(9) C. J. Weschler and E. Deutsch, *Inorg. Chem.*, **15**, 139 (1976).
(10) R. J. Balahura and R. B. Jordan, *J. Am. Chem. Soc.*, **92**, 1533 (1970).
(11) R. J. Balahura and N. A. Lewis, *J. Chem. Educ.*, **53**, 324 (1976).
(12) V. M. Kothari and D. H. Busch, *Inorg. Chem.*, **8**, 2276 (1969).
(13) R. J. Balahura and L. S. Hutley, *Can. J. Chem.*, **51**, 3712 (1973).
(14) N. A. Lewis, Ph.D. Thesis, University of Guelph, 1977.
(15) L. E. Asher and E. Deutsch, *Inorg. Chem.*, **11**, 2927 (1972).
(16) R. H. Lane, Ph.D. Thesis, University of Florida, 1971.
(17) F. A. Sedor, Ph.D. Thesis, University of Florida, 1971.
(18) M. J. Gilroy, Ph.D. Thesis, University of Florida, 1971.
(19) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).
(20) A. Laing and E. S. Gould, *J. Am. Chem. Soc.*, **92**, 6791 (1970).

(21) D. A. Buckingham, J. M. Harrowfield, and A. M. Sargeson, *J. Am. Chem. Soc.*, **95**, 7281 (1973).
(22) E. Deutsch and L. E. Asher, submitted for publication in *Inorg. Chem.*
(23) R. Lane, F. Sedor, M. Gilroy, and L. Bennett, *Inorg. Chem.*, **16**, 102 (1977).
(24) F. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, **90**, 1162 (1968).
(25) L. E. Asher and E. Deutsch, *Inorg. Chem.*, **15**, 1531 (1976).
(26) P. George and J. S. Griffith, "The Enzymes", Vol. I, Academic Press, New York, N.Y., 1959, p 347.
(27) H. Taube and E. S. Gould, *Acc. Chem. Res.*, **2**, 321 (1969).
(28) R. Lane, F. Sedor, M. Gilroy, P. Eisenhardt, J. Bennett, Jr., R. Ewall, and L. Bennett, *Inorg. Chem.*, **16**, 93 (1977).

Metal Ion Catalyzed Oxidation of o-Dihydroxy Aromatic Compounds by Oxygen. 1. Redox and Acid–Base Properties of the System 1,2-Naphthoquinone-4-sulfonate/1,2-Dihydroxynaphthalene-4-sulfonate

JACQUES BUFFLE and ARTHUR E. MARTELL*

The redox and acid–base equilibria of the oxygen-sensitive couple 1,2-naphthoquinone-4-sulfonate (Q)/1,2-dihydroxynaphthalene-4-sulfonate (PH$_2$) have been determined at 25 °C and 0.10 M ionic strength. The successive proton formation constants of PH$_2$, $10^{12.66\pm0.02}$ and $10^{8.14\pm0.04}$ M^{-1}, were obtained by spectrophotometric and potentiometric measurements, respectively. The same values were obtained with both classical and pulsed polarography, and with the latter method the pK of the quinone hydrate was found to be $10^{10.51\pm0.05}$ M^{-1}. From the variation in the slope of the log plot of the polarographic curves with pH, the equilibrium constant for semiquinone (SQ) formation was evaluated as $K(Q + P \rightleftharpoons 2SQ) = 10^{3.2}$. The optical spectrum of the semiquinone was also determined. A special cell was used to carry out simultaneously electrochemical synthesis, potentiometric measurements, and spectrophotometric determinations.

Introduction

Although several authors[1-5] have studied the oxidation reactions of o-dihydroxy aromatic compounds and their metal complexes by dioxygen and by hydrogen peroxide, all of these investigations have been made using benzene derivatives.[6-11] Our preliminary studies[12] have shown that the oxidation of o-phenols such as tiron and catechol by oxygen, even in the presence of a catalyst such as Fe(III), is very slow around neutral pH values. This behavior was attributed to the fact that the standard potential of the Fe^{2+}/Fe^{3+} couple ($E_{Fe}° = 0.749$ V[13]) is lower than the standard potentials of these two catechols.

The literature values[14-19] of the standard potentials of o-dihydroxy aromatic compounds indicate that compounds possessing fused aromatic rings should oxidize more readily than o-diphenols at neutral pH values, i.e., under conditions similar to those found in naturally occurring systems. However, not much work regarding the systematic study of the oxidation–reduction, acid–base, and complexation properties of these compounds has been reported. The practical difficulty of preventing the oxidation of these compounds by atmospheric oxygen has probably been a major deterrent for undertaking such studies.

This paper describes a study of the 1,2-naphthoquinone-4-sulfonate (II)/1,2-dihydroxyhaphthalene-4-sulfonate (I)

I, PH$_2$ II, Q
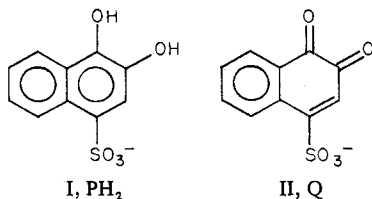
couple, Q/PH$_2$, and also describes the properties of this system

from the redox and acid–base points of view.

Experimental Section

Instruments and Reagents. The major apparatus used in this study includes a Beckman pH meter, Model 1019, a Metrohmn pH meter, E 500, Cary 14 and Beckman DBG spectrophotometers, PAR (electrochemistry system No. 170) and Tacussel (modules PRT 30 and UAP 4) polarographs, and a Beckman Electroscan 30 controlled-potential electrolyzer. The cell is described below.

Unless otherwise stated all reagents used were of analytical grade. Solutions were deaerated by purging them with nitrogen gas of 99.99% purity as certified by Bertholet S. A.

Syntheses. Potassium Salt of 1,2-Naphthoquinone-4-sulfonic Acid (Q). A commercially available sample of the potassium salt of 1-amino-2-naphthol-4-sulfonic acid was oxidized to the o-quinone with concentrated nitric acid. The product was recrystallized from water in the presence of bromine.[20,21] Golden yellow needles of the potassium salt of 1,2-naphthoquinone-4-sulfonic acid were obtained and their purity was determined by the UV–visible spectrum of the compound which was found to be identical with that obtained by Rosenblat et al.[22] and by the Danielson test.[23]

Lithium Salt of 1,2-Dihydroxynaphthalene-4-sulfonic Acid (PH$_2$). Two methods (SO$_2$[20] or Na$_2$S$_2$O$_4$[24]) for reducing Q to PH$_2$ are described in the literature. In our laboratories neither of these methods gave satisfactory results. The SO$_2$ reduction was incomplete, and in the second method, the product obtained was found contaminated. PH$_2$ was therefore prepared by reducing Q with a slight excess of Na$_2$S$_2$O$_3$ at pH ~2 using a minimum of water.

After filtration the product was separated from the solution by the addition of a saturated solution of LiCl. If too much LiCl is added, it coprecipitates with the product. The pH of the reaction must be kept at about 2 since the oxidation by air is rapid at higher pH values. For the same reason, filtration must be carried out very rapidly.

Colorless needles of PH$_2$ were obtained and the following tests showed that the purity of the compound was satisfactory: (1) the UV–visible spectrum obtained after oxidizing an 8×10^{-5} M solution in PH$_2$ with 1.6×10^{-4} M Ce(IV) in the presence of sulfuric acid (0.005 M) was identical with that of an 8×10^{-5} M solution of Q in the same

medium. (2) It was found that the half-wave potentials of the reduction wave of Q and oxidation wave of PH_2, in the pH range 1–6, were identical at a given pH. Moreover, the limiting diffusion currents of the two polarographic waves were equal when the concentrations of Q and PH_2 were equal. These results are in agreement with the report in the literature that the redox system PH_2/Q is a reversible system.[15] As the diffusion coefficients of Q and PH_2 are expected to be equal, this result taken together with that obtained from the UV–visible spectrum shows that that the impurities in PH_2, if present at all, are less than 1–2%. No report on the entire UV–visible spectrum of PH_2 could be found in the literature; however, the spectrum of this compound in aqueous acidic medium was found to resemble the spectrum of 1,2-naphthalenediol taken in a mixture of 95% ethanol and 5% aqueous HCl and in benzene[25,26] and is also in agreement with the spectrophotometric maxima reported by Kano and Matsuo.[27]

Electrochemical Synthesis of PH_2. In order to ensure a total oxygen-free environment during experimental runs in order to avoid oxygen contamination during isolation, transfer, and solution preparation, PH_2 was synthesized by electrochemical reduction of Q under nitrogen in a cell which could be used subsequently to study its properties. This method enables one to avoid the introduction of trace metal impurities by the reagents used as well as to avoid the precipitation step which is rather difficult to carry out in the chemical preparation of this compound.

Apparatus. The electrolysis was carried out with a platinum electrode whose potential was controlled with respect to an Ag/AgCl/NaCl 1 M reference electrode which was connected to the solution by means of a 0.1 M $NaClO_4$ salt bridge. The volume of the experimental solution was 40 mL. The auxiliary electrode was connected to the solution by an agar–agar salt bridge. The bridge was removed without opening the cell prior to any measurement made after the electrolysis, thus avoiding diffusion losses into the agar–agar bridge. Experimentally it was found that diffusion into the bridge was negligible during the electrolysis period (1 h). The reagents were added by means of a microburet with a polyethylene capillary tube. To carry out spectrophotometric determinations, solutions were withdrawn by means of an N_2-purged tube and a peristaltic pump without opening the measuring cell. The pH was continuously monitored with a micro glass combination electrode.

The glass electrode was calibrated to read $-\log [H^+]$ by titrating $HClO_4$ with a standardized solution of NaOH under the same experimental conditions as those used in subsequent measurements. The constant $K_w/\gamma_H\gamma_{OH}$ required for the computation of the concentration of OH^- ions, where K_w is the dissociation constant of water at 25 °C and γ_H and γ_{OH} are the activity coefficients of H^+ and OH^- under the conditions used, was determined in the same way. Hence the equilibrium constants reported are "concentration" constants, which may be considered thermodynamic constants in the electrolyte medium employed. All measurements were made in 0.10 M $NaClO_4$ solution and at 25 ± 0.1 °C.

Electrolytic Procedure. A solution containing Q and $HClO_4$ at slightly greater than twice the concentration of Q was placed in the measuring cell. The solution was deoxygenated with nitrogen and then electrolyzed by applying to the working electrode a potential of 0.00 V vs. the reference electrode and measuring the current as a function of time. The current, I, decreases exponentially with time, following first-order kinetics[28]

$$\ln = (I/I_0) = -kt \tag{1}$$

where the subscript 0 refers to the initial values of the appropriate parameters. The decay constant k was calculated to be 2.8×10^{-3} s^{-1}. The electrochemical reaction is

$$Q + 2e^- + 2H^+ \rightleftharpoons PH_2 \tag{2}$$

The hydrogen ion concentration at any time t is given by

$$[H^+] = [H^+]_0 - 2([Q]_0 - [Q])$$

and the proportionality between I and $[Q]$ leads to

$$\ln \frac{I}{I_0} = \ln \frac{[Q]}{[Q]_0} = \ln \left(1 - \frac{[H^+]_0 - [H^+]}{2[Q]_0}\right) \tag{3}$$

Equations 1 and 3 were experimentally verified. Thus the current

efficiency of electrolysis is 100% and the pH variations observed during electrolysis are attributable to reaction 2 indicating that the diffusion of H^+ or Q into the agar–agar bridge is negligible during electrolysis. The UV–visible spectrum of the reduced compound obtained after electrolysis was identical with that of the compound obtained by chemical preparation of PH_2.

Results and Discussion

Stability of Aqueous Solution of Q. Aqueous solutions of *o*-benzoquinone are known to be unstable. For example we observed that the spectra of pyrocatechol solutions which have been oxidized to various extents with Ce(IV) at pH 3 possess two clear isosbestic points indicating the presence of two components—pyrocatechol and its corresponding quinone. With time (17 h) these deteriorate considerably with the disappearance of the peak at 390 nm corresponding to the quinonoid group and the appearance of a peak at 275 nm corresponding to the phenolic group. This deterioration does not seem to be light dependent.

This type of decomposition also occurs in aqueous solutions of Q as was recently reported.[12,27] Similar changes in the UV–visible spectra with time were observed, i.e., disappearance of the quinonoid peak and appearance of the phenolic band. When the spectra were compared, it was seen that the observed changes depend slightly on pH and mainly on the amount of light. These results show that solutions of Q can be considered to be sufficiently stable during the course of the experiment (a few hours) if the solutions are kept in the dark at not very acidic pH values.

Acid–Base Properties. The two protonation equilibrium constants for P are defined by (4) and (5) where PH and P

$$K^H_1 = [PH]/[P][H^+] \tag{4}$$

$$K^H_2 = [PH_2]/[PH][H^+] \tag{5}$$

are the corresponding species obtained from the dissociation of one and both hydroxy groups, respectively. Of relevance to the redox chemistry of PH_2 a third constant involving the proton dissociation of the hydrated form of Q depicted by eq
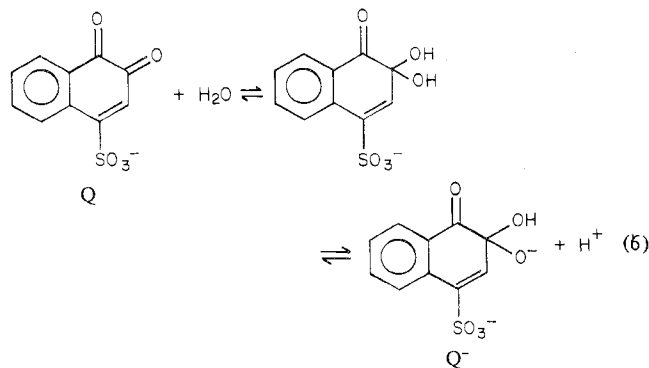
6 and defined by eq 7 should be considered. Since the values

$$K_Q = [Q]/[Q^-][H^+] \tag{7}$$

of these constants had been determined[15] at an unspecified temperature, for the purposes of this work they were redetermined under controlled conditions.

Potentiometric Determination of K^H_2. K^H_2 was determined by potentiometric titration at 6.09×10^{-4} M PH_2, obtained on reducing Q electrochemically as described above, with 0.0997 M NaOH. Since $K^H_2/K^H_1 \ll 1$ the mass balance and proton balance equations were computed by neglecting the first reaction step, and when combined yielded an expression which was a function of known or measured parameters and of K^H_2. A computer least-squares refinement was applied over the central 60% of the buffer region to yield the best value of K^H_2,

Table I. Proton Association Constants of PH_2 and Q

Methods used for determination	$\log K^H_1$	$\log K^H_2$	$\log K_Q$
Polarography[a]	12.64 ± 0.03 c		10.51 ± 0.05
Spectrophotometry[a]	12.66 ± 0.02		
Potentiometric measurement of $[H^+]$		8.14 ± 0.04	
Redox potentiometry[b]	$\gg 11$	8.2	10.0

[a] This work. [b] Reference 15. [c] $\log K^H_1 K^H_2 = 20.78 \pm 0.03$.

which is listed in Table I along with the old literature value. The potentiometric equilibrium curve obtained using this constant compares well with that obtained experimentally (Figure 1 of ref 32).

The computation was performed with the Fortran program MALIK on the CDC 3800 computer of the University of Geneva.

Spectrophotometric Determination of K^H_1. Since K^H_1 is very large, it cannot be determined potentiometrically. Furthermore, these measurements are difficult to carry out since in the presence of trace amounts of oxygen at pH >10 the oxidation of any diphenol is instantaneous. The apparatus described in the Experimental Section was designed to enable one to determine K^H_1 by Agren's spectrophotometric method,[29] using the changes observed in the UV spectrum as a function of hydrogen ion concentration. These spectra show that only the unprotonated species P absorbs at λ 4.20 nm. The application of Agren's method at this wavelength yielded a linear relationship which made possible the determination of the molecular extinction coefficient of P, $\epsilon_P = 10^{3.4 \pm 0.5}$, and the constant $\log K^H_1 = 12.66 \pm 0.02$ (Table I).

It should be noted that the determination of K^H_1 may not be rigorously correct, as the ionic strength of the medium for sodium hydroxide concentrations greater than 10^{-1} M could not be kept constant. However the good linearity yielded by Agren's method indicates that this factor may not be very important. $[H^+]$ was calculated by using $K_w = 1.01 \times 10^{-14}$,[30] the activity coefficients of H^+ and OH^- at 0.10 M ionic strength,[30] and the concentration of added NaOH.

Polarographic Determination of K^H_1, K^H_2, K_Q, and $E°$ of the System PH_2/Q. The results of Michaelis,[15] as well as the work carried out in this laboratory indicate that the determination of K_Q by potentiometric measurement of hydrogen concentration is inaccurate because the value of $\log K_Q$ is high (Table I) and Q decomposes in alkaline medium. This decomposition was therefore investigated polarographically by recording the maximum diffusion current corresponding to the polarographic reduction of Q on the mercury drop (Figure 1). It was found that the decomposition process is first order with respect to Q and the rate constant increases rapidly with pH. The constant K^H_1, K^H_2, and K_Q were determined polarographically by measuring the variation in half-wave reduction potential ($E_{1/2}$) of Q with pH (Figure 2).

The buffers CH_3COO^-/CH_3COOH, $HPO_4^-/H_2PO_4^{2-}$, triethanolamine/triethanolammonium, HCO_3^-/CO_3^{2-}, and PO_4^{3-}/HPO_4^{2-} were used in the pH ranges pH <6, $6 <$ pH < 8, $8 <$ pH < 8.9, $8.9 <$ pH < 10.3, $10.3 <$ pH < 11.8, respectively. NaOH solutions were used for pH >11.8. In all of these cases the ionic strength was maintained constant using 0.10 M $NaClO_4$.

It was found experimentally that the decomposition of Q is negligible during the time required for recording the dc polarogram (5–10 min), at pH <11.5. For higher values of pH, square-wave-pulse polarography was used. In this way a very fast rate of increase of impulses can be used enabling the recording of a complete polarogram in a very short time (ca. 30 s) after the addition of Q to the deaerated buffered solution. In this set of experiments, the maximum error due to decomposition of Q was observed for 0.15 M NaOH and
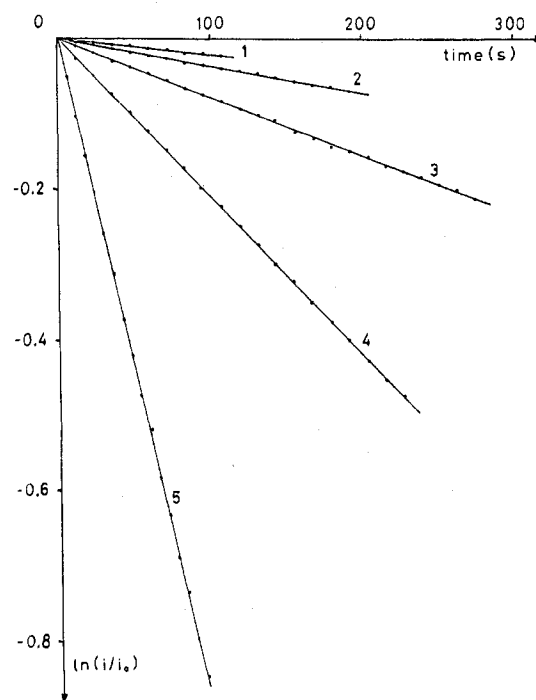

Figure 1. Rate of the decomposition reaction of Q in alkaline medium; $[Q]_T = 1.6 \times 10^{-4}$ M. NaOH concentration: 1, 0.041 M; 2, 0.070 M; 3, 0.30 M; 4, 0.64 M; 5, 2.00 M. I is the maximum diffusion current for reduction of Q at time t; I_0 is this current at time $t = 0$.
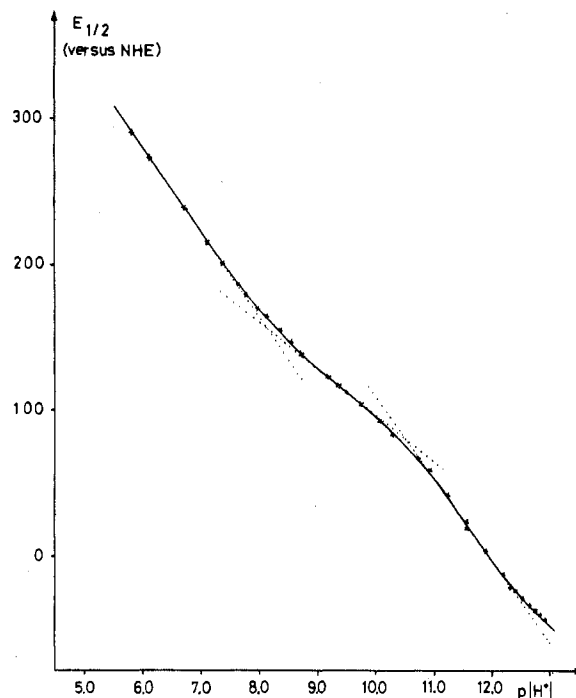

Figure 2. Relationship between half-wave reduction potentials of Q and pH; $[Q]_T = 1.6 \times 10^{-4}$ M. Buffers used for making studies at different pH values were acetate, $H_2PO_4^-/HPO_4^{2-}$, triethanolamine, HCO_3^{2-}/CO_3^{2-}, and HPO_4^-/PO_4^{3-}. For pH values greater than 11.8, NaOH solution was used. Ionic strength was always adjusted at 0.1 M with $NaClO_4$ except for pH greater than 13. The points are experimental data; the curve is adjusted.

was shown to correspond to a 3% decrease in the concentration of Q.

The $E_{1/2}$ values in Figure 2 were obtained by using log plot transformation of polarograms. The slope of the resulting straight lines gave a value equal to $2.303RT/2F$ ($=29.5$ mV)
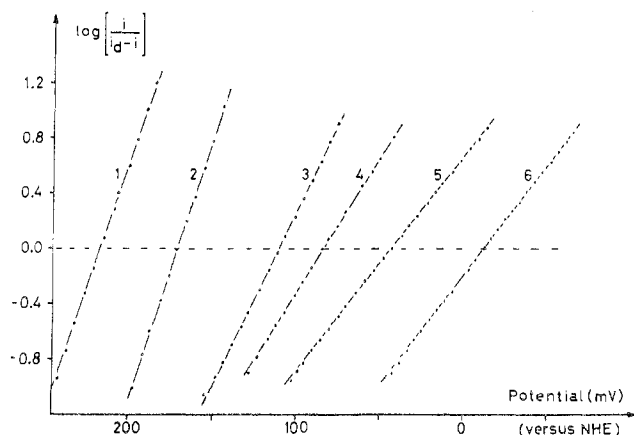
Figure 3. Log plot transformations of some polarograms at various pH values: 1, 7.11; 2, 7.96; 3, 9.19; 4, 10.28; 5, 11.22; 6, 12.20.

for pH <10 (Figure 3) which shows that under these pH conditions the redox system PH_2/Q is indeed a reversible one and that a two-electron-transfer reaction occurs. At pH >10 the slope was found to be larger than $2.303RT/2F$ which probably indicates the formation of semiquinone (vide supra). If the overall system is reversible and if the diffusion coefficients of Q, Q⁻, P, PH, and PH_2 are considered to be equal, the expression relating $E_{1/2}$ and pH is given by Heyrovsky and Kuta.[31] Irrespective of pH

$$E_{1/2} = E_Q{}^\circ + 2.303 \frac{RT}{2F}\left(\log \frac{\alpha_{Red}}{\alpha_{Ox}}\right)$$

where Red and Ox are the species subjected to electron transfer, $E_Q{}^\circ$ is the potential of the redox couple, and α is the degree of protonation of Ox or Red species. The profile of the curve $E_{1/2} = f(pH)$ (Figure 2) indicates that the charge transfer takes place between Q (=Ox) and P (=Red). Then the following equilibrium scheme probably applies at the electrode surface

$$PH_2 \overset{K^H{}_1}{\rightleftharpoons} PH \overset{K^H{}_2}{\rightleftharpoons} P \overset{2e^-}{\rightleftharpoons} Q \overset{K_Q}{\rightleftharpoons} Q^-$$
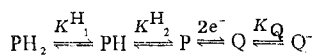
Therefore

$$E_{1/2} = E_Q{}^\circ +$$

$$2.303 \frac{RT}{2F} \log\left[\frac{1 + K^H{}_1[H^+] + K^H{}_1 K^H{}_2[H^+]^2}{1/K_Q[H^+] + 1}\right] \quad (8)$$

The parameters $E_Q{}^\circ$, s ($=RT/2F$), $K^H{}_1$, $K^H{}_2$, and K_Q were calculated using the program MALIK by minimizing the function

$$\sum_i [(E_{1/2})_i - F'_i(E_Q{}^\circ, s, K^H{}_1, K^H{}_2, K_Q)]^2$$

where F'_i is the right-hand term of eq 8, corresponding to ith point ($E_{1/2}$, [H⁺]).

The values of the acid dissociation constants given in Table I agree with those obtained by potentiometric and spectrophotometric measurements. The values cited in the literature also agree, with the exception of the value for K_Q which is $^1/_2$ log unit lower than the present value. The value of s obtained is 12.8 ± 0.1 mV which is in good agreement with that obtained theoretically. The value of $E_Q{}^\circ$ of the Q/P couple is found to be $+20.8 \pm 0.5$ mV (vs. NHE). It is apparent from Figure 2 that the experimental points fit well with the theoretical relationship (eq 8).

Formation of Semiquinone. The variations in the slope of the log plot of the polarographic curves with pH (Figure 3)
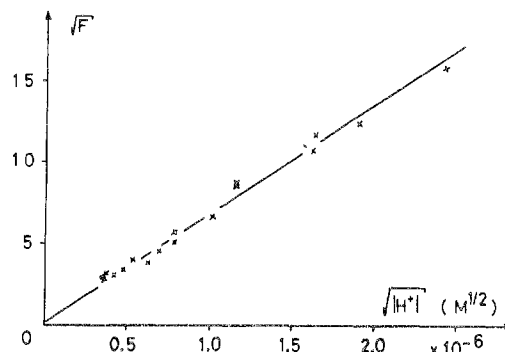
Figure 4. Relationship between F (see eq 14) and proton concentration. Values of K'_{SQ} were calculated from the slopes of the log plot transformations of polarograms used to obtain Figure 2. (Some of them are shown in Figure 3.)

may be explained in terms of the formation of semiquinone, as has been pointed out previously by Michaelis[15]
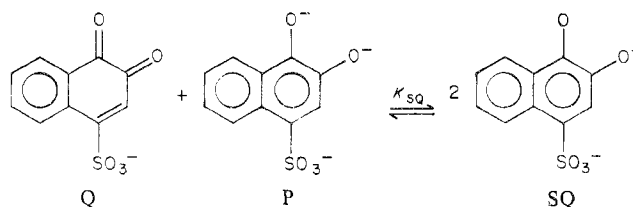
For this reaction, the equation of the polarograms can be derived,[31] i.e.

$$I = \frac{I_d}{2}\ \frac{[K'_{SQ}Y]^{1/2} + 2}{P(E) + [K'_{SQ}Y]^{1/2} + 1} \quad (9)$$

where

$$Y = \exp\left[\frac{2F}{RT}(E - E_{1/2})\right] \quad (10)$$

and

$$K'_{SQ} = [SQ]_T{}^2/[P]_T[Q]_T \quad (11)$$

where $[SQ]_{T'}$, $[P]_{T'}$, and $[Q]_T$ are total concentrations of semiquinone, dinaphthol, and quinone, respectively. Taking into account the corresponding mass balance equations, one obtains

$$K'_{SQ}$$

$$= K_{SQ}\frac{(1 + K^H{}_{SQ}[H^+])^2 K_Q[H^+]}{(1 + K^H{}_1[H^+] + K^H{}_1 K^H{}_2[H^+]^2)(1 + K_Q[H^+])} \quad (12)$$

$K^H{}_{SQ}$ is the acid dissociation constant of the semiquinone.

It can be shown from eq 9 and 10 that when $E = E_{1/2}$, K'_{SQ} is directly proportional to the slope of the log plot, i.e.

$$K'_{SQ} = -\frac{4F}{RT}\left[\frac{dE}{d\ln\left(\dfrac{I}{I_d - I}\right)}\right]_{E=E_{1/2}} - 2 \quad (13)$$

As K'_{SQ} is pH dependent, the slopes of the log plot will be a function of pH (Figure 3). By rearranging eq 12, one obtains

$$F^{1/2} = (K_{SQ}K_Q)^{1/2}[H^+]^{1/2} + (K_{SQ}K_Q)^{1/2}K^H{}_{SQ}[H^+]^{3/2} \quad (14)$$

If $K^H{}_{SQ}[H^+] \ll 1$, then the relation $F^{1/2} = f([H^+]^{1/2})$ will be linear, where F is defined as

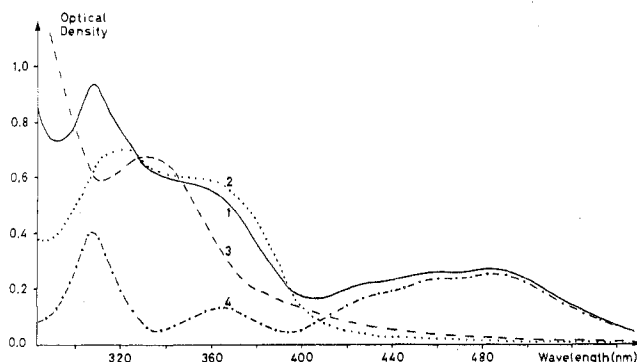$$F = K'_{SQ}(1 + K^H{}_1[H^+]) + K^H{}_1 K^H{}_2[H^+]^2(1 + K_Q[H^+])$$

Figure 5. Spectra of (2) 1.5×10^{-4} M PH, (3) 1.5×10^{-4} M Q⁻, (1) an equimolar mixture of diphenol and quinone each having a total concentration of 1.5×10^{-4} M, and (4) semiquinone alone at concentration 1.7×10^{-4} M. In each case pH was 11.79. For the determination of spectrum 4, see the text.

Figure 4 indeed shows a linear relationship over the working pH range. Therefore $K^H{}_{SQ} \ll 10^{10}$. From Figure 4 the value of K_{SQ} can be evaluated and was found to be $10^{3.2}$. Although traces of SQ were observed by ESR in the neutral pH range, the polarographic results have shown that relatively large quantities of semiquinone form only in the interval $10.8 <$ pH < 12.4. Figure 5 shows the spectra of PH (curve 2) and Q⁻ (curve 3) at pH 11.79 as well as spectra of equimolar concentrations of PH and Q⁻ (curve 1) at the same pH. From the total concentrations of diphenol and of quinone which were initially added (1.5×10^{-4} M) and by using the value of K_{SQ} given above and eq 11, it is possible to calculate $[P]_T$, $[Q]_T$ and $[SQ]_T$ in the mixture. By correcting the spectrum 1 (Figure 5) to eliminate the contribution of PH and Q⁻, one obtains spectrum 4 for SQ.

Conclusions

The above results seem to indicate that, from the point of view of redox properties, the PH_2/Q system is well suited for the study of the catalytic oxidation of aromatic o-dihydroxy compounds by dioxygen in aqueous solutions. Indeed, its normal potential is sufficiently low so that a catalytic effect of Fe(III) may arise during oxidation and that the reaction rate is sufficiently high at neutral or acidic pH value, for making measurements. This latter experimental condition allows the elimination of secondary reactions such as hydrolysis of Fe(III) or radical reactions which arise during oxidation

in alkaline medium. Particularly, from the fact that the decomposition process of Q is negligible below pH 11.5 and that the formation of semiquinone is not appreciable below pH 10.8, it may be concluded that no uncatalyzed secondary reaction will take place if oxidation is performed below pH 10.

References and Notes

(1) G. A. Hamilton, *Adv. Enzymol. Relat. Areas Mol. Biol.*, **32**, 55 (1969).
(2) (a) G. A. Hamilton, R. J. Workman, and L. Woo, *J. Am. Chem. Soc.*, **86**, 3390 (1964); (b) G. A. Hamilton, *ibid.*, **86**, 3391 (1964).
(3) G. A. Hamilton and J. P. Friedman, *J. Am. Chem. Soc.*, **85**, 1008 (1963).
(4) (a) G. A. Hamilton, J. P. Friedman, and P. M. Campbell, *J. Am. Chem. Soc.*, **88**, 5266 (1966); (b) G. A. Hamilton, J. W. Hanigin, and J. P. Friedman, *ibid.*, **88**, 5269 (1966).
(5) M. M. T. Khan and A. E. Martell, "Homogeneous Catalysis by Metal Complexes", Vol. I, Academic Press, New York, N.Y., 1974.
(6) E. Pelizetti, E. Mentasti, and G. Saini, *J. Chem. Soc., Dalton Trans.*, 721 (1974).
(7) C. A. Tyson and A. E. Martell, *J. Am. Chem. Soc.*, **94**, 939 (1972).
(8) R. R. Grinstead, *Biochemistry*, **3**, 1308 (1964).
(9) C. A. Tyson and A. E. Martell, *J. Phys. Chem.*, **74**, 2601 (1970).
(10) E. Mentasti and E. Pelizetti, *J. Chem. Soc., Dalton Trans.*, 2605 (1973).
(11) E. Mentasti, E. Pelizetti, and G. Saini, *J. Chem. Soc., Dalton Trans.*, 2609 (1973).
(12) J. Buffle, report handed in to Fonds Philippe Chuit (unpublished work), 1973.
(13) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. 17 (1964).
(14) J. B. Connant and L. F. Fieser, *J. Am. Chem. Soc.*, **46**, 1858 (1924).
(15) L. Michaelis, *J. Am. Chem. Soc.*, **58**, 873 (1936).
(16) L. Michaelis and M. P. Schubert, *J. Biol. Chem.*, **119**, 133 (1937).
(17) C. M. Wheeler and R. P. Vigneault, *J. Am. Chem. Soc.*, **74**, 5232 (1952).
(18) J. Doskocil, *Collect. Czech. Chem. Commun.*, **15**, 599 (1950).
(19) L. Michaelis and E. S. Fetcher, *J. Am. Chem. Soc.*, **59**, 2460 (1937).
(20) M. Boniger, *Ber. Dtsch. Chem. Ges.*, **27**, 23 (1894).
(21) L. F. Fieser, *Org. Synth.*, **21**, 91 (1941).
(22) D. H. Rosenblatt, P. H. Epstein, and J. Epstein, *Anal. Chem.*, **27**, 1291 (1955).
(23) I. S. Danielson, *J. Biol. Chem.*, **101**, 505 (1933).
(24) L. F. Fieser, *J. Am. Chem. Soc.*, **48**, 1104 (1926).
(25) C. Daglish, *J. Am. Chem. Soc.*, **72**, 4861 (1950).
(26) A. Gemant, *J. Chem. Phys.*, **22**, 1705 (1954).
(27) K. Kano and T. Matsuo, *Tetrahedron Lett.*, **49**, 4323 (1974).
(28) P. Delahay, "New Instrumental Methods in Electrochemistry", Interscience, New York, N.Y., 1966.
(29) A. Agren, *Acta Chem. Scand.*, **9**, 49 (1955).
(30) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths, London, 1959.
(31) J. Heyrovsky and J. Kuta, "Principles of Polarography", Publishing House of the Czechoslovakian Academy of Sciences, Prague, 1965, pp 163, 183.
(32) J. Buffle and A. E. Martell, *Inorg. Chem.*, following paper in this issue.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Metal Ion Catalyzed Oxidation of o-Dihydroxy Aromatic Compounds by Oxygen. 2. Complexes of 1,2-Dihydroxynaphthalene-4-sulfonate with Iron(III) and Iron(II)

JACQUES BUFFLE and ARTHUR E. MARTELL*

The interactions of Fe(II) and Fe(III) with 1,2-dihydroxynaphthalene-4-sulfonic acid (PH₂) are studied with a specially designed cell at 25.0 °C and $\mu = 0.100$ ionic strength. At pH <2 the ferric ion was found to spontaneously oxidize PH₂ to the quinone (Q). With Fe(II) ion, the complex species of importance were identified as FeP and FeP₂, and no protonated or hydrolyzed species were found to be present. With Fe(III) ion, the important complexes formed were found to be FeP, FeP₂, FeP₂H, and a "FeP₂(OH)" species. The hydrolyzed species is probably polynuclear. The thermodynamic stability constants for the equilibrium interconversion of these species are reported.

Introduction

Recent studies on the oxidation of ascorbic acid[1] and o-dihydroxy aromatic compounds[2,3] by oxygen in the presence of a metal catalyst have demonstrated complex formation

between the metal ion and these organic substrates. Before attempting the study of the catalytic oxidation of 1,2-naphthalenediol-4-sulfonate (PH₂) in the presence of Fe(III) it was found necessary to quantitatively determine the