Ch 80 REPORT

UNDERGRADUATE CHEMICAL RESEARCH

by

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I. ABSTRACT

Five distinct anodic chronopotentiometric waves are found for solutions of p-hydroquinone in 10-16F sulfuric acid. Reverse-current chronopotentiometry shows only two oxidation products although the reverse-current transition time equals one-third the anodic electrolysis time. All chemical species represented by these waves have been identified by means of UV and NMR sprectra and comparison with electrochemical properties of compounds synthesized according to the literature. The pK_a of hydroquinone and several rates of sulfonation have been approximately evaluated.

The electrochemical properties of durohydroquinone and ferrocene in sulfuric and other acid solutions were briefly investigated.

II. CREDITS

I am indebted to the National Science Foundation for an Undergraduate Summer Fellowship, and to Dr. Fred C. Anson for employment for part of the period, as well as for laboratory space and helpful suggestions. Preliminary research suggesting the original conception of this work was done by Dr. Harry B. Mark, Jr., and he and I have worked together in characterizing the hydroquinone-sulfuric acid system. Essentially all of the grindy experimental part of this work is mine, and the rest was done in collaboration with Dr. Mark. He suggested some experiments, helped to interpret them, and did the actual writing of our appended paper with my consultation and from part of my results.

III. STATEMENT OF PURPOSE, BACKGROUND, AND RESULTS.

Inasmuch as the principal results, etc., of the hydroquinone work are all in the appended paper, the balance of this report will consist of the original conception of the problem, some rate studies, two related systems, and conclusions, rather than of an amplification

of a preliminary summary of results presented to Dr. Anson in September, 1963.

Notes refer to the bibliography in the appended paper.

Preliminary investigations by Dr. Mark have shown that anodic chronopotentiometry of hydroquinone in 10-12F sulfuric acid gives a doublet wave which persists even after dilution to acid strengths which ordinarily show only a singlet anodic wave for hydroquinone. It was thought that this might be a long-lived protonated species similar to the σ-complex phenonium ion, or ring-protonated phloroglucinol (22, 41). This study was undertaken to identify this supposedly protonated hydroquinone species with an eye to developing a practical chronopotentiometric measure of the Hammett acidity function H_o (35,49) (phloroglucinol does not give an anodic wave), as there are few satisfactory acidity function indicators for very acid solutions ($H_o < -5$). Sulfuric acid was chosen as a medium because its H_o scale is the best defined of the strong acids. It was thought that the concentration of this supposed long-lived ion, and thence H_o, might be determined chronopotentiometrically by Dračka's (7) or Delahay's (8) methods after sorting out interfering sulfonation and decomposition reactions (2,14,16,40,44). Also, it was intended to compare any protonation phenomena of hydroquinone with those found for p-phenylenediamine by Mark and Anson(29).

A. HYDROQUINONE-SULFURIC ACID

It was found that the species forming the second anodic wave is in fact a sulfonic acid derivative of hydroquinone. In all, three sulfate derivatives of hydroquinone were identified, and one sulfate derivative of quinone postulated. The pK_a for O-protonation of hydroquinone was evaluated at approximately -2.5 by UV spectrometry, and no evidence was found for any other protonated organic species. It was also shown that protonation of hydroquinone has no detectable effect on its $E_{1/4}$,

similarly to the monoprotonation of phenylenediamine (29). (See appended paper for complete results and interpretation of the above, and appended Figure #1 summarizing the species and their waves).

Several rate constants were evaluated which were not included in the paper. Hydroquinone sulfonates slowly, and apparently, irreversibly in sulfuric acid; chrono of diluted solutions shows no diminution in concentration of the species identified as 2,5-dihydroxybenzenesulfonic acid over a 24 hour period. A formal first-order rate constant for sulfonation of hydroquinone (actually oxonium ion of hydroquinone at the acid strengths used) was evaluated as follows:

For two consecutive chronopotentiometric oxidations Delahay (4, p.191) gives:

R_1 = hydroquinone
R_2 = 2,5-dihydroxybenzenesulfonic acid

$$(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2} = \frac{\pi^{1/2} n_2 \mathcal{F} D_{R_2}^{1/2} C_2}{2 i_0}$$

Division of this equation by the Sand equation for the first wave (4,p.184), knowing that $n_1 = n_2$ (cf. "Current Reversal Chrono.," in attached paper) and assuming that $D_{R_1} = D_{R_2}$, yields upon rearrangement:

$$\frac{C_2}{C_1} = \left(\frac{\tau_1 + \tau_2}{\tau_1}\right)^{1/2} - 1$$

If the sulfonation reaction is first order in R_1, and there are no electroactive species other than R_1 and R_2, the formal first-order rate constant ("formal" because concentration of acid not included) is derived by:

$$R_1 \xrightarrow{k} R_2 \quad \Rightarrow \quad C_1 = C_1^{\circ} e^{-kt}$$

$$kt = \ln\left(\frac{C_1^{\circ}}{C_1}\right) = \ln\left(\frac{C_2}{C_1} + 1\right) = \frac{1}{2} \ln\left(\frac{\tau_1 + \tau_2}{\tau_1}\right)$$

Experimentally a plot of $\ln((\tau_1+\tau_2)/\tau_1)$ vs. age of the solution gives a straight line--confirming the first-order derivation--the slope of which is 2k. This procedure gave k = 0.015 ± 0.001 hour^{-1} for 13.2F sulfuric acid at 25°C.

In fresh solutions of the monosulfonate R_2 and its sulfate ester R_3 (no disulfonate or other hydroquinone species present; see Figure #1-D), there is found a dependence of $i\tau_{\frac{1}{2}}^{\frac{1}{2}}$ upon i. Assuming only that the reaction

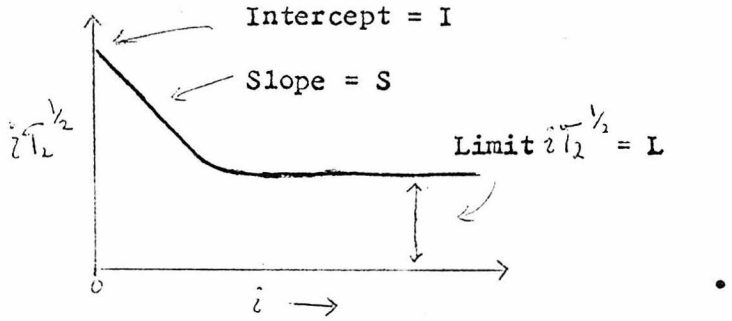
$$R_3 \underset{k_e}{\overset{k_d}{\rightleftharpoons}} R_2 \xrightarrow{ox.} O_2$$

is first-order in R for esterification and deësterification, the rate constants k_e and k_d may be derived from a plot of $i\tau_{\frac{1}{2}}^{\frac{1}{2}}$ vs. i via the following approximate equations derivative from Delahay's (4, p.200) solution of the case:

$$K = L/(I - L) = k_d/k_e$$

$$k_e = \pi / S^2K^2(1 + K)$$

where L,I and S are defined as:



This method gives k_e = 0.3 sec.$^{-1}$, and k_d = 1 sec.$^{-1}$. This determination is hampered by formation of the disulfonate, but worse by the imprecision caused by the variable state of electrode-surface activation.

Anodic chrono of solutions containing the disulfonate shows a small wave merging into the background which may be due to an ester of the disulfonate, just to make everything symmetrical, but of course this is only a guess.

B. RELATED SYSTEMS

Durohydroquinone and tetrachlorohydroquinone, two hydroquinones which cannot sulfonate, were synthesized to determine if they possessed interesting electrochemical properties, particularly protonation phenomena in strong sulfuric acid. Tetrachlorohydroquinone is too insoluble.

Durohydroquinone gives yellow solutions, but no anodic chrono wave upon addition to already-deaerated sulfuric acid solutions. The compound is either oxidized to duroquinone by the solvent--the electron donating character of the four methyl groups would make it very labile to oxidation--or the color is due to some unknown complex or decomposition product. The equilibrium potential of durohydroquinone-sulfuric acid solutions is right at the hydrogen evolution potential, so it is not possible to take a cathodic chrono wave either.

Anodic chronopotentiometry of hydroquinone in perchloric acid solutions of varying concentrations showed no complications, no kinetic dependences--nothing of interest.

Having been told by Mr. Whitesides of Caltech that the pseudo-first-order rate of protonation of ferrocene is of the order of 10 in BF_3-H_2O, this student tried several experiments. It was found that ferrocene sulfonates in concentrated sulfuric acid; nitrates in nitric acid; is too insoluble in perchloric, 10F sulfuric, and 50% tetrafluoboric acids; gives very irreversible singlet anodic waves in acetic, trifluoroacetic, and tetrafluoboric-trifluoroacetic acids; and shows no apparent change in its electrochemical properties as it protonates in tetrafluoboric-trifluoroacetic acid mixtures.

Ultimately it was decided that the pK_a of ferrocene must be greater than about 9.8, and could not really be determined until such time as the H_o scale is defined for some very strong acid, such as tetrafluoboric in acetic acid, or trifluoroacetic acid.

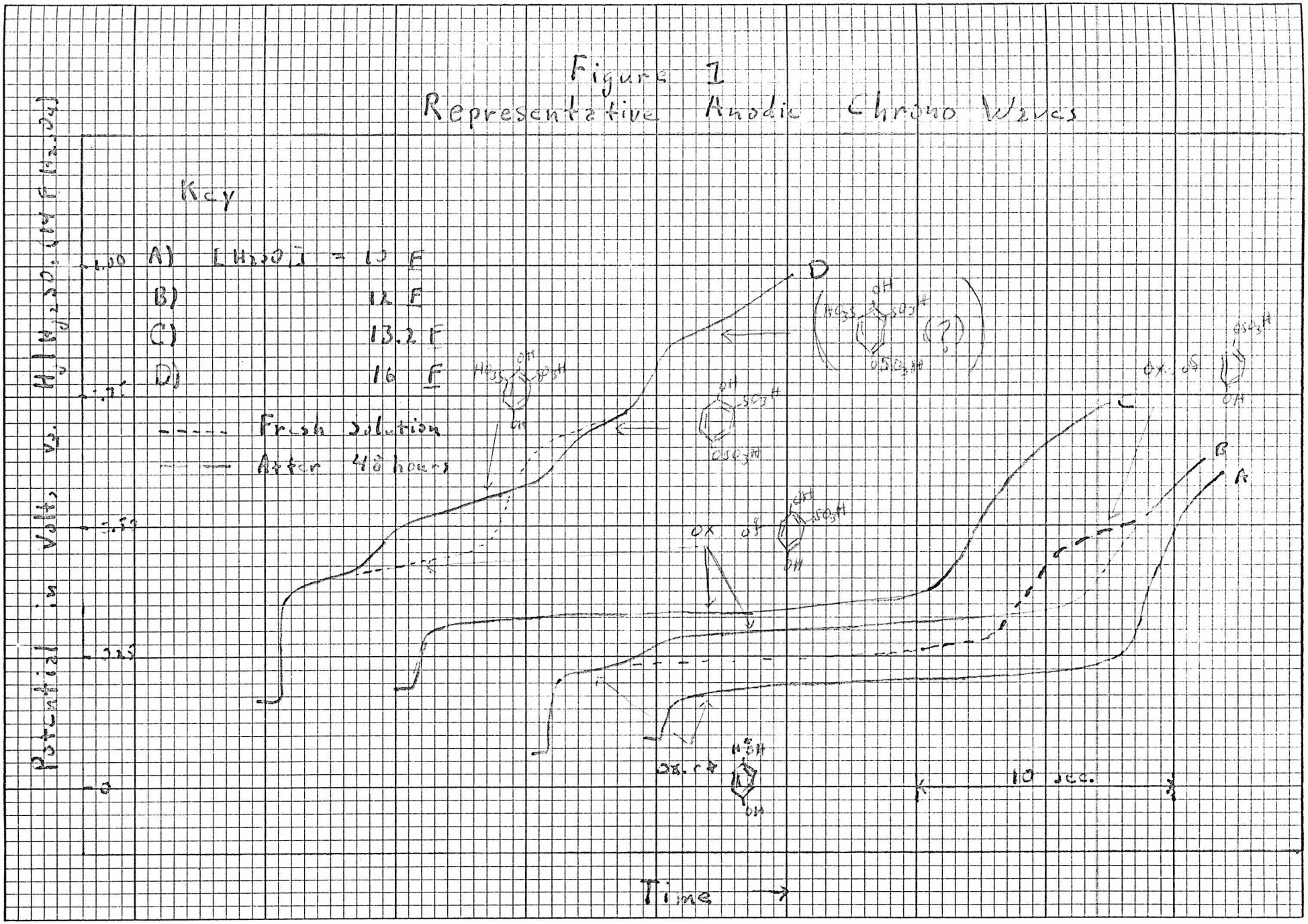
IV. CONCLUSIONS

This study failed in its original intent of finding an acidity function indicator for use with chronopotentiometry, i.e., an electroactive compound which protonates or deprotonates slowly or otherwise has distinctive electrochemical properties in its protonated form.

The preliminary work should have been done in perchloric acid, eliminating problems of sulfonation and electrode activation at one stroke, and also the line of inquiry taken as an approach to the original problem. The study became one of qualitative organic chemistry as soon as so many different waves were found. The chemistry of hydroquinone in concentrated sulfuric acid has been somewhat elucidated, and it was not altogether an uninteresting piece of research.

Curtis L. Atkins

Figure 1
Representative Anodic Chrono Waves



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Electrode Reactions of Aromatic Compounds in Strong Acid Solutions

Chronopotentiometric and Spectrometric Studies of the *p*-Hydroquinone–H_2SO_4 System at Platinum Electrodes

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▶ The electro-oxidation of *p*-hydroquinone and the subsequent reduction of the electro-oxidation products at platinum electrodes has been studied chronopotentiometrically in supporting electrolytes of varying sulfuric acid concentration. Five distinct anodic waves are found between 10 and 16*F* H_2SO_4 which represent the oxidation of hydroquinone and four new species formed at high acid strengths. Reverse current chronopotentiograms reveal that only two oxidation products are observed in this acid strength range even though the total reverse transition time was in all cases equal to $^1/_3$ the anodic electrolysis time. Ultraviolet and nuclear magnetic resonance spectra as well as electrochemical evidence indicate that the four new species are sulfonation products rather than protonation compounds. The four compounds and their oxidation products are identified.

THE ELECTRODE reactions of aromatic compounds such as the phenylenediamine isomers and related diamines (*23, 29, 34, 36*), *p*-aminophenol (*43, 45*), *N,N*-dimethylaniline (*9, 11, 31*), chloropromazine (*36*), and nitrobenzene compounds (*12, 28, 36*) have been the subject of considerable interest in recent years. Quite often the electrode mechanisms of this type of compound involve the formation of short-lived intermediates such as both negative and positive free radicals (*28, 36*), carbonium ions (*9, 11, 31*) and imines (*9, 11, 31, 45*). The nature and reactions of some of these intermediates can be studied by means of such electrochemical techniques as reverse current chronopotentiometry (*7, 38, 45, 46*), rotating disk electrodes (*10, 11, 24*), and cyclic voltametry (*11, 19, 31, 39*). These techniques are generally employed in conjunction with electron paramagnetic resonance (EPR) (*12, 28, 36*) and spectrophotometric (*31*) studies. Such investigations have not only elucidated the electrode behavior of many organic compounds but have also shed considerable light on the chemistry of these short-lived intermediates. This information is very useful also to the organic chemist as it results in a better understanding of homogeneous organic reaction mechanisms in general.

A recent study of the anodic oxidation of phenylenediamine compounds (*29*) as a function acid strength of the supporting electrolyte showed that total protonation of the basic amine groups had a very large effect on the oxidation potential. Protonation of just one amino group (one free amino group remains) had no observable effect on the

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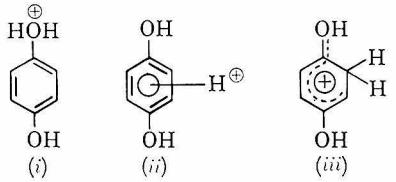
quarter wave potential, $E_{1/4}$, but total protonation (no free pair of electrons) shifted the $E_{1/4}$ about 250 mv. The present study of the effects of acid strength on the electro-oxidation and *p*-hydroquinone was undertaken to determine if any protonation phenomenon could be observed and, if so, to compare them with those observed for *p*-phenylenediamine.

As the phenolic (—OH) group is a very weak base (*2*), this study was carried out in solutions of high acid strength; 1 to 18*F* H_2SO_4 [H_0, Hammett's acidity function (*15*, *35*) = −0.26 to −11.1 (*35*)]. According to current theory three types of conjugate acids of phenolic compounds can form at these high acid strengths (*13*, *15*, *32*, *35*): an oxonium compound (*i*), a π-complex (*ii*), or a σ-complex, (*iii*):



It has been shown that phenol is protonated primarily on the oxygen atom [type (*i*) conjugate acid] in strong acids (*2*) bu tphloroglucinol (1,3,5-trihydroxybenzene) is protonated on a ring carbon [type (*iii*) conjugate acid] (*22*, *41*). To the best of our knowledge, no previous studies of the protonation of *p*-hydroquinone have been made; thus, the possible formation of all three types of conjugate acid had to be considered in interpreting the results of this investigation. Also, other investigators have found that phenolic compounds are extremely sensitive to sulfonation (*2*, *14*, *16*, *44*), oxidation (*40*), and other decomposition reactions (*2*). The formation of such sulfonation or oxidation products could also affect the characteristics of the chronopotentiograms. Thus, because of the complex nature of the system, the ultraviolet spectra as well as the nuclear magnetic resonance (NMR) spectra of the *p*-hydroquinone–H_2SO_4 solutions were studied in conjunction with the potential–time curves obtained by anodic and reverse current chronopotentiometry. As a result of this chronopotentiometric and spectrometric study, the various species formed in the *p*-hydroquinone–H_2SO_4 system have been defined and their electrochemical behavior described.

EXPERIMENTAL

Apparatus. The chronopotentiometric circuitry followed the standard practice (*25*) and complete descriptions of the circuit components have been previously reported (*1*). A Mosely Autograph Model 3-S recorder was employed. The applied electrolysis current was determined by measuring the voltage drop across a precision (0.05%) resistor of appropriate value which was connected in series with the electrolysis cell. A Leads and Northrup direct-reading pH meter, operating as a millivoltmeter, was employed to measure the potential drop across the resistor.

A Hg_2SO_4 (14*F* H_2SO_4)/Hg reference electrode was used and all potential values given in this paper are reported (unless otherwise stated in the text) with reference to this electrode. The potential of this reference electrode was +0.2560 volt *vs.* the saturated calomel electrode (SCE). The reference electrode made electrical contact with the sample solutions through a liquid bridge which contained an H_2SO_4 solution of the exact same acid concentration as that of the sample solution (a medium sintered glass frit separated the liquid bridge and the sample solution). The liquid bridge arrangement eliminated any appreciable change in the acid concentration of the sample solution resulting from the diffusion caused by the difference in acid strengths of the electrolytes of the sample and reference electrode. The working electrode was a Beckman Model 39273 platinum button electrode which had an exposed surface area of approximately 0.23 sq. cm. The working electrode was pretreated before each measurement by successively anodizing and cathodizing it to 1.6 and to −0.2 volt *vs.* the SCE, respectively, in approximately 1*F* H_2SO_4 in a cyclic manner (*30*). The final cycle was cathodic and the current was interrupted as soon as the potential reached hydrogen ion reduction (approximately −0.2 volt *vs.* SCE). This pretreatment results in the formation of finely divided platinum on the surface (*27*). The pretreated electrodes were then immediately used to record the chronopotentiograms of the sample to be investigated. As platinum oxides form in the potential regions of the experiments, the electrode must always be pretreated before each measurement. The auxiliary electrode was a coiled 3-inch length of 0.020 inch in diameter platinum wire. The ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer and the proton magnetic resonance spectra were obtained with a Varian A-60 nuclear magnetic resonance spectrometer.

The sample solutions were de-aerated in the electrolysis cell by bubbling prepurified nitrogen gas through the solution prior to the experiment. A nitrogen atmosphere was maintained over the surface of the solution during the actual experiment. All measurements were made at room temperature (25° ± 1.0° C.).

Preparation of Solutions and Materials. All chemicals, with the exception of those specifically listed below, were reagent grade and were used without further purification. All solutions were prepared with triply distilled water. The H_0 values of the standard acid solutions, from which the samples for measurement were prepared, were determined by measuring the density with a pycnometer and then determining the weight per cent sulfuric acid from a wt. %–density plot constructed from the density tables in the International Critical Tables (*17*). The H_0 was then estimated from H_0 tables of Paul and Long (*35*). The hydroquinone (or related species) solutions were prepared by dissolving weighed amounts of solid sample in a specific volume of standard acid solution. The 2,5-dihydroxybenzenesulfonic acid (*16*), 2,5 - dihydroxybenzene - 1,3 - disulfonic acid [it is assumed although not proved that the predominant product will have the sulfonic acid groups in the 1 and 3 position (*20*)], and the monosulfonic acid ester of *p*-hydroquinone (*48*), were synthesized and purified by standard methods found in the literature (*16*, *20*, *48*).

RESULTS AND DISCUSSION

Anodic Chronopotentiometry. Figure 1 shows the anodic chronopotentiograms of *p*-hydroquinone solutions of various H_0 values between −4.84 and −8.14 (10 to 16*F* H_2SO_4). At H_0 = − 4.89 (curve *A*), only one wave, 1, corresponding to the oxidation of species, *I*, is observed; both for a freshly prepared solution and for a solution that has been allowed to age for over 48 hours. At H_0 = − 5.87 (curve *B*), however, the chronopotentiogram of a freshly prepared solution (indicated by the dashed line) shows two distinct waves; 1 and 3. By examining the chronopotentiograms at intermediate H_0 values, wave 1 of curve *B* was shown to correspond to the electro-oxidation of *I*. The slight positive shift of the $E_{1/4}$ of wave 1 between H_0 = −4.89 and −5.87 is the result of the change in the acidity of the solution. This is not unexpected, as protons are undoubtedly involved in the electro-oxidation mechanism of hydroquinone (*26*). Wave 3, however, must represent the electro-oxidation of a new species, *III*, which is formed at this higher acid strength. As the solution of H_0 = −5.87 is allowed to age (in a sealed container) a new wave, 2, begins to appear which represents the formation of another species, *II*, which is oxidized at a potential intermediate to those of waves 1 and 3. The transition times, τ_1, τ_2, and τ_3, of waves 1, 2, and 3, respectively, change with time: τ_1 and τ_3 decrease, while τ_2 increases. The chronopotentiogram of the H_0 = −5.87 after 48 hours (indicated by the solid line of curve *B*) shows that *II* is now the predominate species in the solution. The concentration of *I* is quite small, and the concentration of *III* has been reduced to zero. It should be noted at this point that the overall transition times (sum of the transition times of individual waves) of the hydroquinone chronopotentiograms in the high acid strength solutions decreases with time (approximately 2% per day at H_0 = −4.89 to about 10% per day at

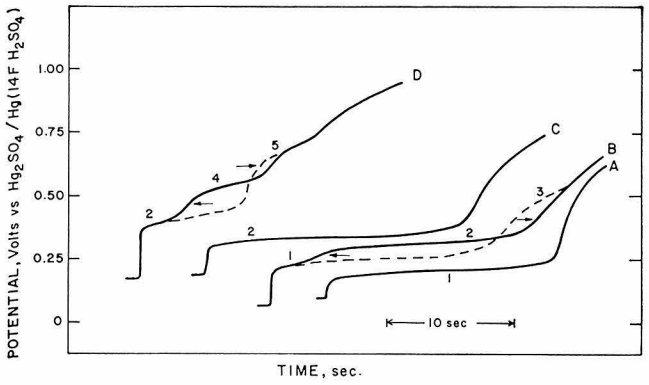


Figure 1. Chronopotentiograms of 0.01F p-hydroquinone at various H_0 values

.... Freshly prepared solutions
—— Solutions aged for 48 hours
A. $H_0 = -4.89$ (10F H_2SO_4)
B. $H_0 = -5.87$ (12F H_2SO_4)
C. $H_0 = -6.51$ (13.2F H_2SO_4)
D. $H_0 = -8.14$ (16F H_2SO_4)

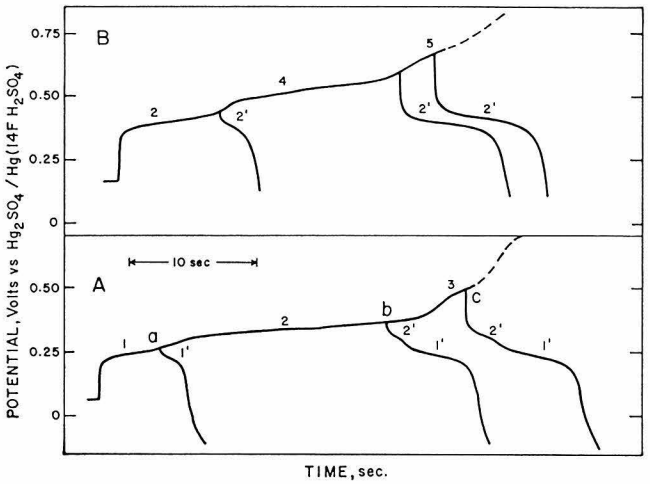


Figure 2. Current reversal chronopotentiograms of 0.01F p-hydroquinone solutions

A. Aged $H_0 = -6.40$ (13F H_2SO_4) solution
B. Aged $H_0 = -8.14$ (16F H_2SO_4) soluion

$H_0 = -11.1$) which indicates that the hydroquinone is also undergoing oxidation and/or decomposition reactions which do not yield electroactive products. At $H_0 = -6.51$, the chronopotentiograms of freshly prepared solutions (not shown in Figure 1) exhibit three distinct waves which correspond to the oxidation of *I*, *II*, and *III*. As the solution ages, however, the transition time of wave 2 increases and those of wave 1 and 3 decrease. After about 12 hours only one wave (wave 2) is observed which does not change on further aging (see curve *C* of Figure 1). At $H_0 = -8.14$ (curve *D*), the freshly prepared solution (indicated by the dashed line) exhibits two distinct waves (2 and 5). The wave at the least positive potential was shown to correspond to the oxidation of species, *II*. The change in acidity again is responsible for the change in $E_{1/4}$ of this wave. Wave 5, however, results from the oxidation of another new species, *V*, formed at the higher acid strength. As the $H_0 = -8.14$ solution is aged, a third wave, 4, representing the oxidation of another species, *IV*, begins to appear and the transition times of waves 2 and 5 decrease, as indicated by the solid line of curve *D* of Figure 1. As the acidity of the solution is increased to $H_0 = -8.75$ and -11.1 (17 and 18F H_2SO_4, respectively), the chronopotentiograms of the freshly prepared solutions exhibit three waves, 2, 4, and 5. The only change in the characteristics of the waves as the acid strength increases is the increase in the rate at which the transition time of wave 4 increases (and that of 2 decreases) with aging.

The chronopotentiograms of *p*-hydroquinone solutions of H_0 between -0.26 and -4.89 exhibited only one wave corresponding to wave 1 of curve *A* of Figure 1. There was no abnormal shift of $E_{1/4}$ (*29*) of this wave indicating that no new species having a different oxidation potential is formed in this acidity range.

Current - Reversal Chronopotentiometry. In an effort to characterize the various species formed in the H_2SO_4 solution whose oxidations correspond to waves 1 through 5, the cathodic waves obtained on reversal of the current after an anodic electrolysis were investigated. A typical set of current-reversal chronopotentiograms are shown in Figure 2. The curves shown in part *A* of Figure 2 were obtained for an aged (10 hours) $H_0 = -6.40$ solution which exhibits three anodic waves: 1, 2, and 3. The cathodic chronopotentiogram obtained on reversal of the current near the end of wave 1 (at point *a*) exhibits only one wave, 1′. The potential of wave 1 at 0.25 τ_1 was found to be equal to the potential of wave 1′ at 0.215 τ_2', which indicates that electrode mechanism for the oxidation of this species, *I*, is reversible (*3*, *6*, *33*). It was found that $\tau_1 = 3\ \tau_1'$; thus, the oxidation product, I_{ox}, was not subject to rapid hydrolysis or decomposition reactions. Plots of $\log\left(\frac{\tau^{1/2} - t^{1/2}}{t^{1/2}}\right)$ *vs.* potential, *E*, (for wave 1) were linear as expected for a reversible reaction (*4*, *19*) and had a reciprocal slope [equal to $\frac{2.3\ RT}{nF}$ (*18*)] that was equal to 0.031 indicating that the numbers of electrons, *n*, involved in the electrode reaction was equal to 2 [for $n = 2$, the theoretical slope of the $\log\left(\frac{\tau^{1/2} - t^{1/2}}{t^{1/2}}\right)$ *vs.* *E* plot is 0.030 (*3*, *19*)]. The expression for the potential–time curve of the current reversal chronopotentiogram of a reversible system (*3*), predicts that plot of log

$$\left\{\frac{\tau_1^{1/2} - [(\tau_1 + t')^{1/2} - 2t'^{1/2}]}{(\tau_1 + t')^{1/2} - 2t'^{1/2}}\right\}$$

vs. *E*, where τ_1 is the transition time of the anodic wave and t' is any time after τ_1, will be linear and have a reciprocal slope of $\frac{2.3\ RT}{nF}$. Such plots for wave 1′ yielded straight lines of slope = 0.030–0.033 indicating the number of electrons, *n*, involved in the reduction reaction is also equal to 2.

If the current is reversed just prior to the transition of wave 2 (at point *b*, Part *A* of Figure 2), two waves, 1′ and 2′, which correspond to the reduction of the products I_{ox} and II_{ox} of the two anodic waves 1 and 2, are obtained. The overall transition time, τ', ($\tau' = \tau_1' + \tau_2'$), of the reverse wave was equal to 1/3 of the overall time duration, t_b, of the anodic wave, indicating that the oxidation products do not undergo a rapid chemical reaction to form electro-inactive species. Palke, Russell, and Anson (*33*) have shown that for reverse wave in this case, τ_1' can be calculated from the expression:

$$\tau'_1 = 1/9\ [8\tau_1 + 3\tau_2 - 4(4\tau_1^2 + 3\tau_1\tau_2)^{1/2}] \quad (1)$$

where τ_1 and τ_2 are the transition times for waves 1 and 2 in this case. Comparison of theoretical values of τ_1' and experimental values showed that the experimental values were 10 to 20% less than the theoretical values. This coupled with the fact that $(\tau_1 + \tau_2) = 3\ (\tau_1' + \tau_2')$ indicates that the species, II_{ox}, produced on the oxidation of *II* undergoes a chemical reaction to form the same species, I_{ox}, produced by the oxidation of *I*. Also, aged solutions of $H_0 = -6.51$ which showed only one anodic wave, 2, were found to exhibit two cathodic waves, 1′ and 2′, on

current reversal; further indicating that II_{ox} was undergoing a chemical conversion to I_{ox}. Studies of the reverse current chronopotentiograms of the same $H_0 = -6.51$ as used above but now diluted to $H_0 = -3.75$ showed that only one anodic wave, corresponding to oxidation of species II, and only one cathodic wave on current reversal. However, in this later case the potential at 0.215 τ' was approximately 90 mv. more negative than $E_{1/4}$ of the anodic wave and was found to be equal to that of the $E_{1/4}$ for the anodic wave of species I, at $H_0 = -3.75$. It was concluded, therefore, that, at this lower acid strength, the oxidation product of II is very rapidly converted to I_{ox}. Furthermore, at higher acid strengths, $H_0 = -7.00$ to -8.00, the reverse current wave obtained after the anodic oxidation of II exhibits only one wave. In this case the $E_{1/4}$ of the anodic wave was exactly equal to the potential at 0.215 τ' which indicates that the electrode reaction is reversible. Also, it was found that $\tau_2 = 3\tau_2'$ Thus, at the higher acid strengths, the chemical reaction of II_{ox} to form I_{ox} does not proceed at an appreciable rate. The apparent influence on the acid strength on the rate of this chemical reaction suggests that this reaction is reversible. It was found that the data obtained at $H_0 = -6.51$ treated by the method of Testa and Reinmuth (*46*) did not yield linear plots as expected for irreversible first-order reactions (*46*). Thus, the reaction is either reversible or second order. No attempt was made to calculate the rate constants by means of the expression for a reversible first-order reaction derived by Dračka (*7*) as the equilibrium constant for this reaction is not known and cannot be determined from the present data.

When the current is reversed just prior to the transition time of wave 3 (at point *C*, Part *A* of Figure 2) only two cathodic waves, 1′ and 2′, are observed which correspond to the reduction of I_{ox} and II_{ox}, respectively. No separate reverse wave was observed for the oxidation product of the oxidation of III. It was found that the overall duration of anodic electrolysis was equal to 3 times the overall cathodic transition time ($\tau_1' + \tau_2'$). Thus, the species produced by the oxidation of III must either be II_{ox} or I_{ox} or undergo an extremely rapid chemical conversion to form II_{ox} or I_{ox}.

Part *B* of Figure 2 shows the cathode waves obtained on reversal of the electrolysis current at three different points, *a*, *b*, and *c*, on the anodic chronopotentiogram of an aged $H_0 = -8.14$ solution. Note that, although the anodic wave suggests that there are three species, II, IV, and V, in the solution, only one cathodic wave, 2′, is obtained on current reversal even

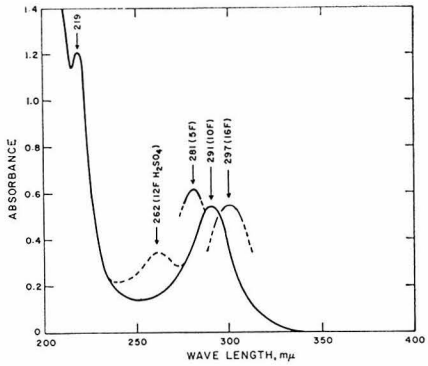


Figure 3. Ultraviolet spectra of 0.2 × 10^{-3}F *p*-hydroquinone at various H_0 values

though all three species have undergone oxidation. The potential of the single cathodic wave, 2′, corresponds to that of the reduction of II_{ox}. No cathodic wave was obtained for a distinct oxidation product of either species IV or V even at $H_0 = -11.1$. It was found that, regardless of the point at which the current was reversed, the duration of the anodic electrolysis was always equal to $3\tau_2'$. Thus, the oxidation product(s) of IV and V must be either II_{ox} or undergo extremely fast chemical conversion to II_{ox}.

$i\tau^{1/2}$ *vs.* *i* Studies. The value of $i\tau^{1/2}$ was studied as a function of i for waves 1 and 2 for a 10m*F* *p*-hydroquinone solution over an H_0 range of -5.87 to -11.1. It was found that for wave 1, $i\tau^{1/2}$ was independent of i (over a τ_1 range of 1 to 35 seconds) for a $H_0 = -5.81$ solution and for both a fresh and aged $H_0 = -6.40$ (see curves *A* and *B* of Figure 1). This shows that the electro-oxidation of I over this acid strength range was diffusion controlled. Thus, if species II and III are in equilibrium with I, the rate constants for the conversion of II and III to I must be quite small. This was substantiated by diluting both fresh (exhibits wave 1 and 3) and aged (exhibits waves 1 and 2) $H_0 = -6.40$ solutions (see curve *B* of Figure 1) with water until the H_0 was equal to approximately -2.0 (at this acid strength, species II and III did not form as explained previously). The anodic chronopotentiograms of the resulting $H_0 = -2.0$ solution showed the same ratio of transition times as obtained for the initial acid strength of -6.40. Thus, the concentration of II and III did not change on dilution, which suggests that these two species are quite stable once formed at the higher acid strength. It was found that ratio of τ_2/τ_1 for the diluted, aged solution did not change even after 24 hours. The species, III, however, was somewhat less stable, as the ratio τ_3/τ_1 (for the diluted fresh solution) had decreased noticeably 10 minutes after dilution and only wave 1 remained after about 30 minutes.

The value of $i\tau_2^{1/2}$ of wave 2 for an aged 10m*F* *p*-hydroquinone solution of $H_0 = -8.14$ (exhibits essentially only waves 2 and 4) were also independent of i and on dilution to $H_0 = -2.0$, the ratio of τ_4/τ_2 did not change even over a 24-hour period. Thus, the wave of species II is diffusion controlled and there is no evidence that IV converts to II once it has formed. The value of $i\tau_2^{1/2}$ for a fresh 10m*F* *p*-hydroquinone solution at $H_0 = -8.27$ (exhibits only waves 2 and 5) decreased linearly with increasing current density; from 340 to 255 μa.–cm.$^{-2}$–second$^{1/2}$ for the current densities of 63 and 20 μa.–cm.$^{-2}$, respectively (τ varied over this current range from 1.4 to 29 seconds).

This variation of $i\tau_2^{1/2}$ with i suggests that in this case the electrode mechanism for the oxidation of II is controlled by a chemical kinetic process that precedes the electron transfer rather than diffusion controlled (*4*, *5*, *29*) process. The reaction is probably the rapid conversion of V to the more easily oxidized species, II. Thus, it appears that species II and V are in rapid equilibrium at H_0 values between about -8 to -11.1. This was further substantiated by diluting several solutions (H_0's between -8 and -11) with water to a H_0 of approximately -6. The chronopotentiograms of the resulting solution were measured as fast as possible (~3 minutes delay) and showed only one wave which corresponds to the oxidation of II. No wave was observed for species V.

Ultraviolet and Nuclear Magnetic Resonance Spectra. To further characterize the nature of the five species found by the chronopotentiometry experiments to form in H_2SO_4 solution between $H_0 = -2.30$ and -8.14, the ultraviolet (UV) adsorption and NMR spectra of solutions containing the five species, either alone or as mixtures, were measured.

The UV spectra of 0.2m*F* *p*-hydroquinone solutions at $H_0 = -2.30$ (contains I only), -4.89 (contains II only), -5.87 (fresh solution, contains I and III), and -8.14 (aged solution, contains II, IV, and V) are shown in Figure 3. In all four solutions, two strong bands are observed; one at approximately 219 mμ which did not appear to be appreciably affected by change in H_0 and one about 275 to 295 mμ which varied with H_0. The peak absorbance, A_{max}, of this band for a $H_0 = -0.26$ solution occurs at 275 mμ and the molar absorptivity, ϵ, is 2.7×10^3. As the acid strength is increased to -4.89, A_{max} shifts to about 290 microns and the absorptivity decreases to 2.2×10^3. It was found that the shift in A_{max} is approximately linear with increasing acidity, but the change

in ϵ took place in a narrow acidity range between $H_0 = -2.30$ and -3.03. Further increase in the acidity function to -4.89 did not result in any appreciable change in ϵ. A similar shift of the 270-mμ band of phenol to longer wavelengths with increasing acidity and a similar decrease of its absorptivity over a narrow acidity range has been reported (*2*). The shift of the peak in both cases to longer wavelengths is probably a medium effect (*8*, *41*) but the change in absorptivity is interpreted to be the result of protonation (*41*). The protonation of phenol is thought to take place on the oxygen atom to form an oxonium conjugate acid, analogous to species (*i*). In both the phenol and *p*-hydroquinone cases such a protonation would reduce or remove the resonance interaction of the free pairs of electrons of the oxygen with the π-electron system of the ring [an $N \rightarrow V$ band (*47*)], and the oxonium ion spectrum would be similar to that of toluene. The spectral evidence suggests that the formation of a π-complex, species (*ii*), or a σ-complex, species (*iii*), does not take place to an appreciable extent in the case of the first protonation of *p*-hydroquinone. A π-complex would result in little spectrum change (*32*) and a σ-complex would exhibit two new bands in the 255- and 355-mμ range). The fact that the change in ϵ in the *p*-hydroquinone case is considerably less than that of the phenol case, 18.5% decrease compared to approximately 40% (*2*), is not unexpected because one of the oxygens of *p*-hydroquinone still remains unprotonated and its electrons are still free to have some resonance interaction with the π-system of the ring. Thus, the UV spectra indicates that the *p*-hydroquinone protonates to form an oxonium conjugate acid which has a $pK_a \cong -2.5$. As the chronopotentiograms of *p*-hydroquinone solutions between $H_0 = -0.26$ and -4.89 showed neither an abnormal shift of quarterwave potential nor a new wave, the protonation of one oxygen must not have any appreciable effect on the electro-oxidation potential of the compound. Similar results were observed for the electro-oxidation of *p*-phenylenediamine (*29*). The $E_{1/4}$ of the mono-protonated form of *p*-phenylenediamine was not appreciably different than that of the free base. However, the $E_{1/4}$ of the diprotonated form was about 310 mv. more positive than that of the mono-protonated species (*29*).

As the acid strength increases from -4.89 to -11.1 there is a further shift of the absorbance maximum to longer wavelengths as shown in Figure 2. At $H_0 = -11.1$, A_{max} occurs at approximately 295 mμ. No appreciable change in ϵ is observed over this acid strength range. At $H_0 = -5.87$, a new peak is observed at 262 mμ, as shown in Figure 3, indicating that a new species is formed at this acid strength. Although it has been shown that the formation of the σ-complexes (species *iii*) of phloroglucinol (*22*, *41*) and mesitylene (*21*) results in a strong band ($\epsilon = 1.11 \times 10^4$) in the region 255 m$\mu$, the peak in this region for *p*-hydroquinone is not thought to be that of a σ-complex. All known σ-complexes also exhibit a strong band at 355 mμ (*21*, *22*, *41*) which was not observed for *p*-hydroquinone. This peak at 262 mμ was also observed in fresh $H_0 = -6.51$ (waves 1, 2, 3) but not observed in an aged solution (waves 1 and 2 only) of the same acid strength. Thus, this peak probably corresponds to that of the species, *III*, whose oxidation is represented by wave 3.

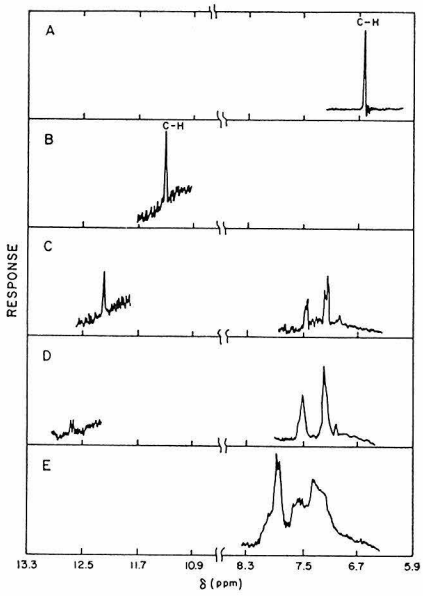


Figure 4. Nuclear magnetic resonance spectra of various *p*-hydroquinone solutions (5%)

A. In CH_3CN
B. In 10*F* H_2SO_4 ($H_0 = -4.89$). Chronopotentiogram of the solution shows only wave 1
C. In aged 12*F* H_2SO_4 ($H_0 = -5.81$). Chronopotentiogram shows waves 1, 2, and 3
D. In aged 13.2*F* H_2SO_4 ($H_0 = -6.57$). Chronopotentiogram shows wave 2 only
E. In aged 16*F* H_2SO_4 ($H_0 = -8.14$). Chronopotentiogram shows waves 2, 3, and 4

The NMR spectra of the ring hydrogens for 5% *p*-hydroquinone in acetonitrile, and sulfuric acid solutions of $H_0 = -4.89$, -5.87, -6.51, and -8.14 are given by Parts *A* to *E*, respectively, of Figure 4. In an aprotic solvent, acetonitrile, the ring carbon line is found to have a chemical shift, δ, of 6.6 p.p.m. ($\delta = 0$ was arbitrarily set equal to the proton resonance line of tetramethylsilane). However, in H_2SO_4 solution of $H_0 = -4.89$, the ring proton line has shifted down field and has a δ of 10.2 p.p.m. This large change in the chemical shift probably is the result of protonation of one of the oxygen atoms of the phenolic groups in the acid medium (*42*). This observation agrees with conclusions drawn from the UV spectral data. Note that the magnitude of this line decreases as the acid strength is increased to -5.87 and the line has practically vanished at -6.81. This change in the concentration of the oxonium conjugate acid concentration between $H_0 = -4.89$ and -6.51 corresponds with the change in the transition time of wave 1 over this acidity range. Thus, there can be little doubt that species *I*, whose oxidation corresponds to wave 1, is oxygen-protonated *p*-hydroquinone. The additional shift of the ring carbon peak over this acidity range, as shown in parts *B* to *D* of Figure 4, is probably a medium effect (*37*). At acid strengths of -4.89, two strong lines begin to appear at 7.17 and 7.40 p.p.m. and a weak line at 6.90 p.p.m. These two lines increase in magnitude at $H_0 = -6.51$. The increase in these two lines is essentially proportional to the decrease in the line of the ring carbons of the oxonium conjugate acid. Thus, the two lines at the 6.17- to 7.40-p.p.m. range probably correspond to the resonance of the ring protons of the species *II*, as at $H_0 = -6.51$ essentially only one wave, 2, is observed for the anodic chronopotentiogram. As the line at 6.90 p.p.m. does not appear to increase in magnitude, it might correspond to the resonance of the ring protons of species *III*. Such small amount of *III* in the aged $H_0 = -6.51$ solution would probably not exhibit a distinct chronopotentiometric wave. The fact that the ring carbon lines for *II* (and presumably *III*) have shifted up field to the 7-p.p.m. range indicates that these species are not oxygen-protonated. The resonance lines fall at approximately the same chemical shift value found for *p*-hydroquinone in aprotic media (see part *A*). At $H_0 = -8.14$ (chronopotentiograms indicate the species *II*, *IV*, and *V* are present) the position of the group of lines is moved slightly down field [which is again probably a medium effect (*37*)] and the spectrum is considerably more complex. There appear to be at least two more lines and perhaps more between 8.0 and 7.0 p.p.m. which suggests the formation of new species. Because the resolution is not good in sulfuric acid media, it is difficult to sort out the new lines from those of species *II*. As the resonance lines for *II*, *IV*, and *V* all appear to fall in the 7- to 8-p.p.m. range, it is probable that these species are not oxygen-protonated either. It should be noted that the above discussion assumes that the same species are formed in 5% (employed in the NMR measurements) and $10^{-3}F$ (in chronopotentiometric measurements) hydroquinone solutions.

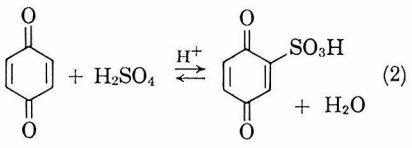
CONCLUSIONS

On the basis of the NMR and the UV evidence, species *I* (corresponding to wave 1) is the oxygen-protonated form of *p*-hydroquinone [see structure (*i*)] for solutions of $H_0 \cong -3.5$ to approximately -5 and simply hydroquinone at lower acid strengths. The chronopotentiograms show that protonation of one of the oxygens has no appreciable effect on the oxidation potential of hydroquinone. The NMR and UV results obtained for solutions of $H_0 = -5$ to -11.1 (range where species *II*, *III*, *IV*, and *V* are formed) indicate that, not only has no further protonation taken place, but that these species are not protonated at all. Thus, it must be concluded that these species are sulfonation products. The fact that $i\tau^{1/2}$ is independent of i for waves 2, 3, and 4 and that the $i\tau^{1/2}$ dependence of wave 5 was not that to be expected for a prior deprotonation chemical reaction supports this conclusion. [Calculated k's, although not precise, were several orders of magnitude less than expected for protonation (*29*)]. To test this conclusion, the chronopotentiograms of 2,5-dihydroxybenzenesulfonic acid were measured. At $H_0 = -5.87$ and -6.51, the $E_{1/4}$'s for this compound were identical with those observed for species *II* (wave 2). Furthermore, it was observed that the chronopotentiograms of a mixture of *p*-hydroquinone and 2,5-dihydroxybenzenesulfonic acid showed two cathodic waves whose potentials corresponded exactly to those of waves 1′, and 2′. Also, the ratio of the anodic transition times of the mixture did not change on dilution to $H_0 = -2.0$. The NMR and UV spectra of 2,5-dihydroxybenzenesulfonic acid in $H_0 = -6.51$ solution corresponded exactly to the lines and peak assigned to *II*. Similarly, the chronopotentiogram of 2,5-dihydroxybenzene-1,3-disulfonic acid in $H_0 = -8.14$ solution had a $E_{1/4}$ which was essentially equal to that of *IV* (wave 4) and the cathodic wave on current reversal showed only one wave whose $E_{0.215\tau'}$ was identical to that obtained for wave 2′. The ratio of the transition times for the chronopotentiograms of a mixture of 2,5-dihydroxybenzenesulfonic acid and 2,5-dihydrobenzene-1,3-disulfonic acid did not vary as the acidity of the solution was varied from -8.14 to -2.0

The chronopotentiogram of a freshly prepared $H_0 = -5.87$ solution of the mono-sulfonic acid ester of *p*-hydroquinone exhibited two waves which were identical to waves 1 and 3 observed for a freshly prepared *p*-hydroquinone solution of the same acid strength (see curve *B* of Figure 1). The ratios of τ_1/τ_3 for both the mono-sulfonic acid ester of *p*-hydroquinone solutions were essentially the same. Further experiments showed that the mono-sulfonic ester hydrolyzed in acid solution and that the hydrolysis went to completion in acid solutions which had acidity function values less than -5. At $H_0 = -5.87$, it was observed that the rate of hydrolysis, although very rapid, did not go to completion but an equilibrium was reached between the mono-sulfonic acid ester and hydroquinone (oxonium ion) itself.

Because the reaction rates estimated from the $i\tau^{1/2}$ *vs.* i for the solution containing species *II* and *V* (see curve *D* of Figure 1) did not compare with those expected for a protonation reaction and because the NMR spectra of the solution did not exhibit a oxonium protonation peak in the 14- to 11-p.p.m. range, it is believed that species *V* is proabably a mono-sulfonic acid ester of 2,5-dihydroxybenzenesulfonic acid. Such a compound was not, however, synthesized independently; its properties would be expected to be similar to that observed for *V*.

The current-reversal chronopotentiograms reveal some very interesting information about the nature of sulfonic acid derivatives of *p*-benzoquinone (the anodic electrode reaction products). First, it is felt that the oxidation product of the oxonium ion of *p*-hydroquinone in the higher acid strength solutions is simply *p*-benzoquinone and not its oxonium ion conjugate acid, because the quinone oxygens would be expected to be considerably less basic than the phenolic oxygens [the pK_a of anthraquinone is about -8.3 (*35*)]. The oxidation product of 2,5-dihydroxybenzenesulfonic acid is undoubtedly *p*-benzoquinone-2-sulfonic as n was found to equal 2 and the reaction was reversible. This sulfonated benzoquinone is not stable, however, in low acid strength solution, but was found to be stabilized in $H_0 = -6.51$ solutions indicating that the chemical reaction between *p*-benzoquinone and sulfuric acid is also reversible:



(2)

At present it is not understood why this reaction is such a rapid equilibrium. The *p*-benzoquinone-2,5-disulfonic acid which would be expected to be the oxidation product of *IV* (2,5-dihydroxybenzene-1,3-disulfonic acid) is evidently quite unstable even in solutions of $H_0 = -11.1$ and decomposes into II_{ox}, a rate sufficiently great to prevent the observation of any cathodic wave for its reduction on current reversal. As expected, the oxidation of the two monosulfonic acid esters, *III* and *V*, would not be expected to show a reverse wave, because the oxidation products will be *p*-benzoquinone and *p*-benzoquinone-2-sulfonic acid, respectively, which necessitates the cleaving of the ester at some point during its formation.

It is also interesting to note that th *p*-hydroquinone–quinone couple shows perfect reversibility at $H_0 > \sim -3$, but it is not reversible, $E_{1/4} \neq E_{0.215\tau'}$ at lower acid strengths. This effect of acid strength on the couple is not understood at the present.

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