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Note

A CDNO/S3 Study of the *p*-Quinonemethide-Phenol Interaction

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The dependence of the electronic structure of *p*-quinonemethide — phenol and *p*-quinonemethide — phenolate anion systems on interplane distance and mutual orientation of the reactants was analyzed on the basis of CNDO/S3 calculations. The approach of two reactants results in a minor change in the charge transfer electron transition. Its high energy indicates a low probability of electron transfer to be the first stage of the chemical reaction.

INTRODUCTION

The reaction of *p*-quinonemethides (π-acids) with phenols (π-bases) is a typical example of donor-acceptor interaction, leading ultimately to the formation of a covalent chemical bond. Such reactions are of technological interest, because they determine the undesirable lignin self-condensation during the wood pulping process.[1,2] Thus, the mechanism of the interaction is of theoretical, as well as of practical significance.

The electronic structure of the simplest molecules entering into this type of reactions (*i. e.* producing a link between the starred atoms), *p*-quinonemethide (*1*) and phenol (in neutral *2* and ionized *3* forms) was analyzed previously.[2–4] The general conclusion was that an interaction of *p*-quinonemethides with electron donors is orbitally controlled, the regioselectivity being determined by distribution, and the rate by energies of frontier molecular orbitals (FMO).[3–6] But, electronic characteristic of electrophile and nucleophile will change when they approach each other, and this alteration may influence conclusions based on the studies of separate molecules.

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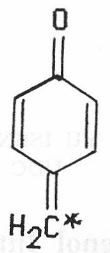

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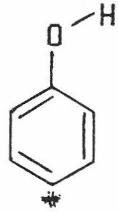

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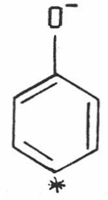

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Another crucial question is that of the initial stage of the donor-acceptor chemical reaction. It may proceed as a »classical« heterolytic reaction, but the possibility of a pre-reaction electron transfer stage cannot be eliminated. Relative probabilities of these two possible mechanisms have to be estimated in order to clarify the reactions governing lignin condensation. This is important because there are different types of catalysts for »classical« heterolytic and ion-radical reactions. Considering the two points mentioned above, we have theoretically examined the dependence of electronic structure of systems *1 . . . 2* and *1 . . . 3* on the mutual orientation and distance between the reagents.

RESULTS

CNDO/S3 calculations[7,8] have been performed for the systems *p*-quinonemethide — phenol (*1 . . . 2*) and *p*-quinonemethide — phenolate anion (*1 . . . 3*) with different mutual orientation and interplane distances (see Figure). Only parallel orientations of planar reagents have been considered. It is clear that the sets of mutual orientations of the reactants have been chosen quite arbitrarily, and it would be better to perform the calculations for a continuous set. But we think that it is enough for qualitative estimations to be based on orientations characteristic of the considered chemical reaction. For the geometry used for *1* see ref.[4] Geometry parameters of *2* and *3* were chosen on the basis of X-ray data[9] and *ab initio* calculations.[10] The bond lengths used were: C—C and C—OH 140, C—O$^-$ 130, C—H 110, O—H 95 pm; all valence angles were taken to be equal to 120°. Wave functions and excited state energies were calculated taking into account 96 and 16 singly excited configurations for systems (*1 . . . 2*) and (*1 . . . 3*), respectively. These correspond to singlet electron excitations from one out of twelve (or out of four, respectively) highest occupied levels to one out of eight (or out of four, respectively) lowest unoccupied levels.

The results are presented in Tables I and II. Since the electronic structure of *1*, as well as that of *2*, was analyzed in detail in other publications,[2–4,10] we are discussing now only the variation of most essential parameters which govern chemical reactivity.

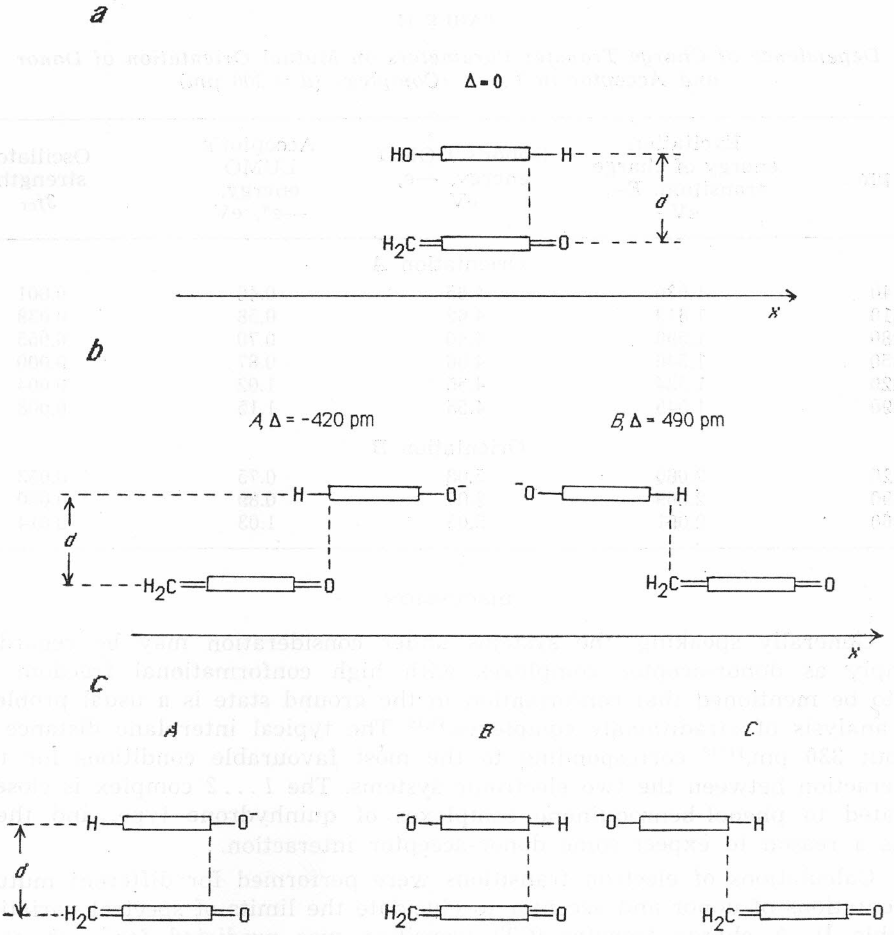

Figure. Orientation of the reagents: *a 1...2* »Complex«, see Table I (disposition presented corresponds to $\Delta = 0$); *b 1...3* »Complex«, see Table II (in both cases Δ takes positive values with moving of *2* or *3*, correspondingly, along x axe in positive direction); *c 1...3* »Complex«, see Table III.

TABLE I

*Electron Transitions for the 1···2 »Complex«, d = 330 pm**

Dominant electron transition	Excitation energy (E), eV	Oscillator strength (3f)				
		Δ pm				
		—70	0	70	140	210
σ (A)→π^* (A)	3.7	0.00	0.00	0.00	0.00	0.00
π (D)→π^* (A)	4.5	0.96	0.48	0.24	0.56	0.77
π (D)→π^* (D)	4.6	0.03	0.23	0.15	0.02	0.02
π (A)→π^* (A)	4.6	1.11	1.39	1.77	1.68	1.60

* For individual molecules: *1*, $\sigma \to \pi^*$ ($E = 3.5$ eV, $f = 0.00$), $\pi \to \pi^*$ ($E = 4.5$ eV, $f = 2.18$); *2*, $\pi \to \pi^*$ ($E = 4.6$ eV, $f = 0.03$).

TABLE II

Dependence of Charge Transfer Parameters on Mutual Orientation of Donor and Acceptor in 1 . . . 3 »Complex« (d = 300 pm)

Δ, pm	Excitation energy of charge transition, E_{CT}, eV	Donor's HOMO energy, —e, eV	Acceptor's LUMO energy, —e^*, eV	Oscillator strength, $3f_{CT}$
		Orientation *A*		
140	1.630	4.65	0.46	0.001
210	1.619	4.62	0.58	0.038
280	1.599	4.60	0.70	0.055
350	1.546	4.56	0.87	0.009
420	1.534	4.55	1.02	0.004
490	1.545	4.55	1.15	0.008
		Orientation *B*		
—420	2.060	5.08	0.75	0.053
—490	2.069	5.07	0.89	0.050
—560	2.061	5.05	1.03	0.014

DISCUSSION

Generally speaking, the systems under consideration may be regarded simply as donor-aceptor complexes with high conformational freedom. It is to be mentioned that conformation in the ground state is a usual problem in analysis of »traditional« complexes.[11,12] The typical interplane distance is about 330 pm,[11–13] corresponding to the most favourable conditions for the interaction between the two electronic systems. The *1 . . . 2* complex is closely related to phenol-benzoquinone complexes of quinhydrone type, and there was a reason to expect some donor-acceptor interaction.

Calculations of electron transitions were performed for different mutual orientations of donor and acceptor to elucidate the limits of spectral variation (Table I). A charge transfer (CT) transition was predicted for each case, suggesting that mutual interactions take place between *1* and *2* practically independently of relative orientation. Hence, there is a possibility of a *1 . . . 2*-type interaction in solutions where individual molecules are present, as well as in polymer matrices where the two participants are connected by carbon chains. The only necessary condition is that the distance between the molecules is sufficiently close. The oscillator strength can be regarded as a measure of interaction since the excitation energies are practically the same in all cases.

The general conclusion concerning *1 . . . 2* interaction is that it takes place but without any noticeable chemical or spectral consequences. Firstly, the $\pi(D) \rightarrow \pi^*(A)$ CT band cannot be observed in UV spectra because of its overlapping with the $\pi(D) \rightarrow \pi^*(D)$ and $\pi(A) \rightarrow \pi^*(A)$ bands. Secondly, it is known that appreciable CT is possible for complexes of neutral molecules having only the ionization potential and electron affinity difference less than 4.3 eV,[13] which is not the case of molecules *1*[3,4] and *2*[2]. The energy of CT transition is in good agreement with the estimations based on frontier orbital calculations[2–4] (see formula[13]) and is too high for thermal electron transfer. Thermal condensation of *p*-quinonemethides with phenols seems to be the »classical« polar reaction without the possibility of an electron transfer playing any significant role (see discussion[14]). But the data presented enable us to propose that the spatial neighbourhood of *p*-quinonemethidic (acceptors) and phenolic (donors) fragments in a polymer makes it sensitive to ultraviolet radiation which would tend to move the system into chemically active excited state with charge separation.

The problem of the *1...3* interaction is of more practical interest because the corresponding condensation is most essential for some processes in alkaline media.[1] On the other hand, ionization appreciably raises the energy of phenol's highest occupied molecular orbital (HOMO)[2] making the compound more reactive and at the same time the CT stage more probable. It is to be noted that CT interaction between the molecule and ion differs from the one between two neutral molecules. In the latter case, charge separation and electrostatic attraction are characteristic. In the former case, there is no pronounced electrostatic interaction. It was pointed out that complexes of »anion-molecule« type have not been thoroughly investigated.[13] In the case under consideration, a real complex may be formed only when the two participants are fixed in a rigid (polymer) framework. In another case *1...3* systems with different geometrical characteristics are regarded as pre-reaction »macroconformations«.

The most essential point in the analysis of the *1...3* interaction is the dependence of the energy of CT transition (E_{CT}) and of donor's HOMO (e) and acceptor's LUMO (e^*) energies on the distance between and mutual orientation of the reactants. Firstly, we tried to estimate the limits of CT transition energies at the usual interplane distance, favourable for the donor-acceptor interaction (Table II). The minimum of E_{CT} corresponds to the configuration unfavourable for chemical bonding. So, even if a fast electron transfer takes place, it has to be followed by a much slower geometry rearrangement in order to lead to consequent formation of the chemical bond. Secondly, we determined the variation of FMO energies and E_{CT} with intermolecular distance (Table III, E_{CT} values in all the cases very precisely correspond to one-configurational electron transition from donor's HOMO to acceptor's LUMO). Calculations were performed for three different orientations (*A*, *B*, *C*).

TABLE III

Energies (eV) of Donor's HOMO (e), Acceptor's LUMO (e) and Charge Transfer Electron Transition (E_{CT}) in 1...3 System**

d, pm	$-e$			$-e^*$			E_{CT}		
	Orientation								
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
300	4.73	4.82	5.08	0.21	0.04	0.75	1.82	2.02	2.06
600	4.75	4.78	4.88	1.07	1.01	1.28	1.87	1.92	1.97
900	4.76	4.78	4.82	1.52	1.50	1.62	1.90	1.93	1.95
10000	—	—	4.77	—	—	2.71	—	—	1.92
∞	—	—	4.77	—	—	2.85	—	—	1.92

* Oscillator strength $f \approx 0.02$ at $d = 300$ pm, in other cases $f = 0.00$.

The data listed in Table III show that the approach of each reactant to the other has no significant influence on donor's HOMO energy. The energy of acceptor's LUMO raises drastically, but E_{CT} remains practically the same. It is essential that $E_{CT} = e^* - e$ at $d = \infty$. There is a characteristic difference in E_{CT} dependence on the donor-acceptor distance between the »complexes« of two neutral molecules and a molecule with anion. In the former case, E_{CT} is very sensitive and falls down during the approach (see the calculation of benzene — tetracyanoethylene complex[12]). The value of E_{CT} is smaller in the case of neutral phenol *2*, but too much for the possibility of ET stage taking a substantial part in the mechanism of thermal *p*-quinonemethide — phenol interaction.

All the conclusions concerning the photochemical influence on *p*-quinonemethide — phenol system are the same for neutral and ionized phenol, but in the latter case all the effects are more pronounced. Thermal condensation of *p*-quinonemethides with phenols and, consequently, all related processes of lignin self-condensation during wood pulping, seem to be »classical« polar processes. In our previous publications this condensation was analyzed on the basis of calculations of isolated donor and acceptor molecules.[2-6] The conclusion was that the reaction was orbitally controlled, and its course and rate could be determined by considering the FMO energies and localizations. In addition, it is to be said that the calculations of atomic orbital contributions to FMO for the orientations listed in Table III show that these parameters remain practically unperturbed during the mutual approach of the reactants. Therefore, the data presented confirm our previous conclusions, demonstrating that the pre-reactional mutual influence of donor's and acceptor's electronic systems does not lead to any effects which could qualitatively change the conclusions about the mechanism based on the analysis of the isolated participants of the reaction.

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SAŽETAK

CNDO/S3 studija interakcije *p*-kinonmetida s fenolom

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Zavisnost elektronske strukture sustava *p*-kinonmetid/fenolat-anion o udaljenosti molekulskih ravnina i međusobnoj orijentaciji reaktanata analizirana je na osnovi rezultata CNDO/S3 računa. Približavanje oba reaktanta ima za posljedicu neznatnu promjenu u elektronskom prijelazu uz prijenos naboja. Visoka pripadna energija pokazuje da je malo vjerojatno da prijenos elektrona bude prvi korak u toj kemijskoj reakciji.