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Kinetic Studies of the Oxidation Reactions of *o*-, *m*-, and *p*-Benzenediols with Tris(1,10-phenanthroline)iron(III). An Estimation of the Redox Potentials of the Organic Radicals by Application of the Marcus Theory

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Kinetic studies of the oxidation of *o*-, *m*-, and *p*-benzenediols (H_2A) by tris(1,10-phenanthroline)iron(III) were made in dilute perchloric acid solution at an ionic strength of 1.0 mol dm^{-3} at four temperatures between 10 and 30 °C. The second-order rate constants (k_0) which follow the observed rate law of $-\mathrm{d}\,[\mathrm{Fe(phen)_3}^{3+}]/\mathrm{d}t=k_0[\mathrm{Fe(phen)_3}^{3+}][H_2A]$ were determined under varied conditions. The order of the rate constants was *m*-<*o*-<*p*-benzenediols, with the ratio being approximately 1 : 10^3 : 10^4. By the application of the Marcus theory to the kinetic parameters obtained, the standard redox potentials of the dihydroxyphenyl radicals ($H_2A^{\dot{+}}$) were estimated in 0.11 mol dm^{-3} perchloric acid solution to be 1.41, 1.10, and 0.97 V for *m*-, *o*-, and *p*-benzenediols, respectively. The energies of the highest occupied molecular orbitals for the H_2A molecules ($\varepsilon_{\mathrm{HOMO}}$) were calculated to be -0.4468, -0.4332, and -0.4224 a.u. for *m*-, *o*-, and *p*-benzenediols, respectively. The differences of the total electronic energies between $H_2A^{\dot{+}}$ and H_2A molecules (ΔE_T) were calculated to be 0.4183, 0.4033, and 0.3957 a.u. for *m*-, *o*-, and *p*-benzenediols, respectively. Thus, the standard redox potentials of the free-radicals estimated are found to be well correlated with the HOMO energies and also with the differences of the total electronic energies between the cation radicals and the parent molecules.

The application of the Marcus theory[1] to kinetics of the reactions involving organic and inorganic substrates has given satisfactory results in the explanation of the observed kinetic parameters. An application of Marcus theory to the investigation of the kinetic data in the outer-sphere electron transfer reactions allows an estimation of the redox potentials of the unstable free-radicals of organic molecules.[2,3] The present paper demonstrates the kinetics of the outer-sphere electron transfer reactions of *o*-, *m*-, and *p*-benzenediols with tris(1,10-phenanthroline)iron(III), and explains the estimation of the standard redox potentials of those free-radicals by means of the application of Marcus theory to the kinetic parameters obtained. We calculated the energy of the highest occupied molecular orbitals (HOMO) of each benzenediol and the difference in the total electronic energy between the cation radical and the parent molecule, by using CNDO/2 MO.[5] The correlation between the theoretically calculated energies and the standard redox potentials estimated by the application of Marcus theory to the kinetic parameters is discussed in the present paper.

Experimental

Chemicals. Reagent-grade *o*-, *m*-, and *p*-benzenediols from Wako Pure Chemical Co. Inc., were used without further purification. The solution of each reagent was prepared just before use. Tris(1,10-phenanthroline)iron(III) perchlorate was prepared by oxidizing tris(1,10-phenanthroline)iron(II) with lead(IV) dioxide in dilute sulfuric acid solution; after removal of lead(IV) dioxide and lead(II) sulfate, the perchlorate salt of the tris(1,10-phenanthroline)-iron(III) was precipitated by the addition of sodium perchlorate solution. The solid obtained was recrystallized from aqueous perchlorate solution. A stock solution of tris(1,10-phenanthroline)iron(III) was prepared by dissolving the perchlorate salt in 70% (v/v) perchloric acid. The stock solution of the blue solution having an absorption maximum at 600 nm was very stable in perchloric acid and no appreciable decomposition occurred for at least 3 months at room temperature in the dark. Sodium perchlorate, used for adjusting ionic strength, was recrystallized twice from aqueous solution. Deionized water was distilled with and without addition of some permanganate in a glass still.

Kinetic Measurements. The kinetic experiments were carried out with a Union Stopped Flow Spectrophotometer RA-401 by following the increase of the absorbance at 510 nm due to the tris(1,10-phenanthroline)iron(II) of a reaction product. The concentrations of *m*-benzenediol were kept at least 10-fold larger than those of tris(1,10-phenanthroline)iron(III) in order to ensure pseudo-first-order conditions. In most of the reactions of *o*- and *p*-benzenediols with tris(1,10-phenanthroline)iron(III), second-order conditions were adopted because these reactions were extremely fast under the conditions of excess benzenediols with respect to tris(1,10-phenanthroline)iron(III). The rate constants were evaluated by treating an average-kinetic curve for 10 runs, the Stopped-Flow apparatus being equipped with a micro-computer system for memorizing and averaging the multiple runs. The acidity was kept constant at 0.055, 0.11, or 1.0 mol dm^{-3} in perchloric acid. The ionic strength was adjusted to be 1.0 mol dm^{-3} by the addition of sodium perchlorate solution. The temperature (with ±0.1 °C) of the cell housing was regulated by circulating the thermostated water.

Results

Stoichiometry. By the titration of 2.6×10^{-5} mol dm^{-3} tris(1,10-phenanthroline)iron(III) with *o*- or *p*-benzenediol monitoring the absorbance at 510 nm due to tris(1,10-phenanthroline)iron(II), the stoichiometry was determined to be 2 : 1 for $[\mathrm{Fe(phen)_3}^{3+}]$: [bezenediol]. Thus, the stoichiometric equation is written as Eq. 1:

$$2\,\mathrm{Fe(phen)_3}^{3+} + \mathrm{H_2A} \longrightarrow 2\,\mathrm{Fe(phen)_3}^{2+} + \mathrm{A} + 2\mathrm{H}^+, \quad (1)$$

where H_2A indicates a benzenediol and A, a quinone. The stoichiometry for the reaction between *m*-benzenediol and tris(1,10-phenanthroline)iron(III) was not determined by the titrimetric method due to the slow reaction. A large excess of *m*-benzenediol was necessary for the reaction to proceed completely.

Kinetics of Reaction. The kinetic runs were carried out in the acid solutions so that the acid dissociation of benzenediols could be completely neglected.4) For the reactions of *o*- and *p*-benzenediols with tris(1,10-phenanthroline)iron(III), when pseudo-first-order conditions were adopted, plots of ln $(A_\infty - A_t)$ *vs.* *t* were linear for at least 80% of a whole reaction. Moreover, when the reaction was started at a second-order condition of $[\mathrm{Fe(phen)_3}^{3+}] = 2[\mathrm{H_2A}]$, plots of $1/(A_\infty - A_t)$ *vs.* *t* were also linear for at least 60% of a whole reaction. This confirms the first-order dependence of each reactant and the stoichiometry given in Eq. 1. Thus, the following empirical rate law can be written:

$$-\mathrm{d}[\mathrm{Fe(phen)_3}^{3+}]/\mathrm{d}t = k_0[\mathrm{Fe(phen)_3}^{3+}][\mathrm{H_2A}], \quad (2)$$

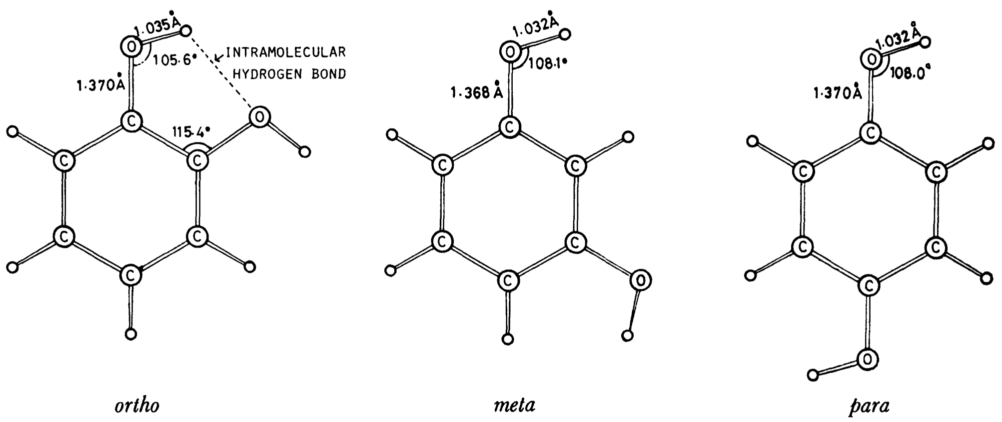
where k_0 is the observed second-order rate constant. In case of the reaction between *m*-benzenediol and tris(1,10-phenanthroline)iron(III), plots of ln $(A_\infty - A_t)$ *vs.* *t* were linear for the initial periods of about 20% of a whole reaction and gradually deviated from the straight line under a pseudo-first-order condition. Thus, the rate constants in this case were evaluated by using the initial slope. The second-order rate constants obtained were, within the experimental error, constant irrespective of the reactants over the wide ranges of 5.0×10^{-5} to 5.0×10^{-2} mol dm^{-3} *m*-benzenediol and of 1.2×10^{-6} to 2.0×10^{-5} mol dm^{-3} tris(1,10-phenanthroline)iron(III). However, when tris(1,10-phenanthroline)iron(II) was added to the reaction solution before starting the reaction, the rate of reaction decreased according to the amounts of tris(1,10-phenanthroline)iron(II) added. Unless the amounts of tris(1,10-phenanthroline)iron(II) exceeded about 10% of the tris(1,10-phenanthroline)iron(III) concentrations, the rate constants obtained from the initial slope of ln $(A_\infty - A_t)$ *vs.* *t* were not influenced.

Temperature Dependence. The observed second-order rate constants k_0 at varied temperatures were determined under given conditions. The forward rate constants k_1 in Reaction 3 (and Eq. 5) are tabulated in

TABLE 1. TEMPERATURE DEPENDENCE OF THE RATE CONSTANTS AT AN IONIC STRENGTH OF 1.0 mol dm^{-3}

Temp / °C	*m*-Benzenediola) $10^{-3}\,k_1$ / dm^3 mol^{-1} s^{-1}	*o*-Benzenediolb) $10^{-6}\,k_1$ / dm^3 mol^{-1} s^{-1}	*p*-Benzenediolc) $10^{-7}\,k_1$ / dm^3 mol^{-1} s^{-1}
10			12.0d)
			9.5e)
			6.3f)
15	6.9d)	9.3d)	13.9d)
	4.5e)	8.7e)	11.6e)
	0.7f)	6.5f)	7.2f)
20	10.3d)	11.6d)	16.4d)
	6.0e)	10.6e)	12.8e)
	1.1f)	7.0f) 8.2f)	8.2f)
25	13.4d)	15.0d)	17.3d)
	8.8e)	13.2e)	15.0e)
	1.0f)	9.2f)	10.2f)
30	18d)	17.7d)	
	11.0e)	16.2e)	
	2.6f)	10.9f)	

a) The initial concentrations of *m*-benzenediol and tris(1,10-phenanthroline)iron(III)were 2.0×10^{-3} and 7.0×10^{-6} mol dm^{-3}, respectively. b) and c) The initial concentrations of benzenediols and tris (1,10-phenanthroline)iron (III) were 7.0×10^{-6} and 1.4×10^{-5} mol dm^{-3}, respectively. d), e), and f) indicate the results in 0.055, 0.11, and 1.0 mol dm^{-3} perchloric acid, respectively.



ortho
−0.4332 a.u.
0.4033 a.u.

meta
−0.4468 a.u.
0.4183 a.u.

para
−0.4224 a.u.
0.3957 a.u.

Fig. 1. The structures of the benzenediols calculated by the CNDO/2 MO, and the values of $\varepsilon_{\mathrm{HOMO}}$ (negative values in the above) and ΔE_{T} (positive values in the below). The small empty circle denotes the hydrogen atom. The C–C distance of 1.40 Å and the C–H length of 1.08 Å in the benzene are common to the three molecules. The structure of the cation (H_2A^+) is assumed to be the same as that of the neutral molecule (H_2A). The energy unit is a.u., where 1 a.u. = 2625.7 kJ mol^{-1}. The larger $\varepsilon_{\mathrm{HOMO}}$ in the absolue and the larger ΔE_{T} correspond to the more difficult oxidation.

TABLE 2. KINETIC PARAMETERS FOR THE OXIDATION OF *m*-, *o*-, AND *p*-BENZENEDIOLS BY TRIS (1,10-PHENANTHROLINE)IRON(III), AND THE ESTIMATED REDOX POTENTIALS (E°)[a]

Benzenediols	$\Delta H^{\neq}$[b] / kJ mol^{-1}	$\Delta S^{\neq}$[c] / J K^{-1} mol^{-1}	ΔG^{*}_{12} / kJ mol^{-1}	ΔG°_{12} / kJ mol^{-1}	E° / V
m-	42[d]	−28[d]	39.2[d]	31.8[d]	1.39[d]
	41[e]	−32[e]	40.4[e]	33.5[e]	1.41[e] 1.39[e,g]
	57[f]	10[f]	45.0[f]	39.8[f]	1.47[f]
o-	29[d]	−10[d]	22.0[d]	3.52[d]	1.10[d]
	28[e]	−15[e]	22.1[e]	3.71[e]	1.10[e] 1.07[e,g]
	23[f]	−35[f]	23.0[f]	5.42[f]	1.12[f]
p-	15[d]	−36[d]	15.7[d]	−9.57[d]	0.96[d]
	19[e]	−25[e]	16.2[e]	−8.44[e]	0.97[e] 0.94[e,g]
	19[f]	−28[f]	17.3[f]	−6.02[f]	1.00[f]

a) $r_1=4.0\times10^{-10}$ m for benzenediols; $r_2=7.0\times10^{-10}$ m for $Fe(phen)_3^{3+/2+}$; $\lambda_{12}=80.8$ kJ mol^{-1}; the potentials estimated for the reaction $H_2A^{\dagger}+e^- \rightleftarrows H_2A$; the error of E° is ±0.01 V. b) The error is ± 1 kJ mol^{-1}. c) The error is ±4 J K^{-1} mol^{-1}. d), e), and f) indicate the results in 0.055, 0.11, and 1.0 mol dm^{-3} perchloric acid at an ionic strength of 1.0 mol dm^{-3}. g) Evaluated by using $\Delta G^{*}_{11}=23$ and $\Delta G^{*}_{22}=20$ kJ mol^{-1} (see Text).

Table 1, where the observed rate constants k_0 are equal to 2 k_1 (*v. i.*).

Calculation of ε_{HOMO} *and* ΔE_T. To evaluate the oxidation potential theoretically, a CNDO/2 MO[5] calculation was made for *o*-, *m*-, and *p*-benzenediols and the corresponding dihydroxyphenyl radicals. The following two energies may be compared to the redox potentials determined experimentally. One is the energy level of the highest occupied molecular orbital of the neutral species (ε_{HOMO}). This gives the ionization potential of benzenediols of H_2A species. The other is ΔE_T, the difference of the total electronic energies between the neutral molecule and its cation radical of $H_2A^{\dagger}$. The ΔE_T corresponds to the energy required to cause $H_2A \rightarrow H_2A^{\dagger}+e^-$, and is described as $\Delta E_T = E_T(H_2A^{\dagger}) - E_T(H_2A)$. The value of E_T of the radical was computed by using the UHF MO. For the calculation of ε_{HOMO} and E_T, the geometries of the molecules were determined through the optimization of the functional group (-OH part). The structure of the benzene ring was fixed throughout this work. The geometries determined in this way are exhibited in Fig. 1, together with the pictures of ε_{HOMO} and ΔE_T.

Discussion

Tris(1,10-phenanthroline)iron(III) is an one-electron oxidizing agent. Thus, the non-complementary oxidation reactions are expected to occur through two successive one-electron transfer reactions, as follows:

$$H_2A + Fe(phen)_3^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2A^{\dagger} + Fe(phen)_3^{2+}, \qquad (3)$$

$$H_2A^{\dagger} + Fe(phen)_3^{3+} \xrightarrow{k_2} Fe(phen)_3^{2+} + 2H^+ + A. \qquad (4)$$

Assuming the steady state conditions for the concentrations of $H_2A^{\dagger}$ species, the following rate equation can be derived:

$$-\,d[Fe(phen)_3^{3+}]/dt = \left\{1 + \frac{k_2[Fe(phen)_3^{3+}]}{k_{-1}[Fe(phen)_3^{2+}] + k_2[Fe(phen)_3^{3+}]}\right\} \times k_1[H_2A][Fe(phen)_3^{3+}]. \qquad (5)$$

When the condition of $k_2[Fe(phen)_3^{3+}] \gg k_{-1}[Fe(phen)_3^{2+}]$ is satisfied, Eq. 5 can be represented by the empirical rate law of Eq. 2 with relationship of $k_0=2\,k_1$. These conditions were fulfilled for the reactions of *o*- and *p*-benzenediols with tris(1,10-phenanthroline)iron(III) for at least 80% of a whole reaction, and for the reactions of *m*-benzenediol with tris(1,10-phenanthroline)iron(III) for about 20% of a whole reaction. In the reaction of *m*-benzenediol, the rate of reaction decreased with increasing the ratios of $[Fe(phen)_3^{2+}]_i/[Fe(phen)_3^{3+}]_i$, and the value of k_{-1}/k_2 was approximately 0.7. According to the Marcus theory[1] for the outer-sphere electron transfer reaction, the excess free energy of activation for a cross reaction (ΔG^{*}_{12}) varies with the standard free energy change (ΔG°_{12}) for the redox step, as shown in Eqs. 6 and 7:

$$\Delta G^{*}_{12} = \omega_{12} + \lambda_{12}(1+\Delta G^{\circ}_{12}/\lambda_{12})^2/4, \qquad (6)$$

$$\lambda_{12} = 2(\Delta G^{*}_{11} - \omega_{11} + \Delta G^{*}_{22} - \omega_{22}), \qquad (7)$$

where ΔG^{*}_{11} and ΔG^{*}_{22} are the activation free energies for the self-exchange electron-transfer reactions, and ω_{11} and ω_{22} represent the work terms involved in the same reactions; ω_{12} is the work term required to bring the reactants onto the activated complex. The work terms can be evaluated from Eq. 8:

$$\omega_{ij} = \frac{Z_1 Z_2 e^2}{D_s r_{ij}} \exp\,[-\kappa r_{ij}], \qquad (8)$$

where Z_1 and Z_2 are the formal charges of reactants, e is the electron charge, D_s is the static dielectric constant, r_{ij} is the distance of the closest approach of the reactants in the activated complex, and κ is the reciprocal Debye radius. According to the Marcus theory,[1] the parameter λ_{12} is equal to $\lambda_o+\lambda_i$, where λ_o is the solvent reorientation term and λ_i is the contribution term from the inner-sphere change in bond lengths and angles in the molecules. When λ_i is negligible, then λ_{12} is set to be λ_0, which is represented as Eq. 9:

$$\lambda_0 = \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{r_{12}}\right)\left(\frac{1}{n^2} - \frac{1}{D_s}\right)(\Delta e)^2, \qquad (9)$$

where r_1 and r_2 are the radii of the reactants, r_{12} is the distance between the reacting centers in the activated state and can be approximately set as (r_1+r_2), n is the refractive index of the medium, D_S the static dielectric constant, and Δe the charge transferred. By assuming $r_1=4.0\times10^{-10}$ m for *o*-, *m*-, and *p*-benzenediols[6,7] and $r_2=7.0\times10^{-10}$ m for tris(1,10-phenanthroline)iron(III),[8] $n=1.342$,[9] and $D_S=78.5$,[10] the value of λ_0 is calculated to be 80.8 kJ mol^{-1}. The work terms for the forward reaction of Eq. 3 are evaluated to be zero for ω_{12} and ω_{11}, and 0.08 kJ mol^{-1} for ω_{22} at an ionic strength of 1.0 mol dm^{-3} at 25 °C. The activation free energy ΔG^*_{12} is described as follows:

$$k_{12} = Z\exp\left[-\Delta G^*_{12}/RT\right], \tag{10}$$

where Z is the collision frequency in solution and is usually taken as 10^{11} at 25 °C. Thus, the ΔG^*_{12} for the forward reaction of Eq. 3 are determined by using the data in Table 1. By using the parameters obtained, the value of ΔG°_{12} can be evaluated by Eq. 6. The ΔG°_{12} allows the estimation of the standard redox potentials of the cation radicals of *o*-, *m*-, and *p*-benzenediols. By using $E^\circ(\mathrm{Fe(phen)_3}^{3+/2+})=1.06$ V,[11] the values of the standard reduction potentials of the cation radicals were estimated; these are shown in Table 2. The potentials of the radicals could be estimated without knowledge of the contributions of ΔG^*_{11}, ΔG^*_{22}, ω_{11}, and ω_{22}. The rate constant for the self-exchange reaction of tris(1,10-phenanthroline)iron(III) and -(II) has been reported to be larger than 3×10^7 dm^3 mol^{-1} s^{-1} at 25 °C.[12] Meisel[13] has reported that the observed self-exchange rate constants for a series of reactions between the organic radicals and the parent molecules fall in the range of 1×10^7 to 1×10^9 dm^3 mol^{-1} s^{-1}. If we adopt the values of 3×10^7 dm^3 mol^{-1} s^{-1} for k_{22} of Fe(phen)$_3{}^{3+/2+}$ and 1×10^7 dm^3 mol^{-1} s^{-1} for k_{11} of $\mathrm{H_2A^{\dagger}/H_2A}$, the activation free energies of ΔG^*_{22} and ΔG^*_{11} are evaluated to be 20 and 23 kJ mol^{-1} for Fe(phen)$_3{}^{3+/2+}$ and $\mathrm{H_2A^{\dagger}/H_2A}$ from Eq. 10, respectively.[14] This leads to the value of 86 kJ mol^{-1} for λ_{12}. Therefore, we can determine the values of $\mathrm{E^\circ(H_2A^{\dagger}/H_2A)}$ to be 1.39, 1.07, and 0.94 V in 0.11 mol dm^{-3} perchloric acid solution for *m*-, *o*-, and *p*-benzenediols, respectively. These values are in good agreement with the corresponding ones which are estimated without using ΔG^*_{11} and ΔG^*_{22} and neglecting λ_i (refer to Table 2). The values of $E^\circ(\mathrm{H_2A^{\dagger}/H_2A})$ increased slightly with increasing acidity in *m*- and *p*-benzenediols. This may indicate some contributions of Reaction 11, which involves a simultaneous transfer of an electron and a proton:

$$\mathrm{HA^{\cdot} + H^+ + e^- \rightleftharpoons H_2A.} \tag{11}$$

The Marcus theory[1] holds for a reaction which occurs adiabaticly by the outer-sphere electron transfer reaction, and thus, the activation entropy is expected to be close to zero. Although the collision frequency (Z) is generally assumed to be 10^{11} dm^3 mol^{-1} s^{-1} in solution, the pre-exponential factor deviates sometimes from the value, indicating some contribution of a non-adiabatic reaction. The activation enthalpy and entropy ΔH^* and ΔS^* can be determined by assuming $\kappa=1$ in Eyring's absolute rate equation:

$$k = \kappa\frac{\boldsymbol{k}T}{h}\exp\left[\Delta S^*/R\right]\exp\left[-\Delta H^*/RT\right], \tag{12}$$

where κ is the probability of the electron-transfer within the activated complex. The values of ΔH^* and ΔS^* were estimated by assuming $\kappa=1$; they are listed in Table 2 together with the other parameters.

It is of interest to interpret theoretically the order of the redox potentials of *o*-, *m*-, and *p*-benzenediols and to compare them to those estimated experimentally. Since the environment effect such as the solvent effect on the potentials is expected to be almost the same among these isomers, the differences of the genuine electronic properties must be related to the order of the redox potentials. According to the results in Fig. 1, both $\varepsilon_{\mathrm{HOMO}}$ and ΔE_{T} indicate that the ease for the oxidation is in the order of *m*-<*o*-<*p*-. This trend is well correlated with that obtained experimentally by the application of Marcus theory to the kinetic parameters. The order of these potentials is ascribed to the positional difference of the O–H group. To apply the orbital interaction scheme to this analysis, benzenediol is regarded as a system of phenol and O–H group. In this respect, the HOMO of benzenediols is mainly composed of the highest occupied MO of phenol (***homo***) and the pπ atomic orbital on the oxygen of the O–H group. Thus, $\varepsilon_{\mathrm{HOMO}}$ is determined by the extent of this orbital interaction. Examining the shape of ***homo*** in

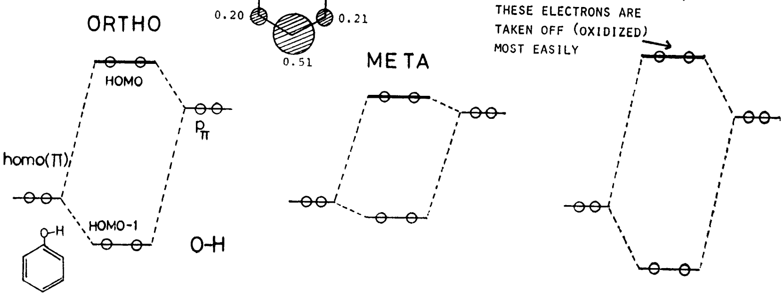


Fig. 2. Schematic sketch of the orbital interaction between homo of phenol and the pπ atomic orbital of the O–H group. The HOMO levels of benzenediols ($\varepsilon_{\mathrm{HOMO}}$) are determined by the extent of this orbital interaction. The degree of the interaction is ascribed to the coefficient attached to the atomic orbital of homo, the coefficient being shown by the absolute value in this figure.

Fig. 2, one may find that the *para* position has the largest coefficient (0.51), the *ortho* is of the second (0.33 or 0.34) and the *meta* is of the smallest one (0.21 or 0.20). Since the position with the large coefficient undergoes the large extent of the orbital interaction (the bigger energy splitting in Fig. 2), the order of the coefficients should be reflected in that of $\varepsilon_{\mathrm{HOMO}}$. This prediction is confirmed by the comparison of the values of $\varepsilon_{\mathrm{HOMO}}$ in Fig. 1. Thus, the order of the ease of oxidation may be interpreted in terms of the orbital interaction and the origin of the difference of $\varepsilon_{\mathrm{HOMO}}$ is basically the same as the *ortho*, *para orientation* for the nucleophilic substitution onto the benzene ring of phenol.

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