrix of the ground state *P* and through the transitional density matrices $P^{[on]}$ (calculated neglecting the differential overlap) according to formulae:

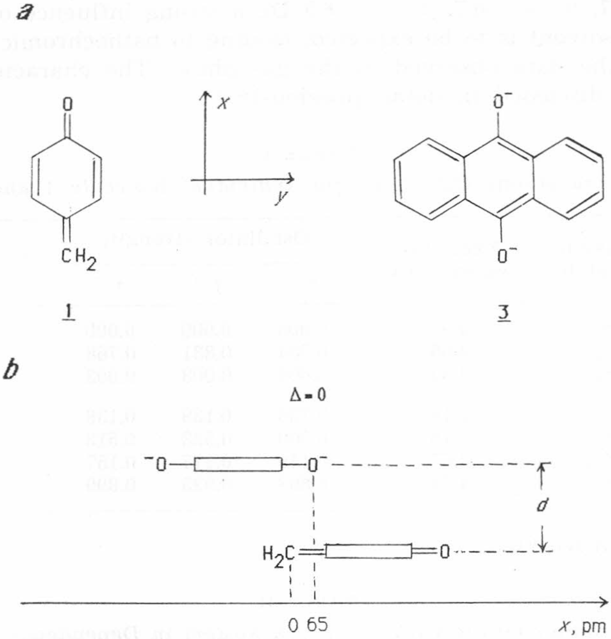

Figure. Orientation of the reagents: *a* Individual molecules, see Table I; *b* Mutual disposition of the reagents, see Tables II and III (disposition presented corresponds to $\Delta = 0$, Δ takes positive values with moving of *1* only along x axe in positive direction).

$$\vec{\mu}_{\mathrm{on}}{}' = -\Sigma_{\mathrm{A}} \; \Sigma \; \langle a \,|\, \vec{r} \,|\, a' \rangle \; P_{\mathrm{a'a}}[on];$$

$$\vec{\mu}_{\mathrm{o}}{}'' = \Sigma_{\mathrm{A}} Z_{\mathrm{A}} \vec{r}_{\mathrm{A}} - \Sigma_{\mathrm{A}} \Sigma_{\mathrm{B}} \sum_{\mathrm{a} \in \mathrm{A}} \sum_{\mathrm{b} \in \mathrm{B}} \langle a \,|\, \vec{r} \,|\, b \rangle \, (S^{-1/2} P \, S^{-1/2})_{\mathrm{ba}};$$

$$\vec{\mu}_{\mathrm{on}}{}'' = -\Sigma_{\mathrm{A}} \Sigma_{\mathrm{B}} \sum_{\mathrm{a} \in \mathrm{A}} \sum_{\mathrm{b} \in \mathrm{B}} \langle a \,|\, \vec{r} \,|\, b \rangle \, (S^{-1/2} P[on] \, S^{-1/2})_{\mathrm{ba}}.$$

Oscillator strengths were calculated according to formula:

$$f_{\mathrm{on}} = 2/3 \, E_{\mathrm{n}} \, \mu_{\mathrm{on}}{}^{2},$$

where E_{n} is the energy of the n-th electron transition. The set (μ_{o}, μ_{on}, f_{on}) corresponds to the simplest point charge approximation, the set ($\mu_{\mathrm{o}}{}'$, $\mu_{\mathrm{on}}{}'$, $f_{\mathrm{on}}{}'$) being more, and the set ($\mu_{\mathrm{o}}{}''$, $\mu_{\mathrm{on}}{}''$, $f_{\mathrm{on}}{}''$) the most precise. In our previous publications only the data for the first set were mentioned.[3,13]

First of all, we calculated the electron absorption spectra of *1* and *3* (Table I) and the dipole moment of *1*. The calculated and experimental[14,15] spectra are in good concordance for *1* as well as for *3*.[3] In the former case, the theoretical spectrum demonstrates a hypsochromic shift in comparison with the experimental one. An explanation of this shift might be the unspecific interaction with the solvent. Because of the great dipole moment of *1* (μ_o = —5.7, μ_o' = —6.7, μ_o'' = —6.5 D), a strong influence of the reactive field of polar solvent is to be expected, leading to bathochromic shift in comparison with the data observed in the gas phase. The character of such an influence was discussed in detail previously.[16]

TABLE I

Electron Transitions Calculated for Individual Molecule 1 *and Ion* 3*

Compound	Excited state	Excitation energy, eV	Oscillator strength			Dominant electron transition
			f_{on}	f_{on}'	f_{on}''	
1	S_1	3.47	0.000	0.000	0.000	$\vert -2\rightarrow 1\rangle$, 78%
	S_2^x	4.06	0.734	0.831	0.768	$\vert 0\rightarrow 1\rangle$, 93%
	S_3^y	4.35	0.004	0.003	0.003	$\vert -1\rightarrow 1\rangle$, 92%
3	S_1^x	2.14	0.136	0.139	0.139	$\vert 0\rightarrow 1\rangle$, 96%
	S_2^y	2.76	0.500	0.523	0.513	$\vert 0\rightarrow 2\rangle$, 92%
	S_{10}^x	4.67	0.149	0.177	0.157	$\vert 0\rightarrow 7\rangle$, 96%
	S_{11}^y	4.74	0.863	0.925	0.899	$\vert -1\rightarrow 1\rangle$, 73%

* For orientation see Figure.

TABLE II

Energies of Frontier Orbitals (eV) of 1 . . . 3 *System in Dependence on Geometry Parameters d and* Δ *(pm, see Figure)*

Geometry parameters		Two highest occupied levels*	Two lowest unoccupied levels*
d	*Δ*		
300	—70	—4.16; **—1.04**	**1.76;** 3.74
	0	—4.14; **—1.04**	**1.54;** 3.45
	70	—4.10; **—1.02**	**1.31;** 3.18
400	—70	—3.99; **—0.89**	**1.19;** 3.18
	0	—4.00; **—0.91**	**1.04;** 3.00
	70	—4.01; **—0.91**	**0.88;** 2.82
500	—70	—3.93; **—0.83**	**0.78;** 2.79
	0	—3.94; **—0.84**	**0.66;** 2.65
	70	—3.95; **—0.85**	**0.53;** 2.51
600	0	—3.90; **—0.80**	**0.34;** 2.35
∞	—	—3.79; **—0.70**	**—2.85;** —0.77

* HOMO and LUMO are indicated in bold figures.

The most essential parameters characterizing the mechanism of reaction between *1* and *3* are the energies of donor's HOMO *e* and acceptor's lowest unoccupied molecular orbital (LUMO) *e**, as well as the energy of charge transfer electron transition E_{CT}. The variation of these parameters with the interplane distance and the mutual orientation of the reactants is presented in Tables II and III. We performed calculations only for a limited set of geometry parameters (*Δ*, *d*, see Figure) to demonstrate the character of the *e*, *e** and E_{CT} dependence on the geometry of the »complex« under consi-

TABLE III

Energies of Electron Transitions (eV) and Oscillator Strengths (in Parentheses) of 1 . . . 3 System in Dependence on Geometry Parameters d *and* Δ *(pm, see Figure)**

d Δ	300	400	500	600
70	**0.24(0.00)** $\vert 0\to 1\rangle$ 2.27(0.25) $\vert 0\to 4\rangle$ 2.32(0.00) $\vert 0\to 2\rangle$	**—0.09(0.00)** $\vert 0\to 1\rangle$ 2.00(0.00) $\vert 0\to 2\rangle$ 2.26(0.24) $\vert 0\to 5\rangle$	**—0.32(0.00)** $\vert 0\to 1\rangle$ 1.76(0.00) $\vert 0\to 2\rangle$ 2.27(0.23) $\vert 0\to 6\rangle$	
0	**0.40(0.02)** $\vert 0\to 1\rangle$ 2.27(0.24) $\vert 0\to 3\rangle$ 2.45(0.00) $\vert 0\to 2\rangle$	**—0.03(0.00)** $\vert 0\to 1\rangle$ 2.06(0.00) $\vert 0\to 2\rangle$ 2.26(0.23) $\vert 0\to 5\rangle$	**—0.27(0.00)** $\vert 0\to 1\rangle$ 1.81(0.00) $\vert 0\to 2\rangle$ 2.26(0.23) $\vert 0\to 6\rangle$	**—0.46(0.00)** $\vert 0\to 1\rangle$ 1.61(0.00) $\vert 0\to 2\rangle$ 2.19(0.00) $\vert 0\to 3\rangle$ 2.25(0.00) $\vert 0\to 4\rangle$ 2.26(0.23) $\vert 0\to 6\rangle$
—70	**0.58(0.06)** $\vert 0\to 1\rangle$ 2.24(0.19) $\vert 0\to 3\rangle$ 2.57(0.00) $\vert 0\to 2\rangle$	**0.02(0.00)** $\vert 0\to 1\rangle$ 2.11(0.00) $\vert 0\to 2\rangle$ 2.26(0.22) $\vert 0\to 5\rangle$	**—0.24(0.00)** $\vert 0\to 1\rangle$ 1.85(0.00) $\vert 0\to 2\rangle$ 2.26(0.22) $\vert 0\to 6\rangle$	

* Charge transfer parameters are indicated in bold figures.

deration. Actually, the reacting donor-acceptor system *1 . . . 3* may be considered in a pre-reaction stage as a complex. Therefore, $d = 300$ pm was chosen as the minimal distance, this value being characteristic of the usual charge transfer complexes.[17] It seems obvious that at $d \gtrsim 600$ pm a variation of Δ leaving the reactants in the vicinity of one another has no appreciable influence on the main electronic parameters. Also, there was no reason to perform calculations at $d = 700$, 800, *etc.* pm, because this could not lead to qualitatively new conclusions.

DISCUSSION

Complexes of »anion — molecule« type have not been investigated sufficiently so far.[17] We have pointed out that there are characteristic differences in the behaviour of systems »molecule — molecule« and »monoanion — molecule«.[1] These features seem to be connected with electrostatic interaction during ET. In the first case, ET results in Coulombic attraction, but there is a negligible electrostatic effect in the second case. The system »dianion — neutral molecule« differs from these two: Coulombic repulsion appears during ET process.

Thus, there is a significant difference between systems *1 . . . 2* and *1 . . . 3*, even when the reagents are separated and their electronic systems are nearly out of interaction. In that case, the difference between donor's HOMO and acceptor's LUMO in the *1 . . . 2* system corresponds to E_{CT}. There is no such coincidence in the *1 . . . 3* system (compare[17]). It is essential that electrostatic interaction depends on the medium; therefore, E_{CT} in the *1 . . . 3* system (unlike the *1 . . . 2* system) is strongly influenced by the solvent, decreasing with solvent polarity.

At infinite distance (*i. e.* without interaction) the HOMO energy of *3* is even higher than the LUMO energy of *1* which suggests a possibility of spontaneous ET. Naturally, in approaching the reactants the acceptor's LUMO energy raises drastically because of the influence of the negatively charged donor on the electroneutral acceptor.

The *1 . . . 3* system demonstrates a behaviour quite similar to the *1 . . . 2* system, donor's HOMO energy being only slightly influenced in both cases. In the *1 . . . 3* system this circumstance leads to crossing of the HOMO and LUMO energies during the reagents' approach. At distances characteristic of a »normal« chemical reaction, HOMO have negative and LUMO — positive values (Table II).

Charge transfer energy at large distances has negative values, providing the possibility of spontaneous ET. But $E_{CT} > 0$ at distances characteristic of the beginning of chemical reaction (Table III). So, E_{CT} decreases in the »molecule — molecule« system,[18] is practically constant in »monoanion — molecule« system[1] and raises in »dianion — molecule« system, when the distance decreases.

At the same d values, changing the Δ value in such a manner that the reagents become closer one to another, E_{CT} raises, too. It is to be pointed out that in the course of chemical reaction between *1* and *3* the chemical bond is forming between the carbon atoms indicated in chemical formulae (see above) because of the pronounced localization of frontier orbitals on these atoms. Calculations have demonstrated that an approach of each reactant to the other has no influence on the localization of LUMO (*1*) and HOMO (*3*), exactly as it is shown in the case of the *1 . . . 2* system.[1] Therefore, the geometry of the »complex« which is favourable both for ET and for formation of a chemical bond corresponds to $-700 \leq \Delta \leq 700$ pm. Calculations performed for such geometries seem to be sufficiently characteristic for a general conclusion on the possibility of pre-reaction ET.

Even at short distance between the reactants ($d = 300$ pm) the value of E_{CT} is low enough for »dark« ET from dianion *3* to p-quinonemethide *1* and, consequently, to various lignin substrates (it has been shown that substitution transforming the simplest *p*-quinonemethide *1* to corresponding lignin subunits has only minor influence on its main electronic characteristics[7]). So, at every distance ET is probable when an interaction of *3* with p-quinonemethides appears, even in the conditions of thermal chemical reaction. At short distances it is possible for an addition reaction to proceed through the ion-radical stage. The barriers of polar reactions of this type correlate linearly with E_{CT} values.[19] This circumstance enables us to explain the well-known pronounced difference between ions *2* and *3* in their affinity to *p*-quinonemethides.[2] The data obtained confirm our previous conclusions concerning the chemical reactivity of reagents *1—3*, based on the analysis of electronic structure of individual reagents.[2,13]

Et at large distances (by tunnelling, for example) from *3* to *p*-quinonemethidic lignin subunits can itself lead to lignin destruction because of the unstability of anion-radicals forming from *p*-quinonemethides.[20] Therefore, in the case of powerful electron donors (such as reduced forms of effective delignification catalysts), close spatial approach to lignin macromolecule is not a necessary condition for a catalytic process to proceed. An indispensable distance interval corresponds to that permiting electron tunnelling.[21,22] It means that steric hindrances may not influence the process of lignin catalytic destruction. Reduced forms of the catalyst may act as an artillery, bombarding lignin with electrons from large distances.

Comparison of the *1* ... *2* and *1* ... *3* systems shows the principal difference between the behaviour of ionized mono- and diphenols in relation to strong electron acceptors. This difference helps us to understand the unsimilar effect of 9,10-anthrahydroquinone and the usual phenols on such technological processes as wood pulping.[2,4]

All the calculations have been performed for individual molecules, corresponding, therefore, to the gas phase. Probably, the solvent effect could change the absolute values of the main characteristics (for example, strong solvation of anions seems obvious), but there is no reason to propose changing of qualitative conclusions. Polar solvent reduces the repulsive Coulombic term of the total energy of the *1* .. *3* interaction, so it may be expected that the value of E_{CT} in such a solvent is even less than the calculated one.

Considering the catalytic system in real technological processes, we have to take into account all the reduced forms of the catalyst. It is quite clear that *3* is most active amongst all the closed-shell systems.[3] The most puzzling problem is the behaviour of the corresponding semiquinoid anion-radical. This problem is especially significant because of a rise of anion-radical concentration with temperature[5,6] significant amounts of this species are expected to be present at conditions characteristic of real technological processes. The possibility of 9,10-anthrasemiquinone to take part in ET reactions with *p*-quinonemethides seems also very probable, but this is a subject of another investigation.

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SAŽETAK

Prijenos elektrona u predreakciji sustava *p*-kinonmetid-9,10-dihidroksiantracen dianion

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Zavisnost elektronske strukture sustava *p*-kinonmetid-9,10-dihidroksiantracen dianion o udaljenosti molekulskih ravnina i o međusobnoj orijentaciji reaktanata analizirana je na osnovi rezultata CNDO/S3 računa. Međusobna smetnja donorskog i akceptorskog sistema uslijed paralelnog približavanja reaktanata ne mijenja kvalitativne zaključke o njihovoj reaktivnosti, dobivene na osnovi analize elektronske strukture pojedinih molekula. Niska energija za prijenos naboja ukazuje na veliku vjerojatnost da je upravo prijenos elektrona prvi korak termičke reakcije.