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Spectra, Ionization Constants, and Rates of Oxidation of 1,4-Dimercaptobenzene and Properties of the *p*-Mercaptophenylthiyl and *p*-Benzodithiyl Anion Radicals[1]

D. A. Armstrong,[2] Qun Sun, G. N. R. Tripathi, and R. H. Schuler*

Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

D. McKinnon

Department of Chemistry, University of Manitoba, Winnepeg, Manitoba R3T 2N2, Canada

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In basic solution, *p*-dimercaptobenzene, which is found to have pK_a's of 6.0 and 7.7, is rapidly oxidized by azide radical ($k = 7.4 \times 10^9$ M^{-1} s^{-1}) to *p*-benzodithiyl radical anion, the sulfur analog of *p*-benzosemiquinone radical anion. This radical has very strong absorption bands at 390 and ~700 nm. In acidic solutions, $CO_2^{\bullet-}$ abstracts a SH hydrogen atom ($k = 3.1 \times 10^9$ M^{-1} s^{-1}) to form the *p*-mercaptophenylthiyl radical, which has absorption maxima at 350 and 585 nm and a pK_a of 2.7. From measurements of its electron-transfer equilibrium with the resorcinol dianion, the reduction potential of the dithiyl radical has been determined to be 0.33 V vs SHE. This value is 0.37 V below the reduction potential of phenylthiyl radical, indicating that resonance stabilization of ~36 kJ/mol results from delocalization of the unpaired spin between the two sulfur atoms. This stabilization energy is, however, ~39 kJ/mol less than that for the analogous difference of 0.78 V between the reduction potentials of *p*-benzosemiquinone anion and phenoxy radicals. At high pH, the dithiyl radical anion decays rapidly in second-order processes ($2k = 2.8 \times 10^9$ M^{-1} s^{-1}), in contrast to the relatively stable *p*-benzosemiquinone radical anion, which, because its reduction potential is below that of quinone, is stable toward disproportionation by electron transfer.

Introduction

A recent publication from this laboratory[3] on the resonance Raman spectrum of phenylthiyl radical ($C_6H_5S^\bullet$) points out interesting differences between its structural features and those of its oxygen counterpart, the phenoxy radical ($C_6H_5O^\bullet$). In particular, the Raman data show that the CS bond in phenylthiyl radical has substantially less double-bond character than does the CO bond in phenoxy radical, indicating that in the former case the unpaired spin population is largely localized on the sulfur atom. In view of this difference, a comparison of the spectroscopic and chemical properties of the radicals derived from 1,4-dimercaptobenzene (PDMB) with their oxygen analogs, *p*-benzosemiquinone radical and its anion, is expected to be of considerable interest. This paper reports the results of a pulse radiolytic investigation of the spectra and chemical properties of the *p*-mercaptophenylthiyl ($HSC_6H_4S^\bullet$, PMPT$^\bullet$) and *p*-benzodithiyl anion radicals ($C_6H_4S_2^{\bullet-}$, PBDT$^{\bullet-}$). Of particular importance is the reduction potential of the latter (0.33 V vs SHE) which indicates that resonance stabilization is considerably less than that in the case of *p*-benzosemiquinone anion radical ($C_6H_4O_2^{\bullet-}$), where the reduction potential is 0.31 V lower. Background information on the ionization equilibria of the parent compound is also reported.

Experimental Section

Pulse Radiolysis Studies. Pulse radiolysis studies were carried out at the Radiation Laboratory LINAC facility by standard methods as previously described.[4] Doses of ~500 rad (5 Gy), calibrated with the N_2O saturated thiocyanate dosimeter,[5] produced an initial radical concentration of ~3 μM. Solutions were purged and saturated with nitrous oxide to convert e_{aq}^- into $^\bullet OH$ radicals. The mercaptophenylthiyl radical and its anion produced in the oxidation of 1,4-dimercaptobenzene by electron transfer to $N_3^\bullet$ or by H abstraction by $CO_2^{\bullet-}$ were examined by time-resolved absorption spectrophotometry. The intermediate radicals were prepared by the reaction of $^\bullet OH$ with 0.05–0.1 M sodium azide or sodium formate. All solutions were prepared with water from a Millipore Milli-Q system. Perchloric acid and potassium hydroxide were used to adjust the pH, and a flow system was used so that each pulse irradiated a fresh solution. Absorption spectra were recorded on a Cary 219 spectrophotometer. An Orion 811 pH meter, calibrated with Fisher buffers, was used for pH measurements, which are generally accurate to better than 0.02.

Preparation of 1,4-Dimercaptobenzene. 1,4-Dimercaptobenzene (PDMB) was not available from commercial sources and had to be synthesized. The starting point for its synthesis was 4-methylmercaptobenzenesulfonyl chloride (Ia). This compound was reduced, following literature methods, to 4-methylmercaptothiophenol (Ib). Cleavage of Ib with sodium in liquid ammonia gave the dimercaptan (I). The syntheses and purifications were carried out by the following methods, which are modifications of literature procedures.[6-8]

Ia has been reported as the product from reaction of thioanisole with chlorosulfonic acid.[6] In our hands, that approach was unsatisfactory owing to the poor crystallization of the sulfonyl chloride. Therefore, the sulfonic acid initially formed was converted into the sulfonyl chloride via reaction of its sodium salt with phosphoryl chloride. Chlorosulfonic acid (Aldrich) (8.7 g, 0.075 mol) was added dropwise to a stirred solution of thioanisole (Aldrich) (6.2 g, 0.05 mol) in chloroform (35 mL) at a rate such that the temperature did not exceed 5 °C. Toward the end of the addition, a solid precipitated from solution and stirring became difficult. This precipitate was collected on a sintered glass funnel, washed with cold chloroform, and added to a vigorously stirred saturated solution of sodium chloride in water. The precipitated sodium salt was collected, dried, and then gently heated with an approximately equal volume of phosphoryl chloride until homogeneous. The mixture was thrown onto ice and stirred until the product solidified. It was then collected by filtration and crystallized from cyclohexane as colorless needles, mp 44 °C, lit. 44–45 °C[6] (63% yield).

The sulfonyl chloride prepared above was reduced as described

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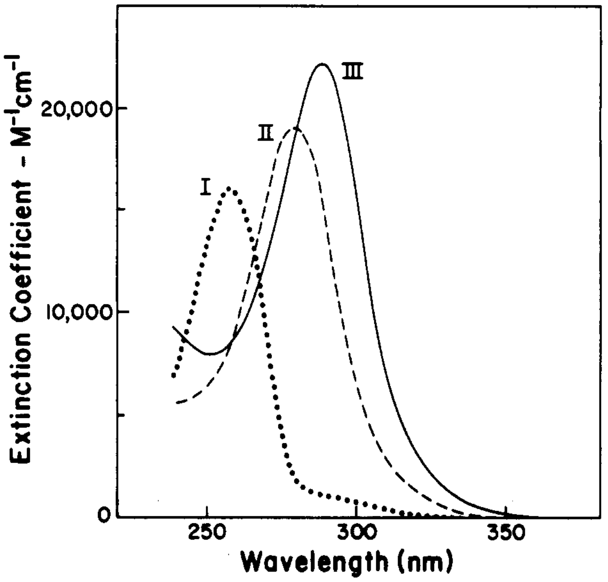


Figure 1. Spectra of dimercaptobenzene (I) and its mono- (II) and dianionic (III) forms in 0.01 M phosphate.

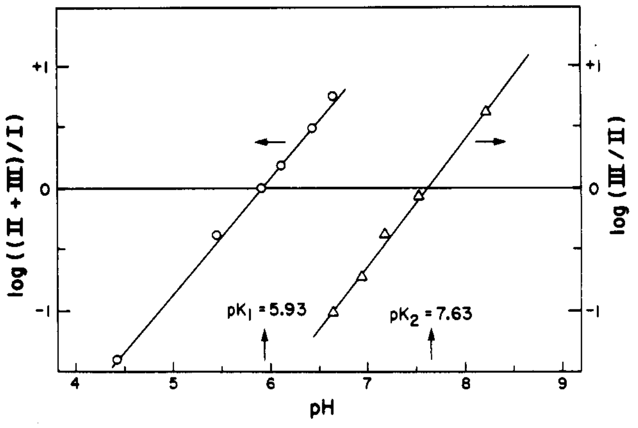


Figure 2. Determination of pK_1 and pK_2 of *p*-dimercaptobenzene. pK_1 was determined from eq 2 using the relative concentrations indicated by absorption measurements at 280 nm (see eq 3); pK_2 from eq 1 using the measurements at 300 nm.

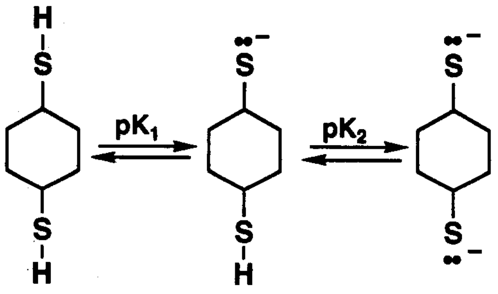
earlier.[7] The product (Ib) was obtained as a colorless oil, which crystallized below 0 °C.

The dimercaptobenzene was prepared from Ib as follows. To 5.6 g (0.05 mol) of Ib in liquid ammonia (100 mL) was added metallic sodium, in small pieces, until the solution acquired a permanent blue color. After 20 min, ether (20 mL) and ammonium chloride (5 g) were cautiously added, and the bulk of the ammonia was allowed to evaporate. The mixture was cautiously acidified with dilute hydrochloric acid and extracted with ether, and the dried extract was evaporated to give the product as a colorless crystalline solid. This was recrystallized from benzene as colorless plates, mp 98 °C, lit. 97.5–98.5 °C[6] (86% yield).

Chromatographic analysis of an aqueous solution of the final product showed only a trace impurity which eluted rapidly on a C_{18} column and had an absorption spectrum similar to that of the dimercaptobenzene. Assuming similar extinction coefficients, this impurity is estimated to be less than 0.2%.

Results and Discussion

Absorption Spectrum and p*K*'s of *p*-Dimercaptobenzene. *p*-Dimercaptobenzene also exists in mono- and dianionic forms which are manifest as the pH is increased from 2 to 10.



I II III

The spectrum of the fully protonated form (I), taken at pH ~ 2, is shown as the dotted spectrum in Figure 1, and that of the doubly ionized form (III), observed at pH > 9, is shown by the solid line. A preliminary examination of the pH dependence of the spectra indicated that pK_1 is greater than 5.5 and pK_2 is less than 8.0. While the singly ionized form (II) contributes in the intermediate pH region, the two p*K*'s are not sufficiently isolated that one is able to obtain a spectrum of this form directly. As the pH was raised above 4, the spectral maximum shifted from 255 to 290 nm with the absorbance at 265 nm being relatively constant over the entire range and that at 280 nm constant over the pH range above 7. The latter is taken as the indication of an isosbestic point at 280 nm between the two ionized forms of PDMB so that the absorption at this wavelength serves as a measure of the sum of II and III. For a simple equilibrium between acid and base forms A and B, one has, of course, the relationship

$$\log([\mathrm{B}]/[\mathrm{A}]) = \mathrm{pH} - \mathrm{p}K_1 \qquad (1)$$

In the present case, eq 1 must be modified to take into account the equilibrium between II and III, i.e.

$$\log(([\mathrm{II}] + [\mathrm{III}])/[\mathrm{I}]) = \mathrm{pH} - \mathrm{p}K_1 + \log(1 + K_2/[\mathrm{H}^+]) \qquad (2)$$

As long as one is at least 1 pH unit below pK_2, the last term in eq 1 is small (<0.04) and can be approximated as $(\ln 10)^{-1} K_2/[\mathrm{H}^+]$. At p$K_1$, this becomes $(0.43)K_2/K_1$. In the present case, the first estimate of the equilibrium constants indicated K_2/K_1 to be ~0.025, so at pK_1 the last term in eq 2 corresponds to only 0.01. One can, therefore, determine pK_1 within experimental error from the pH at which ([II] + [III])/[I] is unity. This latter ratio can be obtained from the data at 280 nm where A is the measured absorbance at this wavelength at a given pH and A_L and A_H are the limiting absorbances at low and at high pH, i.e.

$$([\mathrm{II}] + [\mathrm{III}])/[\mathrm{I}] = (A - A_\mathrm{L})/(A_\mathrm{H} - A) \qquad (3)$$

The data, plotted in the form of eq 2 in Figure 2, give pK_1 as 5.93. The data at 258 nm, where it turns out that the ionic forms II and III have a second isosbestic point, exhibit a similar dependence corresponding to a pK_1 of 5.90. However, the difference between the extinction coefficients at this latter wavelength is small, so the possible error is somewhat larger than for the data at 280 nm.

The value of pK_2 was obtained from a plot in accord with eq 1 with [A] = [II] and [B] = [III]. A preliminary survey of the spectra indicated from changes observed above pH 6.5 that the extinction coefficients of forms II and III were significantly different at ~300 nm. The ratio [III]/[II] was obtained from the values of A, A_L, and A_H measured at 300 nm after correction for the contribution of I, which was small and could be derived at a given pH from its extinction coefficient and the known value of pK_1. The plot of the data in Figure 2 gives pK_2 as 7.63.

Correction of the above p*K*'s for ionic strength gives pK_1 as 6.0 ± 0.1 and pK_2 as 7.7 ± 0.1 at zero ionic strength. Both of these pK_a's are 3.8 units lower than those for the comparable equilibria in hydroquinone, where the corresponding pK_a's are 9.8 and 11.5.[9] The spectrum of II given in Figure 1 was obtained from the

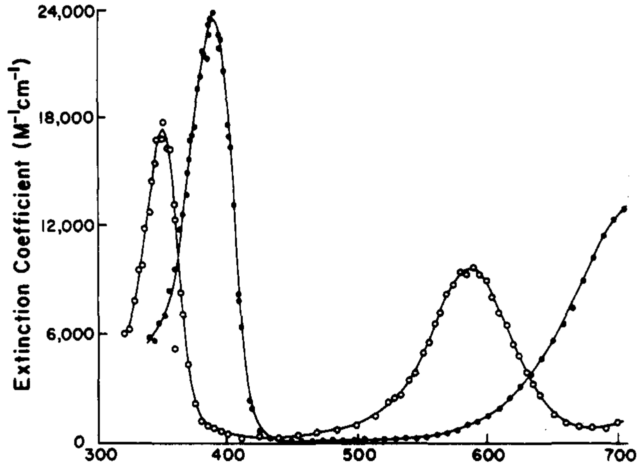
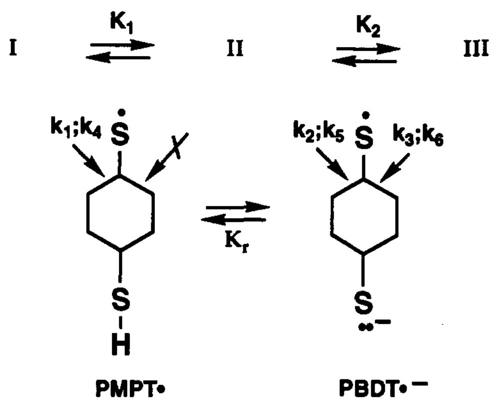


Figure 3. Absorption spectra of p-$HSC_6H_4S^{\bullet}$ (○) and p-$C_6H_4S_2^{\bullet -}$ radicals (●) as determined 4 μs after pulse irradiation of a N_2O-saturated 0.4 mM solution of PDMB containing 0.1 M sodium formate at pH 0 and at pH 7.5. Extinction coefficients are based on thiocyanate dosimetry with the radical yield at time zero taken as 6.0.

recording at pH 6.5 with corrections made for the contributions from I and III as given by their spectra and the values of K_1 and K_2.

Absorption Spectra of the Radicals. It is expected that PDMB should be readily oxidizable to produce the p-mercaptophenylthiyl radical in acidic solution or p-benzodithiyl radical anion in basic solution, i.e.



Although •OH also oxidizes PDMB, because of its selectivity, we have used $CO_2^{\bullet -}$ to abstract H from the SH group of I and II in acidic solutions[10,11] and $N_3^{\bullet}$ to oxidize II and III in basic solutions by electron transfer.[12] Because the pK of the radical (pK_r) is considerably below pK_1 (see below), one cannot, as indicated, oxidize the anions directly to the neutral radical.

The spectra shown in Figure 3 were obtained 4 μs after pulse irradiation of a N_2O-saturated solution containing 0.4 mM PDMB and 0.1 M sodium formate at pH 0 and 7.5. The spectrum at the lower pH is attributed to the neutral radical and that at the higher pH to the radical anion. A spectrum essentially identical to the latter was observed in neutral and basic solutions on oxidation of PDMB by $N_3^{\bullet}$. Its assignment to $C_6H_4S_2^{\bullet -}$ is confirmed by Raman studies, which will be reported separately.[13] These spectra contrast with those of p-benzosemiquinone radical ($HOC_6H_4O^{\bullet}$) and its anion ($C_6H_4O_2^{\bullet -}$), which have their lowest energy absorption bands at 415 and 430 nm, respectively.[14,15] From the fact that the absorption of phenylthiyl radical at 460 nm is ~0.4 eV lower in energy than the related 400-nm band in phenoxy,[3] one expects a considerable shift to the red in the present case. The bands at 585 and ~700 nm very likely represent electronic transitions related to those observed in the p-benzosemiquinone radicals but lower in energy by ~1 eV. The narrower bands at 350 nm for $HSC_6H_4S^{\bullet}$ and 385 nm for $C_6H_4S_2^{\bullet -}$ almost certainly cannot be correlated with the 415- and 430-nm absorptions of the benzosemiquinone radicals. More likely they are related to bands which are considerably further into the UV in the latter case.

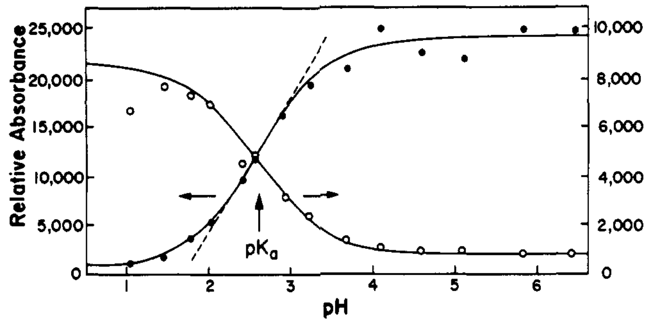


Figure 4. pH dependences of the absorbance at 390 nm (●, left scale) and at 585 nm (○, right scale). The slope of the data at 390 nm expected from eq 4 at the inflection point (see text) is indicated by the dashed line. The inflection points correspond to a pK_a of 2.6 at an ionic strength of 0.1.

pK_r of p-Mercaptophenylthiyl Radical. The pH dependences of the absorbances at 390 and 585 nm are displayed in Figure 4. Both dependences exhibit sigmoidal curves which correspond to a simple equilibrium between PMPT• and PBDT•−. Near the inflection points at pH ~ 2.6, the slope of the pH dependence of the extinction coefficient should be given by the relation[16]

$$\frac{\Delta\epsilon}{\Delta \mathrm{pH}} \geq \frac{\epsilon_A - \epsilon_B}{1.737} \qquad (4)$$

where ϵ_A and ϵ_B are the extinction coefficients of the acidic and basic forms of the radical. Using eq 4, the limiting slope for the data at 390 nm, calculated from the difference between the extinction coefficients of the two forms of the radical, is given by the dashed line in figure 4. Using this slope to correct the data between pH 2.0 and 3.3, we obtain pK_a for the p-mercaptophenylthiyl radical (also referred to as pK_r) as 2.62 ± 0.12 from the measurements at 390 μm. A pK_r of 2.52 ± 0.12 was obtained by a similar treatment of the data at 585 μm, where there is, however, somewhat more scatter. Giving the former a weight 3 times the latter leads to a net pK_r of 2.60 ± 0.07. Correcting for ionic strength, one obtains a pK_r of 2.70 at zero ionic strength. Assuming normal acid–base equilibrium dynamics between the two forms of the radical, this low pK indicates that equilibration should be complete on the nanosecond time scale. There is no evidence in the kinetic traces that this is not the case.

Oxidation Rates. The oxidation rates were determined by following the pseudo-first-order buildup of the absorptions at the appropriate maxima. As shown in Figure 5, these rates were found to be strongly dependent on pH for both $CO_2^{\bullet -}$ and $N_3^{\bullet}$. The pK's of PDMB expected at the high ionic strength in these experiments (~0.1 M) are given by the arrows in the figure. As indicated below, the observed rate constants reflect differences in the rate of reaction with the different forms of PDMB.

The rate for the reaction with $CO_2^{\bullet -}$ falls with increasing pH. At low pH, the rate constant (k_1) for abstraction of H from PDMB by CO_2^-

$$C_6H_4(SH)_2 + CO_2^{\bullet -} \xrightarrow{k_1} HSC_6H_4S^{\bullet} + HCO_2^-$$

is found to be (3.1 ± 0.3) × 10^9 M^{-1} s^{-1}. The reaction was not observed above pH 9, indicating that $CO_2^{\bullet -}$ does not react rapidly with the PDMB dianion; i.e., $k_3 < 10^8$ M^{-1} s^{-1}. Taking into account the shift in K_1 because of the high ionic strength, the rates observed in the region of pH 7-8 indicate that k_2 for reaction

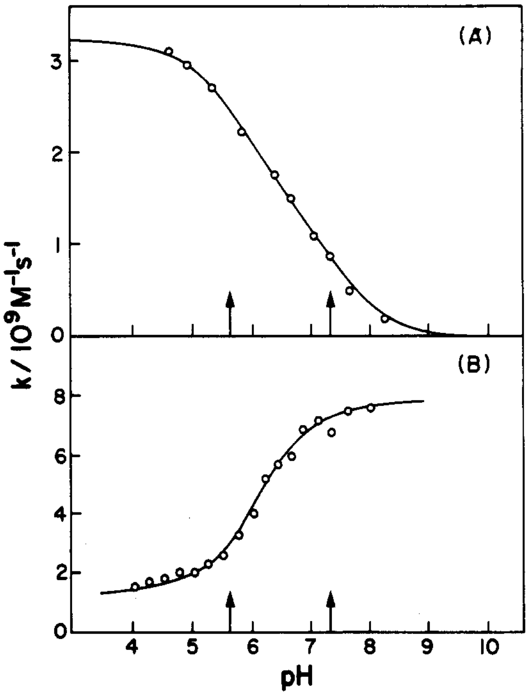


Figure 5. pH dependence of the rate constants for oxidation of PDMB by (A) $CO_2^{\bullet -}$ and (B) $N_3^\bullet$. These dependences are described well by the weighted average of the different ionized forms of PDMB, as indicated in the text.

of CO_2^- with the monoanion

$$HSC_6H_4S^- + CO_2^{\bullet -} \xrightarrow{k_2} C_6H_4S_2^{\bullet -} + HCO_2^-$$

is $(1.5 \pm 0.2) \times 10^9$ M^{-1} s^{-1}. The appropriately weighted average of these values describes the pH dependence as shown by the solid curve in Figure 5A.

Azide radical oxidizes neutral phenols somewhat slowly in acidic solution,[12] so it is not surprising that the rate constant observed for reaction of $N_3^\bullet$ with PDMB below pH 5 is relatively low. From the rates observed in the region of pH 4, the rate constant for electron transfer from the neutral substrate (k_4) is 1.8×10^9 M^{-1} s^{-1}. In this case, electron transfer is followed by loss of a proton to produce the radical anion, but the equilibrium data given above indicate that this latter step should be sufficiently rapid that it will not be rate determining. In basic solutions, the measured rate constant (k_6) is $(7.4 \pm 0.4) \times 10^9$ M^{-1} s^{-1}. The data in the region of pH 7 indicate that k_5 cannot be appreciatively less. The fact that the inflection point in Figure 4 is slightly above pK_1 of PDMB indicates that k_5 is ~10–20% below k_6. The solid curve represents the weighted average rate constant based on the above values for k_4 and k_6 taking k_5 as 6.0×10^9 M^{-1} s^{-1}. This latter value is, however, estimated to be accurate to only ~20%.

Second-Order Decay of the Radicals. Because *p*-benzosemiquinone radical anion does not undergo rapid second-order decay, it was somewhat surprising to find that even at micromolar concentration its sulfur analog decayed appreciably on the microsecond time scale. The decay observed at pH 7.5, illustrated in Figure 6, fits extremely well to second-order kinetics with $2k$ equal to 2.8×10^9 M^{-1} s^{-1} (solid curve in Figure 6). Similar, but even more rapid, decay of the neutral radical is also observed. The data at pH 0 can be fitted with $2k$ taken as 4.0×10^9 M^{-1} s^{-1}. This high value is less surprising than that for the radical anion since the phenylthiyl radical has been observed to undergo second-order decay with a rate constant of 9.6×10^9 M^{-1} s^{-1}.[3] The fact that the rate constant observed here is lower than that of phenylthiyl radical shows that the SH substituent has some effect on the electronic structure, as is, of course, also manifested in the absorption spectra.

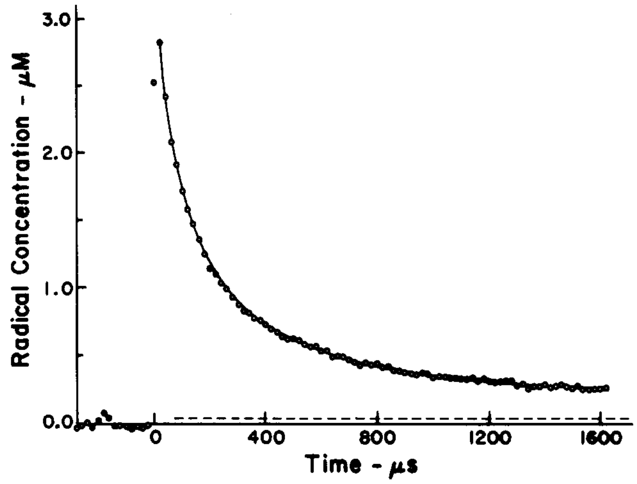


Figure 6. Decay at pH 7.5 of the signal of *p*-$C_6H_4S_2^{\bullet -}$ at 390 nm. Solid curve corresponds to second-order decay with a rate constant ($2k$) of 2.8×10^9 M^{-1} s^{-1} superimposed on a small background signal, indicated by the dashed line.

Reduction Potential of *p*-Benzodithiyl Radical Anion.[17,18] Because of the central importance that the *p*-benzosemiquinone radical anion has in electron-transfer chemistry, the reduction potential of its sulfur analog, $C_6H_4S_2^{\bullet -}$, should provide important information on the electron-transfer properties of aromatic sulfur radicals. We have used pulse radiolysis methods to examine directly the electron-transfer equilibria between several substituted phenoxy radicals and PDMB in basic solution to determine the one-electron reduction potential for the half-cell reaction

$$^-SC_6H_4S^\bullet + e^- \rightleftarrows SC_6H_4S^-$$

In view of the limited amount of PDMB available, design of appropriate experiments required that electron transfer from the PDMB dianion to the phenoxy radical be examined in the forward direction, i.e.

$$XC_6H_4O^\bullet + {}^-SC_6H_4S^- \underset{k_{-T}}{\overset{k_T}{\rightleftarrows}} XC_6H_4O_6^- + {}^-SC_6H_4S^\bullet$$

This requirement means, in turn, that the reference radical must have a reduction potential 0.1–0.2 V higher than that of $PBDT^{\bullet -}$. Because of the rapid decay of the dithiyl radical anion, the rate of electron transfer must also be sufficiently rapid that equilibration be essentially complete within 100 μs after the pulse at PDMB concentration of $\sim 10^{-4}$ M.

The initial experiments were carried out with *p*-methoxyphenoxy and *p*-aminophenoxy radicals prepared by the $N_3^\bullet$ oxidation of the corresponding phenols at pH 13. The experiments with *p*-methoxyphenoxy radicals, for which E^0 has been reported to be 0.54 V,[19,20] indicated that the electron-transfer equilibrium lay too far to the right for an accurate determination of K_T to be made readily with the amount of material available. In the case of *p*-aminophenoxy radical, for which E^0 is 0.22 V,[21] it was found that the equilibrium lay somewhat to the left. The rate of approach to equilibrium in this latter case also was very slow, precluding a detailed study. These preliminary measurements place limits of ~0.2 and 0.5 V on the reduction potential of $C_6H_4S_2^{\bullet -}$.

The resorcinol radical anion, which has a reduction potential of 0.48 V at pH 13.5,[22] was ultimately chosen as an appropriate electron acceptor. This radical has an absorption band at 425 nm where $C_6H_4S_2^{\bullet -}$ absorbs only weakly (but significantly relative to the resorcinol radical anion) and has an almost negligible absorption at 390 and 700 nm, where the production of $C_6H_4S_2^{\bullet -}$ could be followed readily. Resorcinol has pK's of 9.3 and 11.1, so protonation equilibria are not involved in the measurments at pH > 13.

The rates of equilibration were determined from the time

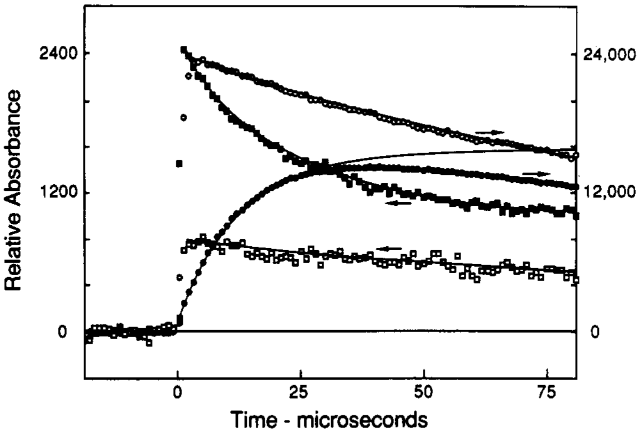


Figure 7. Time dependence of the absorption at 390 nm (●, ○; right scale) and at 425 nm (■, □; left scale). Open points are for a 0.1 mM PDMB solution at pH 13 and solid points for a solution containing 20 mM resorcinol. In the latter case, electron transfer from the *p*-dimercaptobenzene dianion to the resorcinol radical anion is manifested by the growth of the absorption at 390 nm with a half-period of 8.9 μs and the complementary decay of signal at 425 nm.

dependences of the absorption of $C_6H_4S_2^{\bullet-}$ at 390 and 700 nm. The data at 390 nm for a solution 0.1 mM in PDMB and 20 mM in resorcinol (RES) are given by the solid circles in Figure 7. It is seen in the figure that the growth of the 390-nm absorption is mirrored by a decrease in the absorption of the resorcinol radical anion at 425 nm (solid squares) with, however, an overall decay of both radicals superimposed at each wavelength. Comparative data for the decay of $C_6H_4S_2^{\bullet-}$, observed when solutions containing only PDMB are irradiated, are also given by the open points in the figure. The half period for the electron transfer determined from the initial growth rate is 8.9 μs, indicating that equilibrium should be 99% complete after ~60 μs. In the absence of PDMB, the resorcinol radical anion does not decay on this time scale. However, it does decay in the mixture by virtue of its equilibrium with $C_6H_4S_2^{\bullet-}$.

The dependence of the electron-transfer rate constant, as measured from the periods for buildup of $C_6H_4S_2^{\bullet-}$, is given in Figure 8 for different relative concentrations of resorcinol and PDMB. The data are plotted in the form of eq 5:

$$\frac{k_{\mathrm{obs}}}{[\mathrm{PDMB}]} = k_{\mathrm{T}} + k_{-\mathrm{T}}\frac{[\mathrm{RES}]}{[\mathrm{PDMB}]} \qquad (5)$$

It is seen that for solutions 0.1 mM in PDMB (solid points in Figure 8) the observed rate constant increases by ~50% with an increase in resorcinol concentration from 1 to 20 mM, so it is clear that at the higher concentrations the back-reaction contributes appreciably to the observed pseudo-first-order rate constant. The plot of Figure 8 allows k_{T} to be determined from the intercept (5.3×10^8 M^{-1} s^{-1}) and $k_{-\mathrm{T}}$ from the slope (1.3×10^6 M^{-1} s^{-1}). The ratio of these two rate constants gives an equilibrium constant of 408 for the electron transfer in reaction 1. While the forward rate constant should be accurate to ~5%, there is a considerably larger uncertainty in the slope, so a probable error of ±50 is assigned to this value of the equilibrium constant as determined from the rate information. Both of these rate constants pertain to solutions having an ionic strength of ~0.2. However, in this case the charge exchange is symmetrical, so the rates of both forward and reverse reactions should be similarly affected by the high ionic strengths present in these experiments, and there should be essentially no effect on the equilibrium constant.

Calculation of the equilibrium constant from the absorption data at long times is somewhat more complicated. The kinetic data indicate that at 0.1 mM PDMB equilibrium is attained only after ~60 μs, at which point the concentration will have decayed by ~25%. However, since resorcinol radicals decay appreciably only by reaction with $C_6H_4S_2^{\bullet-}$ radicals, the overall radical decay will be delayed and will depend on the relative level of the two radicals. As a result, the fractional decay will be less in the mixed system than for a system containing only PDMB. Also, because of interference with intratrack processes, the total radical yield will increase with resorcinol concentration. From the initial absorbance at 425 nm, we estimate that the total radical concentration increases by 8% at 10 mM and 10% at 20 mM resorcinol. These complications make it virtually impossible to determine the concentration ratio at equilibrium with meaningful accuracy from simple differences in the absorbance.

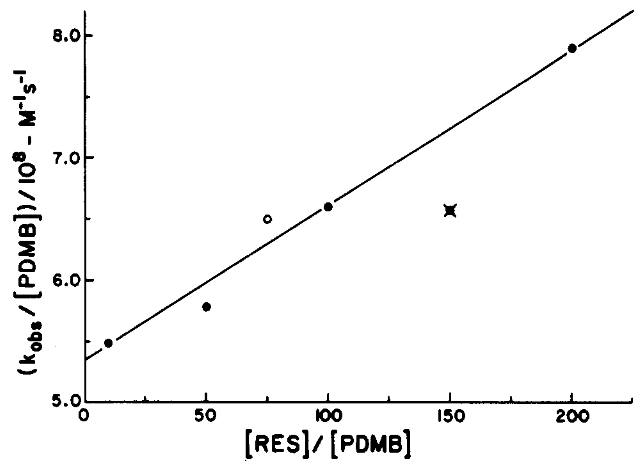


Figure 8. Dependence of the pseudo-first-order rate constant for electron transfer on the relative concentrations of *p*-dimercaptobenzene (PDMB) and resorcinol (RES): ● for solutions 0.1 mM in PDMB, ○ for a solution 0.2 mM in PDMB and 15 mM in RES, and ⊗ for a solution 0.07 mM in PDMB and 10 mM in RES. The forward rate constant (k_8) is given by the intercept as 5.3×10^8 M^{-1} s^{-1} and the reverse rate constant (k_{-8}) by the slope as 1.3×10^6 M^{-1} s^{-1} (cf eq 5 in text).

We have taken the approach of relating *f*, the fraction of the radicals in the form of the dithiyl radical, to *R*, the ratio of the relative absorbances at 390 and 425 nm, assuming that the decay factor *D* in the mixed system is the same for both radicals. While this latter assumption is not rigorous, it should be a reasonably good approximation since the concentration of the resorcinol radical anion is controlled by its equilibrium with $C_6H_4S_2^{\bullet-}$. With these definitions, the relative absorbance at 390 nm is given by

$$A_{390} = [f\epsilon_{390}(\mathrm{S}) + (1-f)\epsilon_{390}(\mathrm{O})]D \qquad (6)$$

and that at 425 nm by

$$A_{425} = [f\epsilon_{425}(\mathrm{S}) + (1-f)\epsilon_{425}(\mathrm{O})]D \qquad (7)$$

The values of $\epsilon(\mathrm{S})$ are the appropriate coefficients for the dithiyl radical anion and those of $\epsilon(\mathrm{O})$ for the resorcinol radical anion at 390 and 425 nm, after correction for the increased yields. Taking *R* as A_{390}/A_{425} eliminates *D* and allows solution of these equations for *f*.

$$f = \frac{R\epsilon_{425}(\mathrm{O}) - \epsilon_{390}(\mathrm{O})}{\epsilon_{390}(\mathrm{S}) - \epsilon_{390}(\mathrm{O}) - R(\epsilon_{425}(\mathrm{S}) - \epsilon_{425}(\mathrm{O}))} \qquad (8)$$

One can then determine *D* from eq 6 to see if this approach gives a decay factor reasonably in accord with expectations.

The most internally consistent data were those presented in Figure 7, where the fraction of radicals found in the form of the dithiyl anion was 0.67 and the decay factor at 75 μs was found to be 0.73, as compared to 0.66 when resorcinol was not present. The equilibrium constant is, of course, given by

$$K_{\mathrm{T}} = \frac{f}{1-f}\frac{[\mathrm{RES}]}{[\mathrm{PDMB}]} \qquad (9)$$

which for the data of Figure 7 is 416. With a similar treatment, an experiment at 0.1 mM PDMB and 10 mM resorcinol gave K_{T}

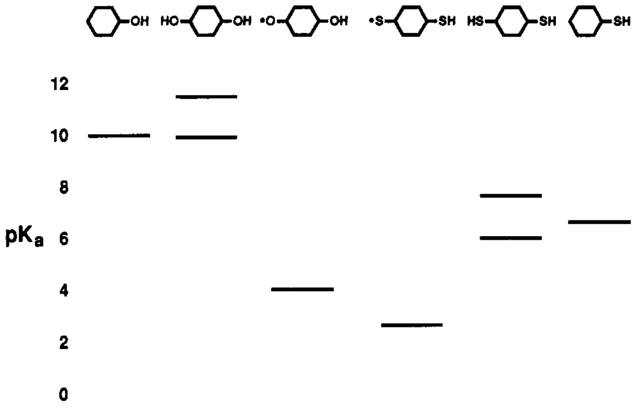


Figure 9. pK_a's for ionization of SH and OH protons.

as 284 and that at 0.2 mM PDMB and 15 mM resorcinol gave K_T as 221. These differences in K_T are largely attributable to the uncertainty in the small contributions from the resorcinol radical at equilibrium. The average of these values gives an equilibrium constant for electron transfer of 310 ± 70. The results for the remaining experiments, while not in disagreement with this value, are regarded as much less reliable because of low concentrations of the resorcinol radical or slowness in the attainment of equilibrium.

The differences in the reduction potential corresponding to the equilibrium constants determined from the kinetic and absorption measurements are respectively 0.154 ± 0.003 and 0.147 ± 0.005 V. Taking the reference potential of the resorcinol radical anion/resorcinol couple as 0.48 V,[22] one obtains 0.33 ± 0.02 V for the reduction potential of the PBDT$^{\bullet-}$/PDMB couple at pH 13.

General Summary

As commented on earlier, the electronic spectra of the PMPT$^{\bullet}$ and PBDT$^{\bullet-}$ radicals are shifted considerably to the red from the spectra of their oxygen analogs, manifesting considerable differences between the electronic structures of these two types of radicals. These differences are manifest in the acid dissociation constants, reduction potentials, and the second-order kinetics, as discussed in this section.

Acid–Base Equilibria. In general, SH protons are considerably more acidic than OH protons, as exemplified by the considerable difference between the pK_a's of methanol (pK_a = 15.5) and methanethiol (pK_a = 10.3) and between phenol (pK_a = 9.9) and thiophenol (pK_a = 6.6).[9] The difference between the protonation equilibria of *p*-dimercaptobenzene and hydroquinone and their radicals is emphasized in Figure 9. It is seen that the pK_a of the *p*-mercaptophenylthiyl radical ($HSC_6H_4S^{\bullet}$) is only 3.3 units lower than pK_1 of its parent compound, while the corresponding difference in the case of *p*-benzosemiquinone (i.e., *p*-hydroxyphenoxy radical, $HOC_6H_4O^{\bullet}$) is 5.8 units. It is clear from this difference that on radical formation the increase in polarity is much less in the SH bond of *p*-$HSC_6H_4S^{\bullet}$ than in the OH bond of the *p*-$HOC_6H_4O^{\bullet}$ radical. This difference is in accord with the relatively higher localization of the unpaired spin on the sulfur atom indicated by the Raman data on phenylthiyl radical.[3] The differences in these free energies of ionization are, of course, reflected in the reduction potentials of the radicals, as discussed in the next subsection.

Reduction Potentials. The reduction potential of 0.33 V given above for the dithiyl radical anion can be compared to the $E^0(C_6H_5S^{\bullet}/C_6H_5S^-)$ value of 0.70 V determined for the half-cell reaction

$$C_6H_5S^{\bullet} + e^- \rightarrow C_6H_5S^-$$

by comparison with the reduction potential of phenoxy radical.[23] The decrease of 0.37 V (36 kJ/mol) is largely attributed to

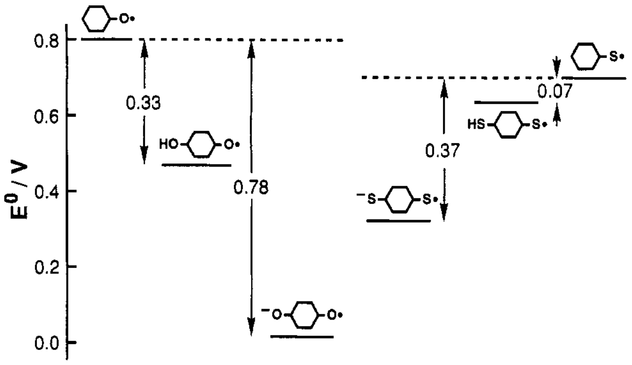


Figure 10. Comparison of the reduction potentials of the phenoxy and phenylthiyl radicals. Reduction potentials for the cases where the products are protonated are given in the text. The reduction potentials of $HOC_6H_4O^{\bullet}$ and $HSC_6H_4S^{\bullet}$ are virtual and given only to indicate their values relative to $C_6H_5O^{\bullet}$ and $C_6H_5S^{\bullet}$ (see text).

stabilization of the radical anion as the result of delocalization of the unpaired spin population. In the analogous case of *p*-benzosemiquinone radical anion, which has a reduction potential of 0.023 V,[18] the stabilization energy is considerably greater, 0.78 V (75 kJ/mol), as measured by the decrease in the reduction potential from that observed for phenoxy radical (0.80 V).[18] These differences are illustrated in Figure 10. We point out here that the reduction potentials of both the phenylthiyl and *p*-phenyldithiyl radicals have, in effect, been measured relative to the reduction potential of phenoxy radical so that the energy differences of the sulfur radicals indicated in Figure 10 should be reasonably accurate (see ref 22). The fact that the stabilization energy is lower by 0.41 V (39 kJ/mol) in the case of the dithiyl radical anion than in the case of $C_6H_4O_2^{\bullet-}$ is the manifestation of a much lower degree of delocalization of the unpaired spin in the former case. At this point we assume that, as is also indicated by the Raman data,[15] the unpaired spin is largely distributed between the two sulfur atoms of PBDT$^{\bullet-}$ rather than being substantially on the ring of PBSQ$^{\bullet-}$, as is indicated by the latter's ring proton hyperfine constant of 2.38 G in aqueous solution[24] and also by Raman data.[25] Unfortunately, because of line broadening by the sulfur atoms, the hyperfine splittings of the ring protons of PBDT$^{\bullet-}$ are not directly available from ESR measurements.

The reduction potential of 0.33 V for PBDT$^{\bullet-}$ can be combined with the free energy differences from the ionization constants given above to obtain half-cell potentials for the cases where the reaction products and/or the radical are protonated. Above pH 9, the reactants on both sides of the electron-transfer equilibrium are essentially fully ionized, so the reduction potential will be constant. At lower pH's, the half-cell potential will increase by virtue of the products being protonated. By adding 0.46 V (i.e., 0.0591pK_2) to correct for the free energy of ionization of $HSC_6H_4S^-$, one obtains a half-cell potential, $E^0({}^{-}SC_6H_4S^{\bullet},H^+/HSC_6H_4S^-)$, of 0.79 V for the reaction

$${}^{-}SC_6H_4S^{\bullet} + e^- + H^+ \rightarrow HSC_6H_4S^-$$

The latter reaction is of prime importance in the pH region between the two pK's of PDMB. The reaction

$${}^{-}SC_6H_4S^{\bullet} + e^- + 2H^+ \rightarrow HSC_6H_4SH$$

becomes important and dominates between pK_1 and pK_r. An additional contribution of 0.35 V (0.0591pK_1) must be added to give 1.14 V for the half-cell potential, $E^0({}^{-}SC_6H_4S^{\bullet}, 2H^+/HSC_6H_4SH)$, for this reaction. In very acidic solutions (below pH 2.7), where the radical is protonated before reduction, contribution of 0.15 V (0.0591pK_r) must be subtracted to give the potential ($E^0(HSC_6H_4S^{\bullet}, H^+/HSC_6H_4SH)$ as 0.99 V for reduction of the protonated radical.

$$HSC_6H_4S^{\bullet} + e^- + H^+ \rightarrow HSC_6H_4SH$$

One can also calculate a value of 0.63 V for the reaction

$$HSC_6H_4S^\bullet + e^- \rightarrow HSC_6H_4S^-$$

by adding 0.0591(pK_2 - pK_r) to 0.33 V, although this reaction does not contribute directly to the observed potentials since the radical is not significantly protonated at any pH where PDMB is ionized. This latter value is, however, important since it can be compared with the reduction potential of 0.70 V for the phenylthiyl radical. The difference of 0.07 V can be compared with the analogous difference of 0.33 V (see Figure 10) between the reduction potentials (0.80 V) of phenoxy radical and *p*-benzosemiquinone (0.47 V). These differences are essentially the same as the corresponding differences of 0.10 and 0.36 V calculated at low pH, where the radicals and products are fully protonated. In the case of phenoxy radical, the substantial decrease in the reduction potential in the case of the semiquinone radical is not surprising since ESR proton hyperfine constants show that there is appreciable unpaired spin (~0.8) on the ring. As a result, one expects a strong interaction between the OH substituent and the radical's electronic system, as also demonstrated by the Raman studies.[25] The much smaller decrease in the reduction potential for the *p*-mercaptophenylthiyl radical is in accord with the conclusion from the Raman experiments[3] that the unpaired spin in phenylthiyl radical is more highly localized on the sulfur atom than on the oxygen atom in the case of phenoxy radical.

Second-Order Kinetics. A final comment must be made on the observed high second-order decay rate for the anionic forms of the radical. This high rate contrasts with the absence of any observable decay of *p*-benzosemiquinone radical anion when it is produced at high pH. In the latter case the reduction potential is lower than that of benzoquinone (0.078 V), so the radical anion is stable toward both oxidation and reduction by interradical electron transfer. While phenylthiyl radicals combine at a diffusion control rate, the observed rapid decay of the dithiyl radical anion can also result from electronic disproportionation between radicals, i.e.

$$^-SC_6H_4S^\bullet + {}^-SC_6H_4S^\bullet \rightarrow {}^-SC_6H_4S^- + SC_6H_4S$$

This reaction will occur only if the free energy of the intermediate radical is above that of the two products. The present measurements suggest an upper limit of 0.33 V for the two-electron reduction potential of the thioquinone.

References and Notes

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