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## Electron Exchange and Electron Transfer of Semiquinones in Aqueous Solutions<sup>1a</sup>

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**Abstract:** Rate constants for self-exchange of electrons between semiquinone radical ions and their parent quinones were measured for four benzoquinone derivatives in aqueous solutions (containing 5 M 2-propanol and 1 M acetone at pH 7). This was accomplished by measuring the effect of the concentration of the quinone on the ESR line width of the semiquinone radical ion produced by in situ photolysis. The quinones studied were benzoquinone, 2,5- and 2,6-dimethylbenzoquinone, and duroquinone. The rate constants for the electron exchange for these couples were found to be in the range of  $0.5\text{--}2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . Electron transfer from one semiquinone to another quinone in this group of benzoquinone derivatives was measured using kinetic spectrophotometry and pulse radiolysis. Since one-electron reduction potentials for all of these quinone/semiquinone couples are known from pulse radiolysis determination of the equilibria, electron transfer rates can be predicted using the Marcus theory from rates of the self-exchange reactions. The calculated rates thus obtained are in good agreement with the experimentally measured rate constants. Reaction radii could be estimated and further correlations between the rates of electron transfer and the free energy changes were checked.

Electron transfer reactions have long been the subject of both experimental and theoretical studies.<sup>2</sup> The experimental results for these reactions are commonly discussed in terms of the Marcus<sup>3</sup> and Hush<sup>4</sup> theory, mainly because of its representation in terms of easily measurable parameters. The theory predicts the existence of a correlation between the free energy of an electron transfer reaction and the rate of this reaction as well as a correlation between the rates of the self-exchange reactions and the rates of cross electron transfer reactions. Although both these predictions have been exhaustively checked for metal ion complexes,<sup>5</sup> the available data for organic systems is rather scarce. A few cases have been checked for the predictions of the Marcus theory,<sup>6-9</sup> but these were confined mainly to organic radicals in aprotic solvents in which the radicals are very long lived. Recent studies, however, have demonstrated that electron transfer equilibria can be measured

even for relatively short-lived radicals in aqueous solutions,<sup>10-13</sup> thus providing the missing free energy of the reaction necessary for these correlations. Indeed it was recently shown that the rate constants for the electron transfer reaction in some systems such as semiquinones, nitroaromatic radical ions, and the superoxide radical ion correlate well with the corresponding free energy of the reaction,<sup>14</sup> as predicted by the Marcus theory. It was estimated in that study that the rate constant for the electron exchange reaction for this type of compounds should be approximately  $5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  in aqueous solution. One aim of this study was to check this estimate.

Electron exchange in such aromatic systems presumably represents the simplest of electron transfer reactions, since no chemical bonds are broken or formed in the transfer and furthermore the changes in bond lengths and angles are rather small. Thus the major contribution to the energy of activation

in this case is the reorientation energy of the solvent molecules around the participating reactants. The pioneering work of Ward and Weissman<sup>15</sup> on exchange rates which used ESR line broadening eliminated the necessity of using isotopic techniques in measuring this zero net reaction. Following their work, numerous studies have been undertaken in order to elucidate the effects of the solvent, temperature, viscosity, charge on the participating particles, and the counterions.<sup>6-9,16-25</sup> Again most of these studies involved aprotic solvents and the interpretation was frequently complicated by the presence of counterions either generated by the chemical method used for production of the radicals or present as a supporting electrolyte in the electrochemical generating technique. When the system was free of this complication, the rate of exchange was often found to be near the diffusion-controlled limit.

In this study, we have measured the rates of electron exchange between benzoquinone (BQ), 2,5- and 2,6-dimethylbenzoquinones (2,5- and 2,6-DMBQ), and the tetramethyl derivative duroquinone (DQ), and their corresponding semiquinone radical ions. This was accomplished by the in situ photolysis ESR technique. The rates of electron transfer from one semiquinone to another quinone of the above mentioned group were measured using the kinetic spectroscopy pulse radiolysis technique. Previous studies have shown that an electron transfer occurs between the semiquinone of 9,10-anthraquinone-2-sulfonate and DQ,<sup>12</sup> but such a transfer has never been observed among benzoquinone derivatives.

### Experimental Section

For measurements of the self-exchange rates we used the in situ photolysis ESR technique. Details of the instrumental setup for these experiments were described previously.<sup>26</sup> Flow rates in these experiments were kept at 15–20 ml/min and no effect of the flow rate on the intensity or line width of the semiquinones was observed in this region. At such flow rates the residence time of the solution in the cell (about 20 ms) is much longer than the half-life of the exchange reaction (<10  $\mu$ s). At the lowest concentrations of quinone used for these measurements the lines of the 2-propanol radical ((CH<sub>3</sub>)<sub>2</sub>CHOH) could be observed at a very low intensity. The presence of this radical could not affect the line width determinations however.

All measurements of the self-exchange rates were taken near the "slow-exchange limit".<sup>15</sup> The microwave power and modulation amplitude were set at levels such that a variation in either produced no significant effect on the observed line width at low concentration of quinone. The line width,  $\Delta H$ , defined as the peak-to-peak separation in the first derivative spectrum could be measured directly and accurately for benzosemiquinone and durosemiquinone. However, for each of the two dimethylbenzosemiquinones some overlap of lines occurred when the lines were broadened. For these cases the width was calculated using computer simulation of the spectra. The differences in line width for different lines of the same radical were taken into account in both the simulation and the conversion of line width to life times. As a result of changes in light absorption by the solution with changes in the concentration of the quinones we found it impractical to use line intensities rather than line width for such measurements.

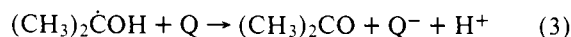
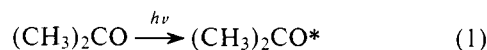
Rates of electron transfer from one semiquinone to another quinone were measured using the pulse radiolysis technique. Pulses of about 1  $\mu$ s length of 2.8 MeV electrons from a Van de Graaff accelerator produced a total of 1–2  $\mu$ M of radicals. The computer-controlled pulse radiolysis set up<sup>27</sup> as well as the rest of the experimental details<sup>10</sup> were described previously. Kinetic data was stored on magnetic tapes and analyzed later on a 9830A Hewlett-Packard calculator. All values given for rate constants were determined by least mean square procedures. Optical spectra of the semiquinones were analyzed using the spectral analysis method developed for this calculator.<sup>28</sup>

The materials used in this study were all of highest purity commercially available and were used without further purification. Water was distilled and the vapor passed with oxygen through a silica oven. All solutions contained 5 M 2-propanol and 1 M acetone in order to facilitate solubility of the quinones and were buffered at pH 7 with

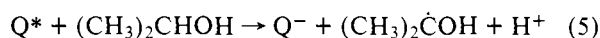
5 mM phosphate. The following procedure was used for all experiments: acetone/2-propanol mixtures and buffered water, at the appropriate proportions, were flushed with prepurified nitrogen for 15 min. The quinones were then dissolved in the deaerated acetone/2-propanol mixture and the deaerated water was added. The resultant solutions were then immediately irradiated or photolyzed. Special care was taken to avoid exposure of the solutions to light before irradiation. A cutoff filter at 360 nm (Corning 0-51) was inserted between the analyzing light source and the solution during the pulse radiolysis experiments to minimize photolysis.

### Results

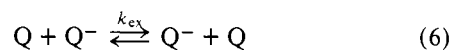
**Electron Exchange Rates.** The semiquinone radical anions were produced in our experiments either from initial excitation of the acetone



or by direct excitation of the quinone, which then is reduced by the alcohol (reactions 4, 5, 3)



The ESR spectra of the semiquinones at low concentration of quinone are shown in Figure 1a. The hyperfine constants are very similar to those previously measured in alkaline alcoholic solutions.<sup>29</sup> The effect of the concentration of the quinone on the line width is illustrated by Figure 1b. Shown here is a portion of the spectrum of 2,6-DMBQ<sup>-</sup> at  $8 \times 10^{-3}$  M of the quinone, where the line width is more than twice that at low concentration. Since the concentration of the radical (several  $\mu$ M) is far below the range where Heisenberg spin exchange can play any role and since the spin exchange rate should not depend on the concentration of the quinone, the broadening of the lines is attributed to the electron exchange reaction:

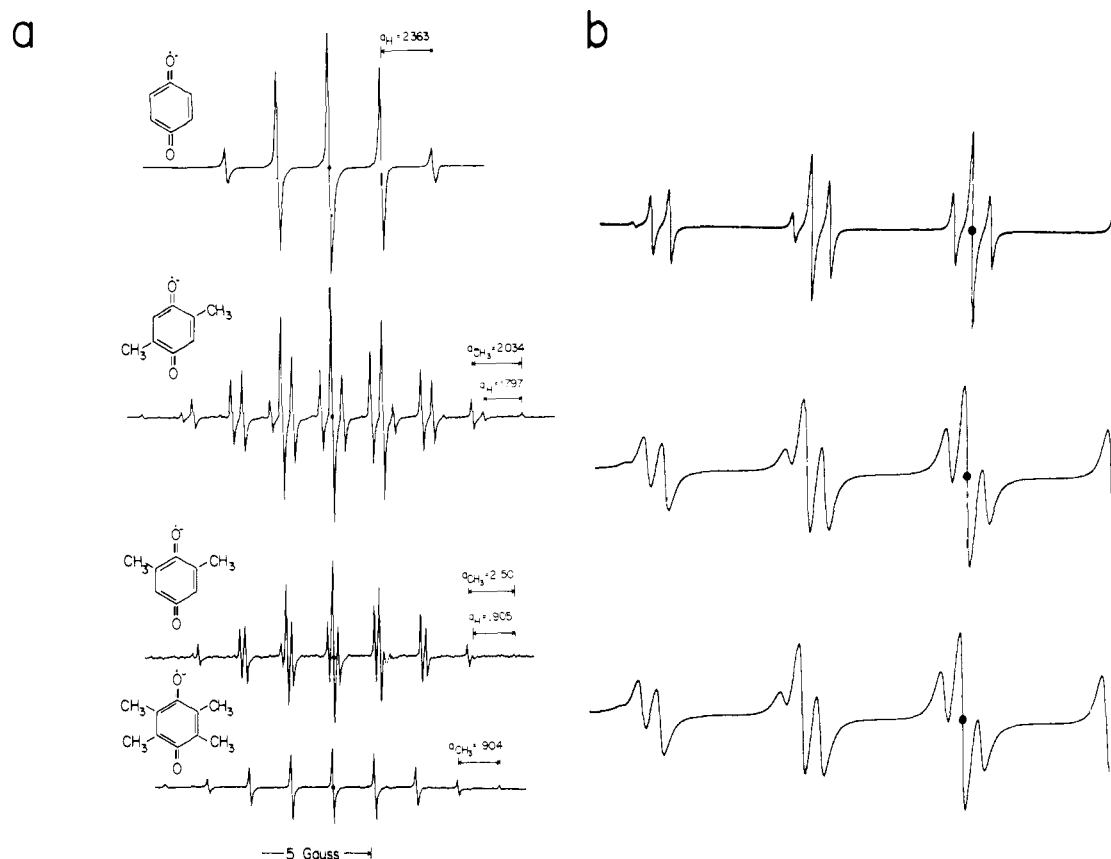


Following Ward and Weissman,<sup>15</sup> in the low exchange limit  $k_{\text{ex}}$  is related to the line width by

$$\Delta H = \Delta H_0 + \frac{k_{\text{ex}}[\text{Q}]}{\sqrt{3}\pi(2.83 \times 10^6)} \left[ 1 - \frac{g_i}{\sum_i g_i} \right] \quad (I)$$

in which the last bracketed term is the intensity correction term, where  $g_i$  is the statistical line intensity of the  $i$ th line. The dependence of  $\Delta H$  on the concentration of the quinone is shown in Figure 2. The linearity represented by eq I is obeyed rather well for all of these semiquinones. However, a pronounced deviation from the expected linearity is observed at a concentration of DQ higher than 5 mM for DQ<sup>-</sup>. The reason for this deviation is as yet unclear to us. One possibility is the formation of a "quinhydrone" type of complex between the semiquinone and the parent quinone. The rate of exchange for this case was derived from the results obtained at concentrations lower than where this departure from linearity occurred and for the same reason no higher concentrations were used in the other experiments. The upper part of Table I summarizes the rate constants for the exchange reaction.

**Electron Transfer Rates.** Although the optical spectra of the four benzosemiquinone derivatives are quite similar,<sup>11</sup> electron transfer could be observed when mixtures of two quinones were pulse irradiated. The computer processed kinetic curves for two such cases are displayed in Figure 3. In these experiments all



**Figure 1.** First derivative ESR spectra of the semiquinones studied: (a) spectra at low quinone concentrations ( $[Q] = 5 \times 10^{-4}$  M); (b) partial spectrum of 2,6-DMBQ $^-$ ; upper spectrum at  $[2,6\text{-DMBQ}] = 0.5 \times 10^{-3}$  M; middle spectrum at  $[2,6\text{-DMBQ}] = 8 \times 10^{-3}$  M, showing the line broadening. The simulated lower curve was calculated with a line width of 135 mG. All solutions contain 5 M 2-propanol, 1 M acetone, and  $5 \times 10^{-3}$  M phosphate buffer at pH 7. Dashed lines represent signals of residual 2-propanol radical.

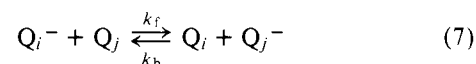
**Table I.** Rates of Electron Exchange and Electron Transfer in Benzosemiquinones

Quinone	Electron Exchange		Electron Transfer		
	$k_{ex}, \text{M}^{-1} \text{s}^{-1}$	$E_7^{\cdot}, ^a \text{V vs. NHE}$	$k_b, ^c \text{M}^{-1} \text{s}^{-1}$		$K_{eq} ^d$
BQ	$(6.2 \pm 0.5) \times 10^7$	0.099			
2,5-DMBQ	$(5.5 \pm 0.5) \times 10^7$	-0.065			
2,6-DMBQ	$(1.7 \pm 0.2) \times 10^8$	-0.080			
DQ	$(2.0 \pm 0.2) \times 10^8$	-0.235			
			$k_f, ^b \text{M}^{-1} \text{s}^{-1}$		
Transfer reaction	Exptl	Calcd	Exptl	Calcd	$K_{eq} ^d$
2,5-DMBQ $^-$ + BQ	$(6.5 \pm 0.3) \times 10^8$	$9.0 \times 10^8$	$9.7 \times 10^5$	$1.3 \times 10^6$	$6.7 \times 10^2$
2,6-DMBQ $^-$ + BQ	$(1.0 \pm 0.1) \times 10^9$	$1.6 \times 10^9$	$8.3 \times 10^5$	$1.3 \times 10^6$	$1.2 \times 10^3$
DQ $^-$ + BQ	$(1.1 \pm 0.05) \times 10^9$	$4.4 \times 10^9$	$1.9 \times 10^3$	$7.7 \times 10^3$	$5.7 \times 10^5$
DQ $^-$ + 2,5-DMBQ	$(1.0 \pm 0.1) \times 10^9$	$1.5 \times 10^9$	$1.2 \times 10^6$	$1.8 \times 10^6$	$8.5 \times 10^2$
DQ $^-$ + 2,6-DMBQ	$(9.6 \pm 1) \times 10^8$	$1.9 \times 10^9$	$2.0 \times 10^6$	$4.0 \times 10^6$	$4.7 \times 10^2$
2,5-DMBQ $^-$ + 2,6-DMBQ		$6.7 \times 10^7$		$1.4 \times 10^8$	0.5

<sup>a</sup>  $E_7^{\cdot}$  is the standard reduction potential at pH 7. <sup>b</sup> Rate constant for the forward reaction. <sup>c</sup> Rate constant for the back reaction. <sup>d</sup> Equilibrium constant.

the reducing radicals ( $e_{aq}^-$  and  $\dot{H}$ ) as well as the  $\dot{O}H$  radicals are converted to 2-propanol radicals. The latter radicals then transfer electrons to the quinones through reaction 3. All these reactions are complete at the end of the pulse. Since the rate constants for reaction 3 with the various quinones are approximately the same,<sup>11</sup> the semiquinone observed at the end of the pulse will be that which corresponds to the quinone which is present in excess (DQ in Figure 3a and 2,5-DMBQ in Figure

3b). However, the initial semiquinone is seen in Figure 3 to transfer its extra electron to the other quinone (BQ in this figure) if the reduction potential of the latter is higher.



The relaxation of the initial conditions to the thermodynamically more favorable situation, i.e., the electron transfer re-

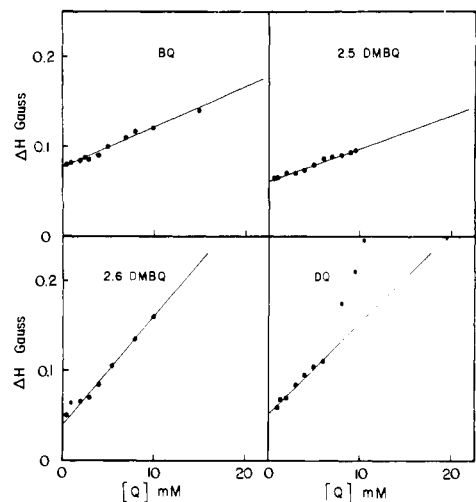


Figure 2. The dependence of the line width on the concentration of the quinone.

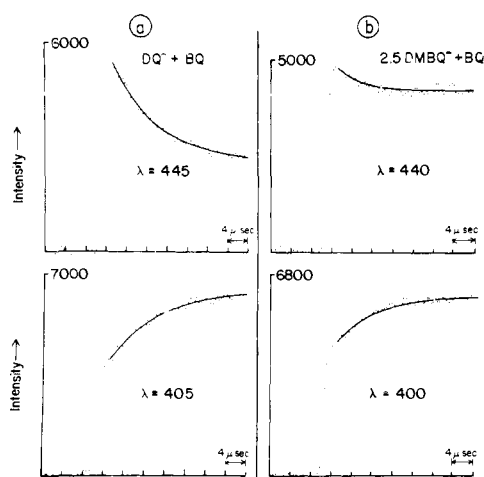


Figure 3. Electron transfer from one semiquinone to another quinone: (a)  $DQ^{\cdot-} + BQ \rightarrow DQ + BQ^{\cdot-}$ ;  $[DQ] = 2 \times 10^{-3}$ ,  $[BQ] = 1 \times 10^{-4}$  M; (b)  $2,5\text{-DMBQ}^{\cdot-} + BQ \rightarrow 2,5\text{-DMBQ} + BQ^{\cdot-}$ ;  $[2,5\text{-DMBQ}] = 3 \times 10^{-3}$ ,  $[BQ] = 2 \times 10^{-4}$  M. The solid line represents the calculated curve giving the least-squares deviation.

action 7, could be followed by both the decay of  $Q_i^{\cdot-}$  and the buildup of  $Q_j^{\cdot-}$ . In Figure 3 are shown the decays of  $DQ^{\cdot-}$  and  $2,5\text{-DMBQ}^{\cdot-}$  at wavelengths where  $\epsilon_i > \epsilon_j$  along with the formation of  $BQ^{\cdot-}$  at wavelengths where  $\epsilon_j > \epsilon_i$ . Both the decay and the buildup have the same half-lives. The spectra obtained immediately the end of the pulse and those obtained after reaction 7 is completed are shown in Figure 4; they indicate that the reaction observed is indeed a pure electron transfer reaction. The dependence of the rates of this reaction on the concentration of the acceptor quinone is in line with this assumption. The rates were found to follow a pseudo-first-order rate law and the observed first-order rate constant was linearly dependent on the concentration of the acceptor quinone. This dependence is shown in Figure 5 for five out of the six possible electron transfer reactions in this group of four quinones. It was not possible to measure the electron transfer reaction between the two dimethyl derivatives because of their similarity. For this couple the reduction potentials are similar (see Table I), while the ratio of the rate constants for reaction 3 is about one.<sup>11</sup> These facts mean that the initial distribution of the radicals is not far from the equilibrium distribution. When the great similarity in the spectra of both semiquinones is also taken into account it is not surprising that reaction 7 could

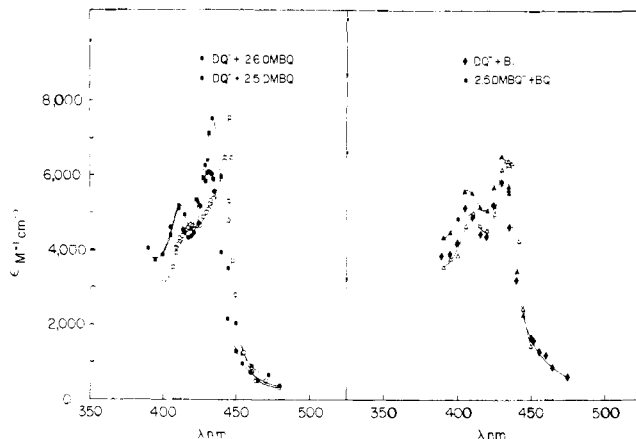


Figure 4. Optical spectra of some semiquinone systems before and after electron transfer. Open symbols taken at  $t = 0$ , solid symbols at  $t = 30 \mu\text{s}$ . Solid lines are the spectra of the corresponding semiquinone taken alone (see ref 11). Concentrations of the donor quinone were  $3 \times 10^{-3}$  M and of the acceptor quinone  $1 \times 10^{-4}$  M.

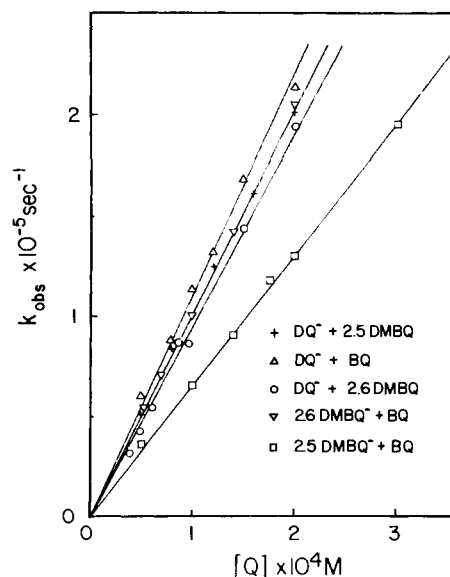


Figure 5. The dependence of the observed rate constants for the transfer reactions on the concentration of the acceptor quinone.

hardly be observed by this technique. The rates of the electron transfer reactions are summarized in the lower part of Table I.

## Discussion

The rates of the exchange reactions and the reduction potentials of the four quinones studied are given in Table I. The values for the one-electron reduction potential were calculated from the two-electron reduction potentials and the semiquinone formation constants as described in ref 10. It is obvious that, in this series of structurally similar and symmetric semiquinones, the reduction potential is of minor importance in determining the rate of the electron exchange. A correlation has been found, however, between half-wave potentials and rates of exchange for a series of phenothiazine radical cations and for some nitrobenzene and benzonitrile radical anions.<sup>7</sup> It seems, therefore, that in the latter systems the half-wave potentials reflect geometrical changes which occur on the transfer of an electron to the parent molecule. In the quinone/semiquinone systems no such change occurs and thus no effect of the reduction potentials is expected.

According to the Marcus theory, the main contribution to the free energy of activation in such cases will be the free energy of reorientation of the solvent molecules. The increase in the rate of exchange in the DQ system by a factor of three as compared to BQ might result from a decrease in the free energy of solvation of  $DQ^-$ . The methyl groups in this semiquinone, and to lesser extent in 2,6-dimethylbenzosemiquinone, seem to block the free approach of water molecules to the main site of solvation, namely the oxygens. All of the exchange rates measured are more than an order of magnitude smaller than the diffusion limit in aqueous solutions. These rates are very similar to the value previously estimated for such an exchange.<sup>14</sup> The rate of exchange of  $BQ/BQ^-$  in DMF was found to be  $3.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , but addition of 10% water to this solvent dropped that value to  $5.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>25</sup> Since this exchange rate is practically the same as the value found in the present study, one infers that 10% water in DMF is enough to produce most of the solvation effect. The rate of exchange of  $DQ/DQ^-$  in DMF is surprisingly lower than in our aqueous solutions.<sup>25</sup>

A more quantitative check to the applicability of the Marcus theory to these systems can be obtained by comparing the rates of the electron transfer between the different systems to those predicted by the theory from the rates of exchanges. The Marcus relation for the rate constant of the electron transfer from semiquinone  $i$  to  $j$ ,  $k_{ij}$ , is given by:

$$k_{ij} = (k_{ii}k_{jj}K_{ij}f)^{1/2} \quad (\text{II})$$

where  $k_{ii}$  and  $k_{jj}$  are the rate constants of the corresponding self-exchanges and  $K_{ij}$  is the equilibrium constant for the transfer reaction. The parameter  $f$  is given by:

$$\ln(f) = (\ln K_{ij})^2 / 4 \ln \left( \frac{k_{ii}k_{jj}}{Z^2} \right) \quad (\text{III})$$

in which  $Z$ , the frequency factor is taken to be  $10^{11} \text{ M}^{-1} \text{ s}^{-1}$ . The observed rate of the electron transfer should, however, be damped by the diffusion limit using the reciprocal relation

$$1/k_{\text{obsd}} = (1/k_{\text{act}}) + (1/k_{\text{diff}}) \quad (\text{IV})$$

where  $k_{\text{act}}$  is the activation-controlled rate constant ( $k_{ij}$  in equation II) and  $k_{\text{diff}}$  is the diffusion-controlled rate constant. The calculated rate constants are given in Table I. The equilibrium constants were calculated from the reduction potentials and  $k_{\text{diff}}$  was estimated from the combined Einstein-Smoluchowski equation

$$k_{\text{diff}} = (8RT/3000)\eta \quad (\text{V})$$

Considering the approximations involved and the uncertainty in  $k_{\text{diff}}$  and  $Z$  the fit between the calculated rate constants and the observed ones is very satisfactory. Although the rate of transfer between the two dimethyl derivatives could not be measured, an estimate of this rate is given in Table I.

Under the above mentioned assumptions, where the major contribution to the free energy of activation,  $\Delta G^*$ , is the solvent reorientation term  $\lambda_0$ , it is easy to show that

$$\Delta G^* = (1/4)\lambda_0(1 + \Delta G^\circ/\lambda_0)^2 \quad (\text{VI})$$

where  $\Delta G^\circ$  is the free energy of the reaction and  $\lambda_0$  is given by

$$\lambda_0 = \left( \frac{1}{2r_a} + \frac{1}{2r_b} - \frac{1}{r_{ab}} \right) \left( \frac{1}{D_o} - \frac{1}{D_s} \right) (\Delta Z e^2) \quad (\text{VII})$$

The quantities  $D_o$  and  $D_s$  are the optical ( $D_o = 1.78$ ) and static ( $D_s = 78$ ) dielectric constants,  $r_a$ ,  $r_b$ ,  $r_{ab}$  are the reaction radii of the reactants and the activated complex, and we assume that  $r_a = r_b = 1/2 r_{ab}$ . The energy of reorientation can thus be calculated from the experimental rates of the exchanges using eq IV-VI and

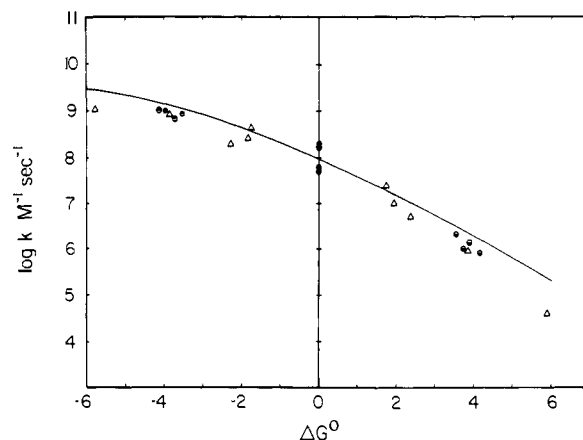


Figure 6. Correlation between the rate of electron transfer and the free energy of the reaction; ●, ⊙, ●, electron transfer between semiquinones and quinones, forward, back, and self-exchange reactions, respectively; Δ, electron transfer between  $O_2^-$  and quinones.

$$k_{\text{act}} = Z \exp(-\Delta G^*/RT) \quad (\text{VIII})$$

We find  $\lambda_0 = 17.8 \text{ kcal/mol}$  for the self-exchange reaction of BQ and  $\lambda_0 = 14.6 \text{ kcal/mol}$  for DQ. The corresponding values of the reaction radii calculated from eq VII are  $r = 5.1$  and  $6.2 \text{ \AA}$ , respectively. These radii might be compared with the molecular radii calculated from the molar volume using the equation<sup>30</sup>

$$(4/3)\pi r^3 = M/\rho N_0 \quad (\text{IX})$$

The values so calculated ( $r = 3.2$  and  $4.8 \text{ \AA}$  for BQ and DQ, respectively) leave about one molecule of solvation layer around each of the reactants during the transfer of the electron.

One can now try to check the correlation between the equilibrium constants and the rate constants for this series of similar quinone/semiquinone systems. Given in Figure 6 is a plot of rate constant against  $\Delta G^\circ$ . Also included are results (taken from ref 14) for the electron transfer reaction between the superoxide radical ion  $O_2^-$  and the same quinones. The solid line in this figure is the calculated correlation obtained using eq IV-VIII with an average value of  $r = 5.6 \text{ \AA}$  as obtained above. The calculated line seems to fit the experimental results quite well. Since the results for the transfer from  $O_2^-$  fall on the same line as for the semiquinones, it might be expected that the rate of self-exchange for the  $O_2/O_2^-$  system is comparable to those for the quinone systems.

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## Transmission of Substituent Effects. Generalization of the Ellipsoidal Cavity Field Effect Model<sup>1</sup>

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**Abstract:** The ellipsoidal cavity field effect model of Westheimer and Kirkwood for transmission of polar substituent effects is extended to remove the constraint of interacting site-focus coincidence. This allows more rational specification of the geometry of the cavity, and hence of the effective dielectric, based upon physically realistic intermolecular (solute-solvent) distances. Significant improvements in the power of the model are noted upon application to several experimentally studied systems, both in terms of the quality of relative reactivity predictions and in internal self-consistency.

One crucial constraint imposed on the ellipsoidal cavity field effect model<sup>2</sup> for transmission of polar substituent effects upon reactivity seriously hampers evaluation of the model's true merit.<sup>3</sup> This involves location of the interacting sites at the foci of the ellipsoid of revolution which, together with specification of the cavity volume or "imbedding" factor, completely determines the size and shape of the cavity, often completely unrealistically. That any doubt presently exists concerning the superiority of the field over the classical inductive (bond falloff) model<sup>8</sup> is likely due to this condition and how it can in fact impede operational improvement of known deficient spherical cavity representations.

What is suggested here is that more directly relevant geometrical information be used in determination of the cavity dimensions. For molecules having axial symmetry with interacting sites located at terminal molecular positions along the axis, as is often the case, at least upon intramolecular rotational averaging, the "imbedding" distance of these sites is usefully retained. It is, however, to be a reasonable physical distance, rather than an empirical value generated from other closely related systems.<sup>13</sup> If the partial molar volume is well known and relatable to cavity volume, it should of course be used. If not, one other internal site to cavity-edge distance, preferably involving a framework locus, would uniquely define the cavity dimensions.

Such physically reasonable ellipsoidal cavities do not conform to the requirement of focus-interacting site coincidence. In fact, for most molecules of interest, particularly those with rigid framework where precise knowledge of geometry is possible, the interacting sites are often predicted to lie significantly away from the foci. To accommodate such cases, partial rederivation of the Westheimer and Kirkwood (WK) electrostatic work equations are necessary and are as follows.

Laplace's equation in prolate spheroidal coordinates for an axially symmetric potential,  $\psi$ , is

$$\frac{\partial}{\partial \lambda} (\lambda^2 - 1) \frac{\partial \psi}{\partial \lambda} + \frac{\partial}{\partial \mu} (1 - \mu^2) \frac{\partial \psi}{\partial \mu} = 0 \quad (1)$$

where  $\lambda = (r_1 + r_2)/R$ ,  $\mu = (r_1 - r_2)/R$ ,  $r_1$  and  $r_2$  are the distances of a point from the ellipsoid foci and  $R$  is the inter-focal distance. As before,<sup>2</sup> the potential inside and outside the cavity fulfilling eq 1 are

$$\psi_{in} = D_i^{-1} \sum_{\text{charges } k} \frac{e_k}{|r - r_k|} + \sum_{n=0}^{\infty} B_n P_n(\mu) P_n(\lambda) \quad (2)$$

$$\psi_{ex} = \sum_{n=0}^{\infty} A_n P_n(\mu) Q_n(\lambda) \quad (3)$$

and the boundary conditions are

$$\psi_{in}(\lambda_0, \mu) = \psi_{ex}(\lambda_0, \mu) \quad (4)$$

$$D_i \left( \frac{\partial \psi_{in}}{\partial \lambda} \right)_{\lambda=\lambda_0} = D_s \left( \frac{\partial \psi_{ex}}{\partial \lambda} \right)_{\lambda=\lambda_0}$$

where  $D_i$  and  $D_s$  are the dielectric constants inside and outside (solvent) of the cavity, both regions considered continuous (structureless),  $\lambda_0$  defines the boundary ellipsoid with  $\mu$  ( $1 \geq \mu \geq -1$ ), and  $P_n$  and  $Q_n$  are, respectively, the  $n$ th order Legendre polynomials of the first and second kind.

It is at this point that the WK derivation is generalized. To match the boundary conditions,  $|r - r_k|^{-1}$  is expanded by the generalized Neumann relationship,<sup>15</sup> valid for  $e_k$  located anywhere on the major axis,<sup>16</sup>

$$|r - r_k|^{-1} = R^{-1} \sum_{n=0}^{\infty} 2(2n + 1) P_n(\lambda_k) P_n(\mu_k) Q_n(\lambda) P_n(\mu) \quad (5)$$

Following solution for  $B_n$ , as in ref 2, the difference in electrostatic work for the compared processes may be computed.

For interaction of two poles located symmetrically away from the foci, i.e., in symmetric dibasic acid ionizations,<sup>18</sup>

$$\Delta W = 2.303kT \Delta pK = e^2/\rho D_c \quad (6)$$

$$D_i/D_c = \left\{ 1 + 2\xi[(D_i/D_s) - 1] \sum_{n=0}^{\infty} \frac{P_n^2(\xi) U_n}{1 - (D_i/D_s) C_n} \right\} \quad (7)$$