Reduction Potentials and Kinetics of Electron Transfer Reactions of Phenylthiyl Radicals: Comparisons with Phenoxyl Radicals¹

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The reduction potentials relative to the standard hydrogen electrode (SHE) for a number of para-substituted phenylthiyl radicals ($E^{\circ}(p-XC_{6}H_{4}S^{-})$) have been derived from pulse radiolytic studies of electron transfer equilibria which compare their values to those of radicals of known reduction potentials. A ladder combining the reduction potentials for both phenylthiyl and phenoxyl radicals has been established. These reduction potentials have been shown to be self-consistent and are intermediate between those of p-benzosemiquinone radical anion at 0.02 V and phenoxyl radical at 0.79 V. The reduction potential decreases as the electron donating power of the para substituent rises. The substituent effect is, however, much weaker for the phenylthiyl radicals than for their oxygen analogs. These observations demonstrate that the electronic interaction between the sulfur atoms and the aromatic ring system is much less than that which occurs with oxygen atoms. Examination of the rates of electron transfer in terms of the Marcus theory indicates that the reorganization energies of both p-XC₆H₄O[•] and p-XC₆H₄S[•] radicals are similarly affected by H, CH₃, and CH_3O substitution. However, the reorganization energies increase substantially for H_2N and O^- para substituents with the effect being much less for the p-XC₆H₄S[•] radicals than for the p-XC₆H₄O[•] radicals. These observations are in accord with structural information from spectroscopic and theoretical studies of the radicals which show that in the latter system the substituent groups interact strongly with the aromatic π system.

Introduction

Phenoxyl radicals are important intermediates in biological systems and in the chemistry of antioxidants, and for that reason have been studied extensively. Their ESR² and resonance Raman spectra³ have been investigated, and theoretical studies of their electronic structures⁴ have been reported. Also the effects of various substituents on their redox potentials and kinetics of reaction have been examined.^{5–9} A comparison of the properties of phenylthiyl radicals with those of their phenoxyl counterparts is of particular interest to give some insight into the effects of replacing oxygen with sulfur. The objective of the present investigation was to examine the effects of para substitution on the reduction potentials of phenylthiyl radicals and to compare the kinetics of their electron transfer reactions with those of phenoxyl radicals.

We point out here that, because of line broadening by the sulfur, ESR data on phenylthiyl radicals are not available. As a result, there is very little information on the delocalization of the unpaired spin in these radicals, so that redox information becomes particularly important. In a recent paper¹⁰ a resonance Raman study of the unsubstituted phenylthiyl radical was presented. Analysis of the vibrational spectra showed that the CS bond has much less double bond character than the CO bond in phenoxyl radical. The Raman studies indicate that the unpaired electron in aromatic thiyl radicals resides primarily on the sulfur atom and that the interaction of the free radical center with the ring orbitals is much less than in the case of the phenoxyl radical. *Ab initio* calculations¹⁰ support this conclu-

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sion. Localization of the unpaired electron on sulfur also causes significant differences in the kinetics of reaction of the two types of radicals and is expected to be reflected in the reduction potentials.

Methods

The radicals were produced in aqueous solution by pulse radiolysis and observed by their characteristic optical absorptions. The pulse radiolysis apparatus and methods used for the measurement of time-resolved optical spectra were as in refs 11 and 12. The electron transfer reactions between electron acceptor radicals and electron donor anions, e.g.,

$$C_6H_5O^{\bullet} + C_6H_5S^{-} \underset{k_r}{\overset{k_f}{\leftrightarrow}} C_6H_5O^{-} + C_6H_5S^{\bullet} \qquad (1/-1)$$

were followed by kinetic spectroscopy at pH's in the range 11-13.5. Concentrations were adjusted so that equilibrium was reached before significant radical decay occurred. Rates for approach to equilibrium were analyzed by a computer program developed in house or by the ORIGIN program.¹³ Rate constants for the forward and reverse reactions were obtained from the usual standard analyses.^{5,6}

The phenylthiyl or phenoxyl radicals were produced at pH 11–13.5 by oxidizing thiophenolate or phenolate ions with azide radicals formed by the reaction of OH• radicals with 0.05–0.1 M N₃⁻. The rate constants for oxidation of these anions by azide are in the region of 4×10^9 M⁻¹ s⁻¹ ^{12,14,15} so that the production of the phenoxyl or phenylthiyl radicals is complete $\sim 0.2 \times 10^{-6}$ s after the pulse. As in ref 14 thiyl radicals were prepared in acidic solutions by abstraction of the SH hydrogen

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TABLE 1: Data for
$$\mathbf{A}^{\bullet} + \mathbf{D}^{-} \stackrel{\sim_{\mathbf{f}}^{\bullet}}{\rightleftharpoons} \mathbf{A}^{-} + \mathbf{D}^{\bullet}$$
 Electron Transfers

						<i>K</i> ₃	
A•	D^{-}	$\lambda_{ ext{A}}{}^a$	$\lambda_{\mathrm{D}}{}^a$	$k_{ m f}{}^b$	$k_{\rm r}{}^b$	$K_{ m kin}$	Kabs
PhO ⁻	PhS ⁻	400	460	14.5	0.29	50	52
PhO ⁻	p-BrPhS ⁻	400	510	17.4	0.74	24	31
<i>p</i> -MePhO [−]	<i>p</i> -MePhS ⁻	406	500	6.4	1.1	5.9	4.4
<i>p</i> -MeOPhS ⁻	<i>p</i> -MeOPhO ⁻	530	415	4.6	1.6	2.9	2.5
$p-NH_2PhS^-$	$p-NH_2PhO^-$	600	435	2.8	0.035	80	
$p-(O^{-})PhS^{-}$	$p-(O^{-})PhO^{-}$	595	427	0.039	$(0.00007)^{c}$		540
$p-NH_2PhS^-$	TMPD	520	360	6.8	0.25	27	36
$p-NH_2PhO^-$	$p-(O^{-})PhS^{-}$	450	590	0.29	0.032	9.0	9.7
RES	$p-NH_2PhS^-$	440	600	1.8	0.03	60	
<i>p</i> -MePhO ⁻	RES	385, 400	440	7.1	0.0027	2630	2270
p-MeOPhO ⁻	RES	330, 400	440				6.8
TMPD	p-NH ₂ PhO ⁻	520	435	1.3	0.34	3.7	3.7

^{*a*} Wavelengths at which equilibria studied. In nm. ^{*b*} Units are 10^8 M⁻¹ s⁻¹. ^{*c*} Calculated from k_f and K_{abs} .

atom from the p-XC₆H₄SH compound with acetone ketyl radical (1-hydroxymethylethyl radical). The ketyl radical was produced by OH• abstraction of H from 1 M 2-propanol.^{16,17}

All solutions were prepared with water from a Millipore Milli-Q system and purged with nitrous oxide. Where necessary, they were buffered with borate or phosphate and the pH's were adjusted with KOH or $HCIO_4$. The substituted phenyl thiols were the purest available from Sigma or Aldrich. Resorcinol (RES) was from Fluka and tetramethylenephenylenediamine (TMPD) was from Aldrich. Absorption spectra were taken on a Hewlett-Packard 8452A diode array spectrophotometer.

Results

pK_a's of *p*-**HOC**₆**H**₄**SH** and **H**₃**NC**₆**H**₄**SH**⁺. The *pK*_a's of *p*-HOC₆H₄SH and H₃**NC**₆H₄SH⁺ were determined from the pH dependences of their absorption spectra. The method was similar to that used in the case of *p*-HSC₆H₄SH in ref 14. The *pK*_a's for dissociation of the SH and OH protons in *p*-HOC₆H₄-SH are, respectively, 7.0 and 10.1. Those of the NH₃ and SH protons in H₃NC₆H₄SH⁺ are 4.0 and 7.1.

Absorption Spectra of the Radicals. As previously observed for C₆H₅S• and *p*-HSC₆H₄S•,^{10,14} the para-substituted phenylthiyl radicals exhibited two absorption peaks in the region between 300 and 700 nm. Extinction coefficients were determined so that the concentrations of the radicals at equilibrium could be calculated (see below). Except for *p*-hydroxyphenylthiyl radical, the absorption spectra of the para-substituted phenylthiyl radicals were independent of pH in the range 3-13.5. They have maxima at the wavelengths reported in Table 1.

 pK_a of *p*-HOC₆H₄S[•]. In the case of *p*-hydroxyphenylthiyl radical the spectra are pH dependent with those of its acid (*p*-HOC₆H₄S[•]) and base (*p*-OC₆H₄S^{•-}) forms given in Figure 1. The absorption in the 500–650 nm region clearly identifies the radicals in both forms as sulfur centered. The change in spectra in the pH 5 region corresponds to ionization of the OH proton (eq 2). The intensities at the peak maxima (see Figure 1) change

$$p \operatorname{+HOC}_{6} \operatorname{H}_{4} \operatorname{S}^{\bullet} \stackrel{K_{t}}{\xleftarrow} \operatorname{H}^{+} + p \operatorname{+OC}_{6} \operatorname{H}_{4} \operatorname{S}^{\bullet^{-}}$$
(2)

as a function of pH. By following these changes, as was done in ref 14 for the *p*-HSC₆H₄S[•] radical, the value of pK_r for *p*-HOC₆H₄-S[•] was determined to be 4.85.



Figure 1. Absorption spectra of radicals formed from p-HOC₆H₄SH: Filled circles, in 0.1 M N₃⁻ at pH 10.5; open circles, in 0.1 M 2-propanol at pH 2.8.

Electron Transfer Equilibria. The electron transfer equilibrium (3/-3) was observed with several acceptor radical (A[•])

$$\mathbf{A}^{\bullet} + \mathbf{D}^{-} \underset{k_{\mathrm{r}}}{\overset{k_{\mathrm{f}}}{\longleftrightarrow}} \mathbf{A}^{-} + \mathbf{D}^{\bullet}$$
(3/-3)

and electron donor anion (D⁻) pairs. For the phenol-thiophenol system preliminary results showed that the equilibrium lay in the direction of phenylthiyl radical formation. Because of this, using azide radical as a secondary oxidant phenoxyl radical can be preferentially prepared by irradiating a solution with excess phenol. The subsequent electron transfer from phenylthiolate is illustrated in Figure 2 where the phenoxyl radical absorption at 400 nm decreases with time, while that of phenylthiyl radical at 460 nm increases. The time dependence of the approach to equilibrium, shown in Figure 2a, follows pseudo-first-order kinetics. The lines through the points are optimized fits to the first-order relaxation process obtained from the computer analysis. The pseudo-first-order rate constants (k_{obs}) for the growth and decay agree very well and give a value of 0.83 \times 10^6 s^{-1} for a solution 16 mM in phenol and 0.25 mM in thiophenol.

The various values of k_{obs} for different conditions are listed in Table 2. The kinetic data for different [A⁻] and [D⁻] were analyzed in accord with eq 4,^{5,6}where A⁻ and D⁻ represent the

$$k_{\rm obs}/[A^-] = k_{\rm f}[D^-]/[A^-] + k_{\rm r}$$
 (4)

anions of PhO⁻ and PhS⁻, respectively. We note that data for phenolate concentrations from 4 to 16 mM follow a common



Figure 2. Changes in absorbance during electron transfer from $C_6H_5S^-$ to $C_6H_5O^-$ produced by oxidation of 16 mM $C_6H_5O^-$ by N_3^- in 0.1 M N_3^- at pH 11.9 and containing 0.25 mM $C_6H_5S^-$. (a) Kinetic traces at 400 (\bigcirc) and 460 nm ($\textcircled{\bullet}$). (b) Spectra taken at 0.5 (\Box), 1.5 (\bigcirc), and 8 (\bigtriangleup) μ s after the electron beam pulse.

TABLE 2: Determination of Equilibrium Constant for $PhO^{\bullet} + PhS^{-} \rightleftharpoons PhO^{-} + PhS^{\bullet}$

[PhO ⁻]/mM	[PhS ⁻]/mM	400 nm	460 nm	$k_{\rm obs}/10^6 \ {\rm s}^{-1}$	$K_{ m abs}{}^a$
16.0	1.00	1036	2163	1.96	56.5
16.0	0.75	1154	2011	1.54	59.2
16.0	0.50	1445	1771	1.20	56.7
16.0	0.25	2038	1338	0.83	54.5
16.0	0.11	2456	791	0.63	57.3
4.0	1.00	592	2496	1.54	49.9
4.0	0.75	639	2280	1.22	49.5
4.0	0.50	803	2307	0.88	46.6
4.0	0.20	1066	1924	0.41	59.8
8.0	1.00	834	2485	1.70	46.9
8.0	0.75	906	2104	1.26	45.7
8.0	0.50	1132	2046	0.95	46.6
8.0	0.20	1616	1520	0.47	52.1
8.0	0.0	3306	68		
0.0	1.00	375	2700		av 52.4 \pm 5.2

 ${}^{a}K_{abs} = [PhO^{-}][{Abs(460 nm) - 68}/{2700 - 68}]/[PhS^{-}][{Abs(400 nm) - 375}/{3306 - 375}].$

plot. The plot of the experimental points with best line obtained by linear regression is shown in Figure 3. The values of k_f at $14.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and of k_r at $0.29 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ derived from the slope and intercept are given in columns five and six of Table 1. The value of the equilibrium constant K_3 from the ratio of k_f and k_r is 50. This result, which is expected to be accurate to about 8–10%, is referred to as K_{kin} and is listed in column seven.

It can be seen from Figure 2a that equilibrium is reached in $\sim 4 \,\mu s$. The plateau values of the absorption traces can be used to calculate the relative equilibrium concentrations of C₆H₅O•



Figure 3. Plot of $k_{obs}/[A^-]$ versus $[D^-/[A^-]$ in accord with expression **4** for $A^- = C_6H_5O^-$ and $D^- = C_6H_5S^-$. $[C_6H_5O^-] = 16 (\Box)$, 8 (Δ), and 4 (\bigcirc) mM, respectively. Slope of 14.5 × 10⁸ corresponds to the forward rate constant and the intercept of 0.29 × 10⁸ to the reverse rate constant.

and $C_6H_5S^{\bullet}$. For each set of conditions these were combined with $[C_6H_5O^-]$ and $[C_6H_5S^-]$ to calculate the values of K_3 given in column six of Table 2 under the heading K_{abs} . The average K_{abs} (52 ± 5), listed in the last column of Table 1, is in excellent agreement with that obtained from the kinetic analysis. This agreement and the absence of any dependence of K_{abs} or K_{kin} on the concentrations of $[C_6H_5O^-]$ and $[C_6H_5S^-]$ indicates that equilibria other than (1/-1) are not involved. Species such as $(C_6H_5O \therefore SC_6H_5)^-$ or $(C_6H_5S \therefore SC_6H_5)^-$ do not appear to play a significant role. This conclusion is in contrast to alkyl thiyl radicals which readily form $(R-S \therefore S-R)^- \sigma\sigma^*$ bonded complexes.¹⁸

Electron transfers for the para-substituted phenylthiols were investigated similarly. Each one was paired with its phenolic analog or with some other suitable standard of known reduction potential. The donor-acceptor combinations and the wavelengths of observation for the radical concentrations have been summarized in Table 1, along with k_f , k_r , K_{abs} , and K_{kin} . These rate and equilibrium constants have been corrected to zero ionic strength using the extended Debye-Hückel equation, where such corrections are needed.

It should be noted that for the identically para-substituted phenylthiyl-phenolate pairs other than H, CH₃, and CH₃O the direction of electron transfer was from phenolate to phenylthiyl radical. For the p-(O⁻)PhO⁻/p-(O⁻)PhS⁻ pair the observed forward rate was $3.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. In this case the overall rates were too slow for a determination of k_r from the intercept of eq 4. From the absorptions at equilibrium K_{abs} is 540, so that k_r is estimated to be only $7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. For resorcinol (RES), where E° for the radical anion was checked, only absorbance data are reported for the *p*-MeOPhO⁻/RES pair. Similarly only kinetic data were available for the *p*-NH₂PhS⁻/p-NH₂PhO⁻ and *p*-NH₂PhS⁻/RES pairs. However, in the instances where K_{abs} or K_{kin} was missing, the data required to calculate reduction potentials were obtained from equilibria involving other donor-acceptor pairs.

Reduction Potentials. In general the $K_{\rm kin}$ and $K_{\rm abs}$ equilibrium constants agree very well. These data were used to obtain the differences in the reduction potentials, ΔE° , from the relation $\Delta E^{\circ} = 2.303(RT/F) \log K$, where 2.303RT/F = 0.0592 V. The reduction potentials of the phenylthiyl radicals in the half reaction 5, $E^{\circ}(p$ -XC₆H₄S⁻/p-XC₆H₄S⁻), were then calculated

$$p - XC_6H_4S^{\bullet} + e^- = p - XC_6H_4S^-$$
(5)

from these differences and the known E° values of the corresponding half reactions of the references used. The data

TABLE 3: Standard Reduction Potentials for RY'/RY⁻ and RY', H⁺/RYH Systems with $R = p-XC_6H_4$ and pK_a 's of RYH

para	E°	E°/V		^c	E°/V	
substituent	$(\mathrm{RO}^{\bullet}/\mathrm{RO}^{-})^{a}$	$(RS^{\bullet}/RS^{-})^{b}$	ROH ^c	RSH ^c	$(RO^{\bullet}, H^{+}/ROH)^{b}$	$(RS^{\bullet}, H^{+}/RSH)^{b}$
Н	0.79	0.69	10.0	6.6	1.38	1.08
Br	0.82	0.71	9.4	6.0	1.38	1.07
CH_3	0.68	0.64	10.3	6.8	1.29	1.04
CH_3O	0.54	0.57	10.1	6.8	1.14	0.97
OH	0.45	0.49	9.9	7.0^{d}	1.04	0.91
SH		0.63^{e}		6.0^{e}		0.99^{e}
NH_2	0.24^{d}	0.36	10.4	7.1^{d}	0.86	0.78
S^-		0.33^{e}	10.1^{d}	7.7^{e}		0.79^{e}
O^-	0.023	0.18	11.4		0.65	

^{*a*} Unless otherwise stated, data are from ref 8. ^{*b*} Unless otherwise stated, data are from this study. ^{*c*} Unless otherwise stated, data are from ref 20. ^{*d*} Data are from this study. ^{*e*} Data are from ref 14.



Figure 4. Reduction potential ladder for phenylthiyl and phenoxyl radicals. E° for each *p*-X para substituent is in boldface next to the formula of X. ΔE° 's are on vertical arrows. The values for X = H, CH₃, CH₃, and HO of *p*-XC₆H₄O[•] are from ref 8, and O⁻ from ref 7. The TMPD value is from ref 19. The X = HS and S⁻ values for *p*-XC₆H₄S[•] are from ref 14. All others are from this study.

have been summarized in the reduction potential ladder in Figure 4, where the E° values are in boldface next to the indicated substituents. The present results for the phenylthiyl radicals are given in the middle column of Figure 4.

The results in Figure 4 clearly connect the E° values for the phenylthiyl radicals with those of the phenoxyl radicals. They also establish consistency over the entire range from 0.02 to 0.79 V and provide valuable reference potentials at intermediate values. The value of 0.24 V for *p*-NH₂PhO[•] measured in the present study relative to TMPD is in reasonable agreement with 0.22 V given in ref 6. However, as indicated in ref 14, the value for RES (0.48 V) measured in the present study differs significantly from the value of 0.38 V previously reported.

The standard (pH = 0) reduction potentials for the thiyl radicals in reaction 6 and their phenoxyl counterparts in reaction

7 are listed in Table 3. These potentials were obtained by

$$p-XC_{6}H_{4}S^{\bullet} + e^{-} + H^{+} = p-XC_{6}H_{4}SH$$
 (6)

$$p-XC_{6}H_{4}O^{\bullet} + e^{-} + H^{+} = p-XC_{6}H_{4}OH$$
 (7)

combining the values of $E^{\circ}(p-XC_6H_4S^{\bullet}/p-XC_6H_4S^{-})$ and $E^{\circ}(p-XC_6H_4O^{\bullet}/p-XC_6H_4O^{-})$ with the free energies of protonation (=p $K_a \times 0.059_2$ V) calculated from the pK_a 's in ref 20. For the *p*-HOC₆H₄S[•] radical $E^{\circ}(p-HO-p-XC_6H_4S^{\bullet}/p-HOC_6H_4S^{-})$ was first obtained from $E^{\circ}(p-OC_6H_4S^{\bullet-}/p-OC_6H_4S^{2-})$ by subtracting the energy of protonation of $p-OC_6H_4S^{\bullet-}$, 0.28₇ V (=p $K_a \times 0.059_2$, where $pK_r = 4.8_5$ was determined above) and adding the energy of protonation of $p-OC_6H_4S^{2-}$ (=p $K_2 \times 0.059_2$, where $pK_2 = 10.1$ determined above).

Analysis of the Electron Transfer Rates. The rate constants in Table 1 for the forward and reverse electron transfers between the phenoxyl and phenylthiyl reactants, that is reactions 8 and -8, cover a range of 5 orders of magnitude. They can be

$$p$$
-XC₆H₄O[•] + p -XC₆H₄S⁻ \Longrightarrow
 p -XC₆H₄O⁻ + p -XC₆H₄S[•] (8/-8)

analyzed in terms of the theory developed by Marcus and others for bimolecular electron transfer reactions.²¹ In general such reactions consist of the set of elementary steps shown in eq 9:

$$\mathbf{A}^{\bullet} + \mathbf{D}^{-} \underbrace{\overset{k_{d}}{\overleftarrow{k_{-d}}}}_{k_{-d}} \mathbf{A}^{\bullet} \cdots \mathbf{D}^{-} \underbrace{\overset{k_{et}}{\overleftarrow{k_{-et}}}}_{k_{-et}} \mathbf{A}^{-} \cdots \mathbf{D}^{\bullet} \underbrace{\overset{k'_{-d}}{\overleftarrow{k'_{-d}}}}_{k'_{-d}} \mathbf{A}^{-} + \mathbf{D}^{\bullet} \quad (9)$$

Here k_d and k_{-d} correspond respectively to the rate constants for formation and breakup of the precursor complex, A^{••••}D⁻, and k_{et} corresponds to the rate of the actual electron transfer process to form the successor complex A^{-•••}D[•]. The primed constants and k_{-et} are for the analogous reverse processes. The relation between these parameters and the observed rate constant in the forward direction is²²

$$\frac{1}{k_{\rm obs}} = \frac{1}{k_{\rm d}} + \frac{k_{\rm -d}}{k_{\rm d} k_{\rm et}} + \frac{k_{\rm -et} k_{\rm -d}}{k_{\rm d} k_{\rm et} k'_{\rm -d}}$$
(10)

Omitting the last term, which is usually negligible, one then has

$$\frac{k_{\rm d} k_{\rm et}}{k_{\rm -d}} = \left[\frac{1}{k_{\rm obs}} - \frac{1}{k_{\rm d}}\right]^{-1}$$
(11)

The quantity $k_{\rm et}k_{\rm d}/k_{\rm -d}$, which is the rate constant when diffusion control is absent, is a function of (i) the standard free energy change for the reaction, ΔG° , which is equal to $-F\Delta E^{\circ}$; (ii) λ , the total reorganization energy; (iii) κ , the electronic factor; (iv)



Figure 5. Plot of log k' (=log $k_{et} k_d/k_{-d}$ or log $k_{-et}k'_d/k'_{-d}$) against ΔE° for forward and reverse electron transfers of the *p*-X substituents H, Me, MeO, Br, H₂N, and O⁻ in the reaction *p*-XC₆H₄O• + *p*-XC₆H₄S⁻ \Rightarrow *p*-XC₆H₄O⁻ + *p*-XC₆H₄O•. The line is calculated for $\lambda = 57.7$ kJ mol⁻¹.

 $A\sigma^2$, the collision frequency term; and (v) w_r and w_p , terms which are associated with the work (normally electrical) required to bring reactants and products into the precursor and successor complexes, respectively. The total reorganization energy, λ , is the sum of the solvent reorganization energy λ_o and the internal reorganization energy λ_i . The parameter $A\sigma^2$ is affected by the structures and lifetimes of the reaction complexes with typical values being $\sim 10^{11}$ M⁻¹ s⁻¹.^{21,23} The relation between $k_{\rm et}k_{\rm d}/k_{\rm -d}$ and the above parameters is

$$\log(k_{\rm et}k_{\rm d}/k_{\rm -d}) = \log(\kappa A\sigma^2) - \{w_{\rm r} + (1/4)\lambda[1 + (w_{\rm p} - w_{\rm r} - F\Delta E^{\circ})/\lambda]^2\}/2.303RT (12)$$

Values of $k_{\rm et}k_{\rm d}/k_{\rm -d}$ for the forward and $k_{\rm -et}k'_{\rm d}/k'_{\rm -d}$ for the reverse electron transfer were obtained from the values of $k_{\rm f}$ and $k_{\rm r}$ in Table 1 by using expression 11 and $k_d = (7.4 \times 10^9) f \text{ M}^{-1} \text{ s}^{-1}$, where f is the electrostatic factor.^{22,24} The differences between the observed $k_{\rm f}$ and $k_{\rm r}$ and the corresponding $k_{\rm et}k_{\rm d}/k_{\rm -d}$ or $k_{\rm -et}k'_{\rm d}/k_{\rm -d}$ k'_{-d} were small; even the largest amounted to only about 20%. The pairs of experimental points, $k_{et}k_d/k_{-d}$ and $k_{-et}k'_d/k'_{-d}$, for reactions 8 and -8 with different para substituents have been plotted in Figure 5 against the values of ΔE° . The line was calculated from eq 12 with $\lambda = 57.7$ kJ mol⁻¹ and ($\kappa A \sigma^2$) = $10^{11} \text{ M}^{-1} \text{ s}^{-1}$. Most of the points fall on this line. In the case of the p-Br and p-NH₂ substituents the lines are parallel. The important feature is that the slopes of the pairs of points are in accord with the theoretical value of 8.45 (=(0.5F/RT)/2.303)^{21,22} shown by the middle portion of the line. This slope holds for $(w_{\rm p} - w_{\rm r} - F\Delta E^{\circ}) \ll \lambda$, a condition which applies here (see λ values below). The present data conform to it very well. The fact that the points for the systems with H, Me, and MeO as para substituents fall on the same line was not expected. This means that for these substituents the values of λ in reaction 8 and -8 must be close to 57.7 kJ mol⁻¹ and that the $\kappa A\sigma^2$ values must also be similar. The rate constants for the systems with O⁻ and NH₂ substituents fall well below the line, and obviously have much larger values of λ , and possibly also smaller values of $\kappa A \sigma^2$.

The reorganization energies for reactions 8 and -8 contain contributions from both the p-XC₆H₄O[•]/p-XC₆H₄O[–] and the p-XC₆H₄S[•]/p-XC₆H₄S[–] couples. More explicit information about the individual reactants can be obtained by separating these components, i.e., by finding the reorganization energies

TABLE 4: Self-Exchange Rate Constants and λ_{se} 's

para	O-syste	ems	S-systems		
substituent	$k_{\rm se}{}^a$	$\lambda_{\mathrm{se}}{}^{b}$	$k_{\rm se}{}^a$	$\lambda_{\mathrm{se}}{}^{b}$	
Br	6.8	50	13	43	
Me	2.4	60	3.2	57	
Н	2.0^{c}	62^c	3.8	55	
H_2N	0.14	88	0.77	71	
O ⁻	0.00026	142	0.019	99	

 a Units are $10^8~M^{-1}~s^{-1}.~^b$ Units are kJ mol $^{-1}.~^c$ Experimental measurement from ref 2. Others obtained by the Marcus cross relation.

for the self-exchange reactions:

p

$$p$$
-XC₆H₄O[•] + p -XC₆H₄O⁻ \rightleftharpoons
 p -XC₆H₄O⁻ + p -XC₆H₄O[•] (13/-13)

$$-XC_{6}H_{4}S^{\bullet} + p - XC_{6}H_{4}S^{-} \rightleftharpoons$$
$$p - XC_{6}H_{4}S^{-} + p - XC_{6}H_{4}S^{\bullet} \qquad (14/-14)$$

In the standard Marcus formalism the rate constant k_{12} for the cross reaction between species 1 and 2

$$\operatorname{red}_{1} + \operatorname{ox}_{2} \xrightarrow{k_{12}} \operatorname{ox}_{1} + \operatorname{red}_{2}$$
(15)

can be related to those for the "self-exchange" reactions 16 and 17:

$$\operatorname{red}_{1} + \operatorname{ox}_{1} \xrightarrow{k_{11}} \operatorname{ox}_{1} + \operatorname{red}_{1}$$
(16)

$$\operatorname{red}_2 + \operatorname{ox}_2 \xrightarrow{k_{22}} \operatorname{ox}_2 + \operatorname{red}_2$$
 (17)

by the cross relation²¹

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$$
(18)

where K_{12} is the equilibrium constant for the electron transfer 15, and f_{12} is a function of k_{11} , k_{22} , K_{12} , and the work terms previously defined.²¹ Several self-exchange rate constants (or k_{se}) were calculated by using eq 18.

The value of $2.0\times 10^8\,M^{-1}\,s^{-1}$ for the rate constant for the self-exchange reaction

$$C_6H_5O^{\bullet} + C_6H_5O^{-} \rightleftharpoons C_6H_5O^{-} + C_6H_5O^{\bullet}$$
 (19/-19)

has been determined by ESR.² The self-exchange rate constants for C₆H₅S[•]/C₆H₅S⁻ and *p*-BrC₆H₄S[•]/*p*-BrC₆H₄S⁻ were obtained from this and the present data in Table 1 for their cross reactions with C₆H₅O[•]/C₆H₅O⁻. The value for *p*-BrC₆H₄O⁻/*p*-BrC₆H₄O⁻ was determined from the rate of the *p*-BrC₆H₄O⁻ + C₆H₅O[•] cross reaction reported in ref 2. Likewise the value for *p*-MeC₆H₄O⁻/*p*-MeC₆H₄O⁻ was obtained from the reaction rates for *p*-MeC₆H₄O⁻ + C₆H₅O[•] given by Lind et al.⁸ The value for *p*-MeC₆H₄O^{*}/*p*-MeC₆H₄S⁻ was obtained from this and the present result for the *p*-Me₆H₄S[•] + *p*-MeC₆H₄O⁻ cross reaction. Where available, both the forward and the reverse cross reaction rate constants were used in the calculations and the average of the two results was taken. Normally they did not differ by more than 30%. The values of k_{se} and λ_{se} calculated from them have been summarized in Table 4.

Table 4 also lists k_{se} and λ_{se} for the H₂N and O⁻ para substituents. They were obtained as follows. The ratio of the k_{12} values for the p-H₂NC₆H₄S[•] + TMPD and p-H₂NC₆H₄O[•] + TMPD cross reactions yields the ratio of the k_{se} values for p-H₂NC₆H₄S[•]/p-H₂NC₆H₄S⁻ and p-H₂NC₆H₄O[•]/p-H₂NC₆H₄O⁻,



Figure 6. Comparison of pK_a 's of p-HOC₆H₄O[•], p-HOC₆H₄S[•], and p-HSC₆H₄S[•] and their parent molecules with those of C₆H₅OH and C₆H₅-SH. Vertical arrows show differences in $\Delta G^{\circ}_{\text{ionization}}$. Data from refs 7 and 14 and this study.

while the rate constant for the p-H₂NC₆H₄S[•] + p-H₂NC₆H₄O⁻ cross reaction yields their product. Thus the k_{se} values for p-H₂- $NC_6H_4S^{\bullet}/p-H_2NC_6H_4S^-$ and $p-H_2NC_6H_4O^{\bullet}/p-H_2NC_6H_4O^-$ can be obtained. The result for $p-H_2NC_6H_4O^{\bullet}/p-H_2NC_6H_4O^{-}$ was used with the cross reaction rates in Table 1 to obtain k_{se} for p-OC₆H₄S^{•-}/p-OC₆H₄S²⁻, and k_{se} for p-OC₆H₄O^{•-}/p-OC₆H₄O²⁻ was then found from that. These k_{se} and λ_{se} values are subject to a greater uncertainty than those found above. However, the uncertainties in λ_{se} (<10 kJ mol⁻¹) are much less than the large increases from the values for the H, Br, and Me para substituents (see Table 4), and they are of theoretical and practical interest. One should note here that for p-OC₆H₄O^{•-}/p-OC₆H₄O²⁻ and p-OC₆H₄S^{•-}/p-OC₆H₄S²⁻ the decrease in $A\sigma^2$ due to the work of bringing the charged reactants together was taken into account when λ_{se} was calculated from expression 18. For the other exchange pairs, all of which involve a neutral reactant, this work term is zero.

Discussion

Acid-Base Equilibria. The effects of para substituents on the ionization of phenols in aqueous solution have been discussed by other authors.^{20,25,26} The p K_a of phenol, 10.0, is reduced by electron-withdrawing substituents. With thiophenols the trend is similar, but the effects of electron-withdrawing para substituents are less pronounced due to the inherently greater acidity of the SH group (p K_1 of thiophenol = 6.6).^{20,25} From its magnitude, the value of 7.0 found here for the pK_1 of p-hydroxymercaptobenzene can clearly be identified as that of the SH group. This value agrees very well with 7.0 predicted from equations based on linear free energy relations given by Perrin, Dempsey, and Serjeant.²⁶ The same is true for pK_1 and pK_2 of 1,4-dimercaptobenzene, viz., 6.0 and 7.7 observed,¹¹ versus 5.9 and 7.6 calculated, respectively. The agreement is not as good for the pK_2 of p-hydroxymercaptobenzene, viz., 10.1 observed here versus 11.5 predicted. However, there is a similar discrepancy for pK_2 of *p*-hydroxyphenol (11.4 observed versus 12.0 predicted) and it appears that the mentioned equations do not work as well for OH ionizations in these disubstituted systems. The fact that the pK_2 value of phydroxymercaptobenzene determined here as 10.1 is lower than the value of 11.4 for hydroquinone indicates that the flow of charge from the S⁻ on to the aromatic ring system is less than for O⁻.

The pK_a of the *p*-HOC₆H₄S[•] radical (4.85) determined here is compared with those of the *p*-HOC₆H₄O[•] and *p*-HSC₆H₄S[•] radicals in Figure 6. The pK_a 's of the radicals may also be compared with the pK_1 values of the appropriate OH or SH substituent of the parent molecules. The radical centers act as electron-withdrawing groups and therefore stabilize the anions, causing the pK_a 's to be reduced below those of the parent molecules. The difference in stabilization of the radical anions



Figure 7. Comparison of the reduction potentials of para-substituted and unsubstituted radicals. (a) $E^{\circ}(p-XC_{6}H_{4}Y^{\bullet},H^{+}/p-XC_{6}H_{4}YH)$ versus $E^{\circ}(C_{6}H_{5}Y^{\bullet},H^{+}/C_{6}H_{5}YH)$; (b) $E^{\circ}(p-XC_{6}H_{4}Y^{\bullet}/p-XC_{6}H_{4}Y^{-})$ versus E° - $(C_{6}H_{5}Y^{\bullet}/C_{6}H_{5}Y^{-})$. Data from refs 7 and 8 and this study.

over the unsubstituted $C_6H_5O^-$ and $C_6H_5S^-$ anions is indicated by the differences in ionization energies in kilojoules per mole, given on the vertical arrows in Figure 6. The decrease in the order p-HOC₆H₄O[•] > p-HOC₆H₄S[•] > p-HSC₆H₄S[•] is consistent with the view that in the para-substituted aromatic systems the unpaired electron is more localized on the S atoms than on the O atoms. Thus the stabilization is greater in the phenoxyl than in the phenylthiyl radicals. This feature is repeated in the other properties discussed below.

Reduction Potentials. The present value of $E^{\circ}(C_6H_5S^{\bullet}/C_6H_5S^{-}) = 0.69$ V in Table 3 may be compared with $E^{\circ}(RS^{\bullet}/RS^{-}) = 0.79$ V for a typical alkylthiyl radical, such as $HOC_2H_4S^{\bullet}.^{27}$ The difference of 0.1 V is substantially less than the difference between the corresponding phenoxyl and alkoxyl radicals ($E^{\circ}(C_6H_5O^{\bullet}/C_6H_5O^{-}) = 0.79$ V⁸ and $E^{\circ}(RO^{\bullet}/RO^{-}) = 1.2$ V²⁸). This smaller difference for the sulfur radicals is a second manifestation of the lesser stabilization of the phenylthiyl radicals as a result of less delocalization of the unpaired electron unto the aromatic ring.

The smaller stabilization of the sulfur radicals is further demonstrated in Figure 7, which shows a comparison of the reduction potentials of radicals of phenol, thiophenol, hydroquinone, *p*-hydroxymercaptobenzene, and 1,4-dimercaptobenzene. The difference of 0.19 V between $E^{\circ}(p-\text{HOC}_6\text{H}_4\text{S}^{\bullet},\text{H}^+/p-\text{HOC}_6\text{H}_4\text{SH})$ and $E^{\circ}(\text{C}_6\text{H}_5\text{S}^{\bullet},\text{H}^+/\text{C}_6\text{H}_5\text{SH})$ in Figure 7a represents the energy of stabilization of the *p*-HOC₆H₄S[•] radical by the *p*-HO substituent. Stabilization energies of the other radicals in Figure 7 have been calculated similarly. It can be seen that they are always greater where oxygen atoms are involved. Also the values for the *p*-HOC₆H₄S[•] and *p*-OC₆H₄S^{•-} radicals are intermediate between those containing only oxygen or only sulfur.²⁹

As a means of making a quantitative comparison of the effects for the other para substituents in the phenylthiyl and phenoxy systems, the values of $E^{\circ}(p-XC_6H_4S^{\bullet}/p-XC_6H_4S^{-})$ and $E^{\circ}(p-XC_6H_4O^{\bullet}/p-XC_6H_4O^{-})$ have been plotted in Figure 8 against the Hammett σ_p^+ parameters³⁰ of the para substituents. The values of the phenylthiyl radicals determined in the present study are plotted as the squares in Figure 8. The values of $E^{\circ}(p-XC_6H_4O^{\bullet}/p-XC_6H_4O^{-})$ for the analogous oxygen containing



Figure 8. Reduction potentials $E^{\circ}(p-XC_6H_4Y^{-}/p-XC_6H_4Y^{-})$ plotted against the σ_p^+ parameter for different *p*-X para substituents. Symbols: \Box , present data for Y = S; O, data of ref 8 for Y = O. Lines are best fits; see text.

radicals, as given by Lind et al.,⁸ are plotted as the circles. The best line through the data from Lind et al. (eq 20) is reproduced

$$E^{\circ}(p-\mathrm{XC}_{6}\mathrm{H}_{4}\mathrm{O}^{\bullet}/p-\mathrm{XC}_{6}\mathrm{H}_{4}\mathrm{O}^{-}) = 0.79 + 0.41\sigma_{\mathrm{p}}^{+}$$
 (20)

in dashed form. The best line obtained by linear regression for the eight thiophenols (solid line in Figure 8) conforms to

$$E^{\circ}(p-\mathrm{XC}_{6}\mathrm{H}_{4}\mathrm{S}^{\bullet}/p-\mathrm{XC}_{6}\mathrm{H}_{4}\mathrm{S}^{-}) = 0.69 + 0.22\sigma_{\mathrm{p}}^{+} \quad (21)$$

with a correlation coefficient of 0.983. From a comparison of the two slopes it is evident that the dependence of $E^{\circ}(p-XC_{6}H_{4}S^{\bullet}/p-XC_{6}H_{4}S^{-})$ on σ_{p}^{+} is about 50% that of $E^{\circ}(p-XC_{6}H_{4}O^{-})$. A dependence of $E^{\circ}(p-XC_{6}H_{4}S^{\bullet}/p-XC_{6}H_{4}S^{-})$ on σ_{p}^{+} , qualitatively similar to that displayed in Figure 8, has been reported previously for reduction potentials of several of the present para-substituted thiophenols in nonaqueous solvents,^{31–33} but quantitative comparison with the present potentials measured in water is not practical.

Where *p*-X substituents have σ_p^+ parameters approaching those of O⁻ and S⁻, it is of interest to compare the observed potentials with those predicted for the X-centered radical species from linear free energy relations. If the latter are lower, this is an indication that the radical is best regarded as X-centered. Jonsson et al.³⁴ have given an equation similar to eqs 20 and 21 above for para-substituted aniline radical cations in water, viz.,

$$E^{\circ}(p-\text{XC}_{6}\text{H}_{4}\text{NH}_{2}^{\bullet+}/p-\text{XC}_{6}\text{H}_{4}\text{NH}_{2}) = 1.02 + 0.33\sigma_{p}^{+} \quad (22)$$

If one uses the σ_p^+ parameter for O⁻ from ref 30 ($\sigma_p^+ = -2.30$), then $E^{\circ}(p-(-0)C_6H_4NH_2^{\bullet+}/p-(-0)C_6H_4NH_2)$ is predicted to be 0.26 V. The present experimental value is only slightly lower (0.24 V), which is in keeping with the view that the radical is a primarily a phenoxyl p-H₂NC₆H₄O[•] species, but, as indicated by the ESR and Raman³⁵⁻³⁷ data, has contributions from both O-centered and N-centered structures (see further below). Unfortunately similar comparisons cannot be made for the p-H₂-NC₆H₄S[•] and p-SC₆H₄O^{•-} radicals, because the $\sigma_p^+ = -2.60$ for S⁻ appears to be seriously in error. For example, if one uses it in eq 22 $E^{\circ}(p-(-S)C_6H_4NH_2^{\bullet+}/p-(-S)C_6H_4NH_2)$ is predicted to be 0.16 V. This is well below the value of 0.36 V observed here and is clearly incorrect. Likewise employing this value for S⁻ in eq 20 predicts -0.28 V for $E^{\circ}(p-\text{SC}_6\text{H}_4\text{-O}^{-/}p-\text{SC}_6\text{H}_4\text{O}^{2-})$. Again this is below the present $E^{\circ}(p-\text{OC}_6\text{H}_4\text{S}^{\bullet-/}p-\text{OC}_6\text{H}_4\text{S}^{2-})$ experimental value (0.18 V) and cannot be rationalized. These observations suggest that $\sigma_p^+ = -2.60$ is too low for S⁻. Placing the value of $E^{\circ}(p-\text{SC}_6\text{H}_4\text{S}^{\bullet-/}p-\text{SC}_6\text{H}_4\text{S}^{2-}) = 0.33$ V from ref 11 on the line in Figure 8 leads to σ_p^+ for S⁻ ≈ -1.5 . This has almost the same difference from that of O⁻ as the one for SH ($\sigma_p^+ = -0.03^{30}$) does from OH ($\sigma_p^+ = -0.92^{30}$), and would appear to be more reasonable for S⁻.

Electron Transfer Kinetics and Radical Structures. Two trends are apparent in the values of λ_{se} in Table 4: (a) they are smaller for the S systems than for the O systems; (b) there is a major increase in going from H to the strongly electron donating H_2N and O⁻ para substituents. The objective of this section is to examine these trends in the light of current knowledge of differences in the structures of these radicals. However, a few comments of a general nature are appropriate first. As pointed out above, the experimental points in Figure 5 conform well to the theoretical slope predicted by the Marcus theory. The fact that the data for the systems with H, Me, and MeO as para substituents fall on the same line is a strong indication that the geometries of the activated complexes as well as the reorganization energies for the electron transfer reactions of these species are similar. Since the magnitude of the charge transferred is always unity and the different para substituents are not large enough to cause major changes in the sizes of the reactants, this is entirely reasonable. Very similar behavior was observed for electron transfers between quinones and semiquinones.³⁸

The similarity in the values of k_{se} and λ_{se} for the individual reactions of the H and Me substituents for both the phenylthiyl and phenoxyl species is apparent in Table 4. The values of these parameters may be compared to the corresponding data for the self-exchange of paraphenylenediamine cation radical with its parent molecule (i.e., p-H₂NC₆H₄NH₂•+ + p-H₂NC₆H₄-NH₂), for which $k_{se} = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $\lambda_{se} = 64 \text{ kJ mol}^{-1}$ measured in acetonitrile.³⁹ Due to the larger solvent polarity, in water k_{se} will be ~30% smaller and λ_{se} a few kilojoules per mole larger. However, the self-exchange parameters of the present H and Me systems are clearly similar to those of the structurally related paraphenylenediamines, which have previously been studied in some detail.⁴⁰

The trend in Table 4 toward smaller λ_{se} for the S systems is best examined in terms of the structures of the unsubstituted phenoxyl and phenylthiyl radicals. Delocalization of the unpaired electron onto the aromatic ring causes a major difference between the structures of the phenoxyl radical and the phenolate anion.⁴ In the phenylthiyl radical, on the other hand, the unpaired spin is primarily localized on the S atom and changes in the bond lengths and angles between the radical and anion are much smaller.¹⁰ As an illustration, the C–O bond length in the phenoxyl radical (0.123 nm) is that of a C=O double bond, while the value in the phenolate anion is much larger (~0.136 nm). On the other hand the C–S bond length in phenyl thiyl radical is computed to be 0.175 nm, almost unchanged from the typical C–S single bond length of 0.176 nm.¹⁰

Experimental verification of these structural differences comes from the fact that the ν_{7a} C–S stretch at 1073 cm⁻¹ in the resonance Raman spectrum of C₆H₅S[•] is virtually unchanged from that of the thiophenolate anion.¹⁰ By contrast the experimental ν_{7a} C–O stretch of C₆H₅O⁻ at 1505 cm⁻¹ is 240 cm⁻¹ larger than in phenolate anion.^{3,41} Other frequencies in the C₆H₅O[•]/C₆H₅O⁻ pair also show larger changes than the corresponding ones in the C₆H₅S[•]/C₆H₅S⁻ pair. Clearly these structural differences will cause λ_i to be significantly larger for $C_6H_5O^{\bullet}/C_6H_5O^{-}$ than for $C_6H_5S^{\bullet}/C_6H_5S^{-}$. The trend toward smaller λ for *all of the S systems* in Table 4 suggests that the effects of stronger localization of the electron on the S atoms also cause the differences in the structural changes in parasubstituted p-XC₆H₄S[•]/p-XC₆H₄SCS⁻ pairs to be lower than in the p-XC₆H₄O[•]/p-XC₆H₄O⁻ pairs. Based on the fact that there is less interaction of the unpaired spin with the ring π system in p-SC₆H₄S^{•-} as well as in C₆H₅S[•], this conclusion is reasonable.^{14,15}

The second trend in Table 4 is the major increase in λ_{se} or decrease in k_{se} on going from H to H₂N and O⁻ para substituents. Here it is possible that, as well as changes in λ_i , there may be alterations in the geometries of the activated complexes that alter $A\sigma^2$ and/or λ_0 and contribute to the decreases in k_{se} . At present, unfortunately, only evidence relating to reasons for increases in λ_i is available. In the case of the *p*-OC₆H₄O⁻/*p*-OC₆H₄O²⁻ pair there will again be changes in the ring carbon structure on electron transfer. Also the C–O bonds, which remain equivalent, change from bond order 1 in *p*-OC₆H₄O²⁻ to 1.5 in *p*-OC₆H₄O^{•-.42} This simultaneous change in two C–O bonds will make a large contribution to λ_i , probably accounting for a major part of the increase over the value of λ_{se} for C₆H₅O⁻.

A contribution to an increase in λ_{se} for the amino-substituted radicals is again found in the structures of the radicals. ESR and Raman spectroscopic studies show that the electronic structure of *p*-aminophenoxyl radical is closely related to that *p*-benzosemiquinone radical anion.^{35–37} The Raman data indicate that the CN and CO bonds are of nearly equal strength and bond order.^{36,37} The change in bond length at the H₂N para substituent on electron transfer will contribute to λ_i . The fact that the increase in λ_{se} for *p*-H₂NC₆H₄O⁻/*p*-H₂NC₆H₄O⁻ is much less than that for *p*-OC₆H₄O^{•-}/*p*-OC₆H₄O²⁻ is, however, an indication that the effects of reorganization are not as strong in the former case.

Unlike the H₂N and O⁻ substituents, the *p*-Br substituents would oppose delocalization of the unpaired electron of the radical onto the aromatic ring, and thus tend to maintain single bond character in the C–O and C–S bonds. While the differences are smaller, the fact that k_{se} tends to *increase* in going from the H or Me to Br as the para substituents (see Table 4) is in agreement with this.

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References and Notes

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$$p-XC_6H_4Y^{\bullet-} + e^- = p-XC_6H_4Y^{2-}$$
 (i)

$$C_6H_5Y^{\bullet} + e^- = C_6H_5Y^-$$
 (ii)

However, the relative energies of the p-OC₆H₄O^{•-}/p-OC₆H₄Y²⁻, p-OC₆H₄S⁴⁻/p-OC₆H₄S²⁻, and p-SC₆H₄S^{•-}/p-SC₆H₄S²⁻ couples would not be affected by this, and the relative values are valid.

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(40) Grampp and Jaenicke³⁹ have carried out studies of self-exchange reactions of the *p*-phenylenediamines in several nonaqueous solvents. If one assumes the same dimensions of the activated complex and reactants in water, the value of λ_0 for *p*-H₂NC₆H₄NH₂•^{+/}*p*-H₂NC₆H₄NH₂ is found to be ~50 kJ mol⁻¹ (λ_0 in acetonitrile is 43 kJ mol⁻¹). The value of λ_i is 21 kJ mol⁻¹, and therefore λ_{se} for *p*-H₂NC₆H₄NH₂•⁺/*p*-H₂NC₆H₄NH₂ in water would be ~70 kJ mol⁻¹. If the reactant and activated complex dimensions for the present systems are similar, then from the λ_{se} 's in Table IV the values of λ_i for the self-exchanges of the H and Me substituents would be ~10 kJ mol⁻¹ for the phenoxyl species and about half that for the phenylthiyl species, respectively.

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