

AN ELECTROCHEMICAL STUDY OF THE KINETICS OF THE ADDITION
OF AROMATIC AMINES TO 4-METHYL-O-BENZOQUINONE

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INTRODUCTION

In a study of the reduction of quinones, Braude and co-workers (1-4) found that the rate of the chemical reduction of a series of quinones by a variety of reducing agents is dependent upon the standard reduction potentials of the quinones and the nucleophilicity of the reducing agents. (The standard reduction potential is that potential where both the oxidized and the reduced species are in standard states having unit activity.) The reaction rates for the catalytic hydrogenation of methyl substituted p-benzoquinones were also found to be dependent upon the standard reduction potentials of the quinones (5).

Ogata, Sawaki, and Gotoh (6) have studied the addition of sodium thiosulfate to p-benzoquinone and observed a dependence upon the formal reduction potential of the quinone. (The formal reduction potential refers to the potential observed under experimental conditions for equal concentrations of the oxidized and reduced species. It is affected by pH, ionic strength, complexation, and solvent or supporting electrolyte.) They observed a straight line with a slope of 0.91 when they plotted the log of the second order rate constant as a function of the formal reduction potential. However, a plot of the log of the second order rate constant vs. pH was said to give a curve. They suggest that these data indicate the rate of thiosulfate addition is a function of the formal reduction potential of p-benzoquinone.

It has been shown that the rate constants for the 1,4-cyclization of oxidized catecholamines are independent of the formal reduction potentials of the catecholamines and are independent of pH above pH 6 (7). Piekarski and Adams (8) have reported that rate constants for 1,4-additions of aromatic amines to quinones in strong acid solutions are specific acid catalyzed.

The purpose of this paper is to expand the investigation of the kinetics of 1,4-additions in an effort to determine the role of pH and formal reduction potentials of the quinones involved in these reactions.

EXPERIMENTAL

Instrumentation

A potentiostat-galvanostat was used to obtain cyclic voltammetric and chronoamperometric data. The instrument was constructed in this laboratory and is a transistorized modification of that reported by Underkofler and Shain (9). The circuitry has been reported previously (10) although compensation for uncompensated iR has been added (11).

Compensation of ohmic potential loss (uncompensated iR) was obtained by adding a positive feedback loop from the output of the current follower to the input of the control amplifier. Optimum feedback was obtained by increasing the feedback until control of potential was lost and then reducing the current slightly until control was re-established.

The techniques suggested by Brown, Smith, and Booman (12) were used to stabilize the potentiostat. In order to reduce the high-frequency noise, the output of the control amplifier was used to drive the shield (ca. 25 pf capacitance) of the feedback loop. For cyclic voltammetry the potential scan was switched at the anodic and cathodic limits by means of a comparator (13) operated by a multipole, mercury wetted relay (Type HG6F-1028, C.P. Clare and Co.).

Moseley 7035B and 7030A X-Y recorders were used to record all current-potential curves. Current-time curves were recorded on a Honeywell Model 19 strip chart recorder. Short time chronoamperometry was obtained using the above potentiostat in conjunction with a Hewlett-Packard Model 3300-3302 function generator. The resulting current-time curves were recorded on a Tektronix Type 564 Storage Oscilloscope which used a Type 2A63 differential amplifier and a Type 2B67 time base. Curves stored on the oscilloscope were photographed with a Dumont Type 2620 camera. Camera settings were f 5.6 with a shutter speed of 1/50 second using Polaroid Type 47, speed 3000 film. All pH measurements were taken with a Corning Model 19 pH meter.

Electrodes and Cells

The working electrode for most cyclic voltammetry and chronoamperometry was a carbon paste electrode (14) which had a geometric area of 0.17 cm^2 . The auxiliary electrode was a small platinum foil. The reference electrode was a saturated calomel electrode (SCE). All potentials are reported vs. SCE. A semi-infinite-linear-diffusion (SILD) electrode was used to study slow reactions. The SILD electrode was constructed in this laboratory. Construction and use of SILD electrodes have been reported previously (15,16).

The cells were glass jars which had a volume of approximately 60 ml. The top of the cell was a number ten rubber stopper with holes for the electrodes and the nitrogen inlet. The cells were thermostated in a water bath having a temperature of $25^\circ \pm 0.1^\circ \text{ C}$. The water bath was cushioned to prevent bench vibrations from stirring the solution in the cell.

Chemicals

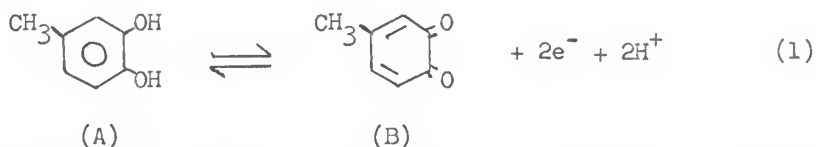
All chemicals, except aniline, were of reagent grade and were used without further purification. Aniline was distilled giving a colorless liquid having a boiling point of $179^\circ\text{-}181^\circ \text{ C}$. Two buffer systems were used; monochloroacetic acid-acetate, and a Britton-Robinson buffer (acetate-phosphate). All solutions were deaerated twenty minutes or more with nitrogen.

Kinetics

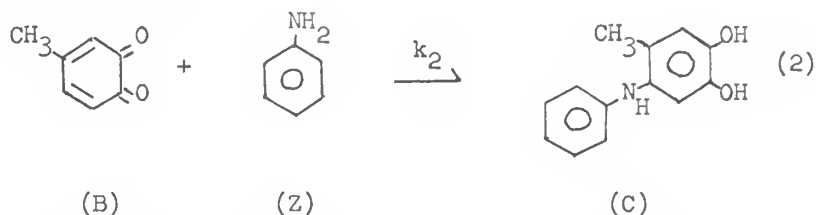
Chronoamperometry, a potentiostatic technique which has been used to determine rate constants (7,8,17-19), was used to study the kinetics of the 1,4-addition of aniline to 4-methyl-o-benzoquinone. Cyclic voltammetry was used to determine the oxidation potential of the compound of interest. A constant potential which was 100-200 millivolts more positive than the peak anodic potential was applied to the electrode and the resulting current-time curve was recorded.

Chronoamperometric $it^{\frac{1}{2}}$ values for 4-methylcatechol were constant with time. Values of $it^{\frac{1}{2}}$ from the strip chart recorder agreed within 2% of the $it^{\frac{1}{2}}$ values from the oscilloscope. The average $it^{\frac{1}{2}}$ value over the time range of interest was then used as $it^{\frac{1}{2}}_{k=0}$.

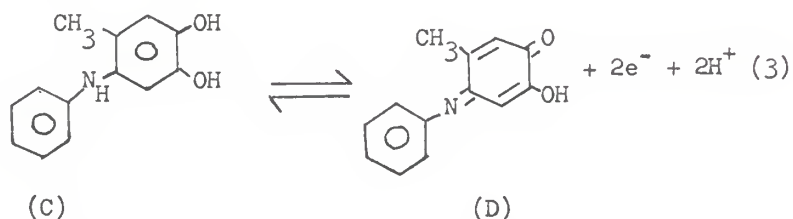
This electrochemical reaction is given below.



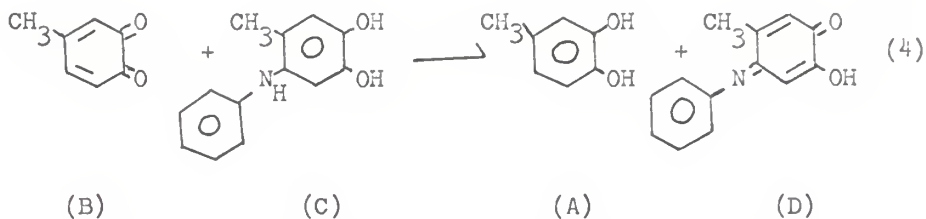
When 4-methylcatechol is oxidized in the presence of a nucleophile, such as aniline, $it^{\frac{1}{2}}$ is a function of $k_1 t$, where k_1 is the pseudo first order rate constant in the presence of excess nucleophile and t is time.



The intermediate formed is then oxidized to complete the ECE mechanism (Electron transfer - Chemical reaction - Electron transfer).



Since the intermediate formed is more easily oxidized than the 4-methylcatechol, a chemical oxidation-reduction reaction occurs. This is seen in equation four.



Alberts and Shain (17) developed the chronoamperometric techniques used to study the kinetics of the ECE mechanism. Improvements have been made to include the chemical oxidation-reduction reaction which was originally neglected (18).

Equations 5-9 describe the mass transfer (diffusion), rate of the follow-up chemical reaction, and the solution redox reaction for the above sequence of reactions. The initial and boundary conditions are listed for chronoamperometry. The solution redox reaction is assumed to be infinitely fast; the equilibrium constant, K , is large (as shown by the separation in peak potentials for the two redox systems).

$$\frac{\partial C_A(x,t)}{\partial t} = D \frac{\partial^2 C_A(x,t)}{\partial x^2} + k [C][B] \quad (5)$$

$$\frac{\partial C_B(x,t)}{\partial t} = D \frac{\partial^2 C_B(x,t)}{\partial x^2} - k [C][B] - k_2 [B][Z] \quad (6)$$

$$\frac{\partial C_C(x,t)}{\partial t} = D \frac{\partial^2 C_C(x,t)}{\partial x^2} - k [C][B] \quad (7)$$

$$\frac{\partial C_D(x,t)}{\partial t} = D \frac{\partial^2 C_D(x,t)}{\partial x^2} + k [C][B] \quad (8)$$

$$i = nFAD \left. \frac{\partial C_A(x,t)}{\partial x} \right|_{x=0} + nFAD \left. \frac{\partial C_C(x,t)}{\partial x} \right|_{x=0} \quad (9)$$

Initial Conditions:

$$C_A(x,0) = C_A^b \quad (10)$$

$$C_B(x,0) = C_C(x,0) = C_D(x,0) = 0 \quad (11)$$

Boundary Conditions:

at $x = 0$

$$C_A(0,t) = C_C(0,t) = 0 \quad (12)$$

$$D \frac{\partial C_A(x,t)}{\partial x} \Big|_{x=0} = D \frac{\partial C_B(x,t)}{\partial x} \Big|_{x=0} \quad (13)$$

$$D \frac{\partial C_C(x,t)}{\partial x} \Big|_{x=0} = D \frac{\partial C_D(x,t)}{\partial x} \Big|_{x=0} \quad (14)$$

at $x = \infty$

$$C_A(\infty,t) = C_A^b \quad (15)$$

$$C_B(\infty,t) = C_C(\infty,t) = C_D(\infty,t) = 0 \quad (16)$$

C_A = equilibrium concentration of A

C_B = equilibrium concentration of B

C_C = equilibrium concentration of C

C_D = equilibrium concentration of D

x = distance from electrode surface

t = time (seconds)

D = diffusion coefficient

k = rate of solution redox reaction (infinitely fast)

i = current

n = number of electrons involved in the electrochemical process

F = Faraday

- A = area of electrode surface
 C_A^b = bulk concentration of A
 [B] = equilibrium concentration of B
 [C] = equilibrium concentration of C
 [Z] = equilibrium concentration of Z

The pseudo first order rate constant, k_1 , is determined by following $it^{\frac{1}{2}}/it_{k=0}^{\frac{1}{2}}$ as a function of k_1t . Values of $it^{\frac{1}{2}}/it_{k=0}^{\frac{1}{2}}$ increase from one at small k_1t when no reaction occurs (eq. 1) to two when k_1t is large and the reaction is complete.

A computer technique has been developed which is a digital simulation of the sequence of reactions (18). It gives a value of k_1t for every $it^{\frac{1}{2}}/it_{k=0}^{\frac{1}{2}}$ value. The pseudo first order rate constant is then obtained from a plot of k_1t vs. t or from an average of k_1 values at several different times (Plate 1). For a first order reaction a plot of k_1t vs. t should give a straight line intercepting the origin. The slope of the line is k_1 .

The second order rate constant, k_2 , was calculated from the following equation,

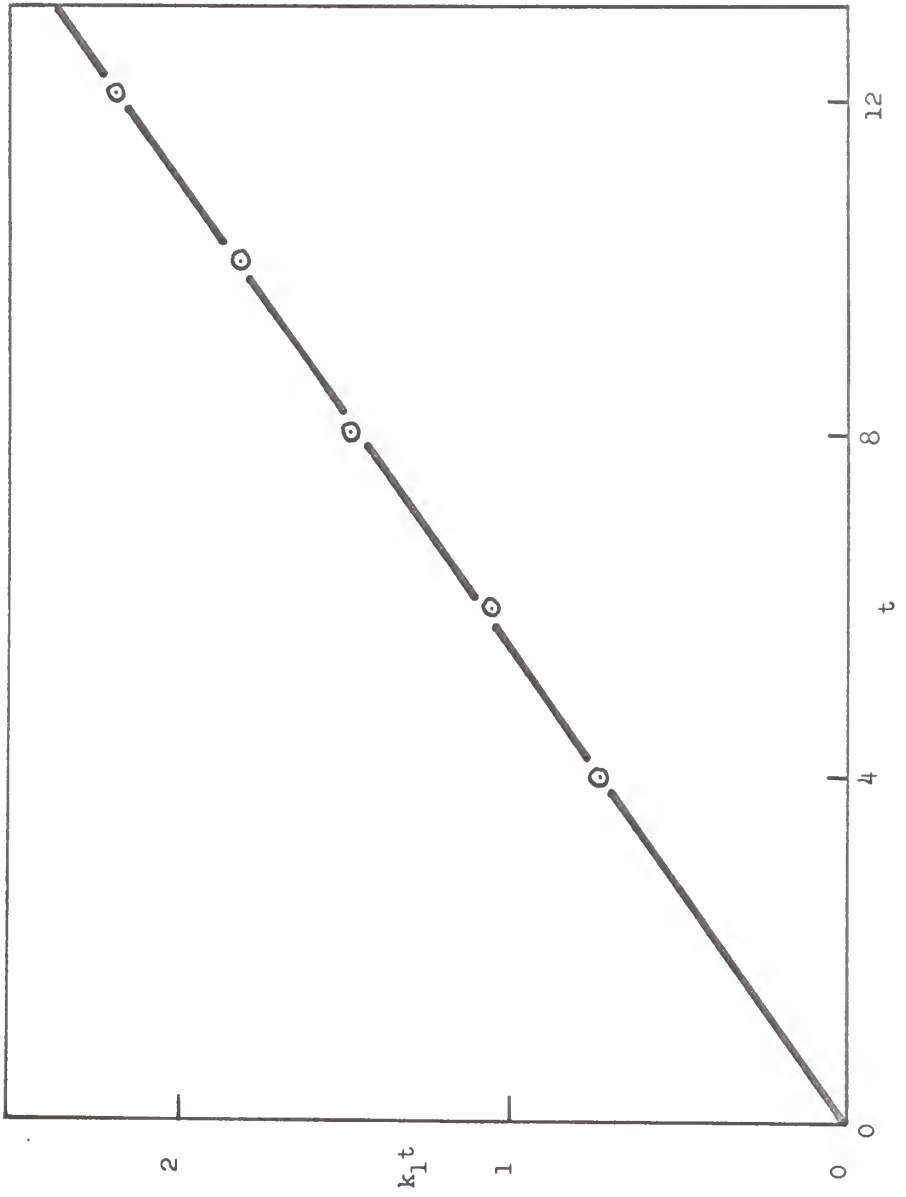
$$k_2 = k_1/[An] \quad (17)$$

where [An] is the equilibrium concentration of aniline. The Henderson - Hasselbalch equation was used to calculate the concentration of aniline in buffered solutions while the Hammett acidity function, H_0 , was used for calculations in strong acid solutions.

$$pH = pK_a - \log \frac{[HB]}{[B]} \quad (18)$$

PLATE 1

Plot of $k_1 t$ vs. $t(\text{sec.} \times 10^{-2})$ for the 1,4-addition of 2.2×10^{-2} M
aniline to 1×10^{-3} M 4-methyl-o-benzoquinone at pH 5.1.



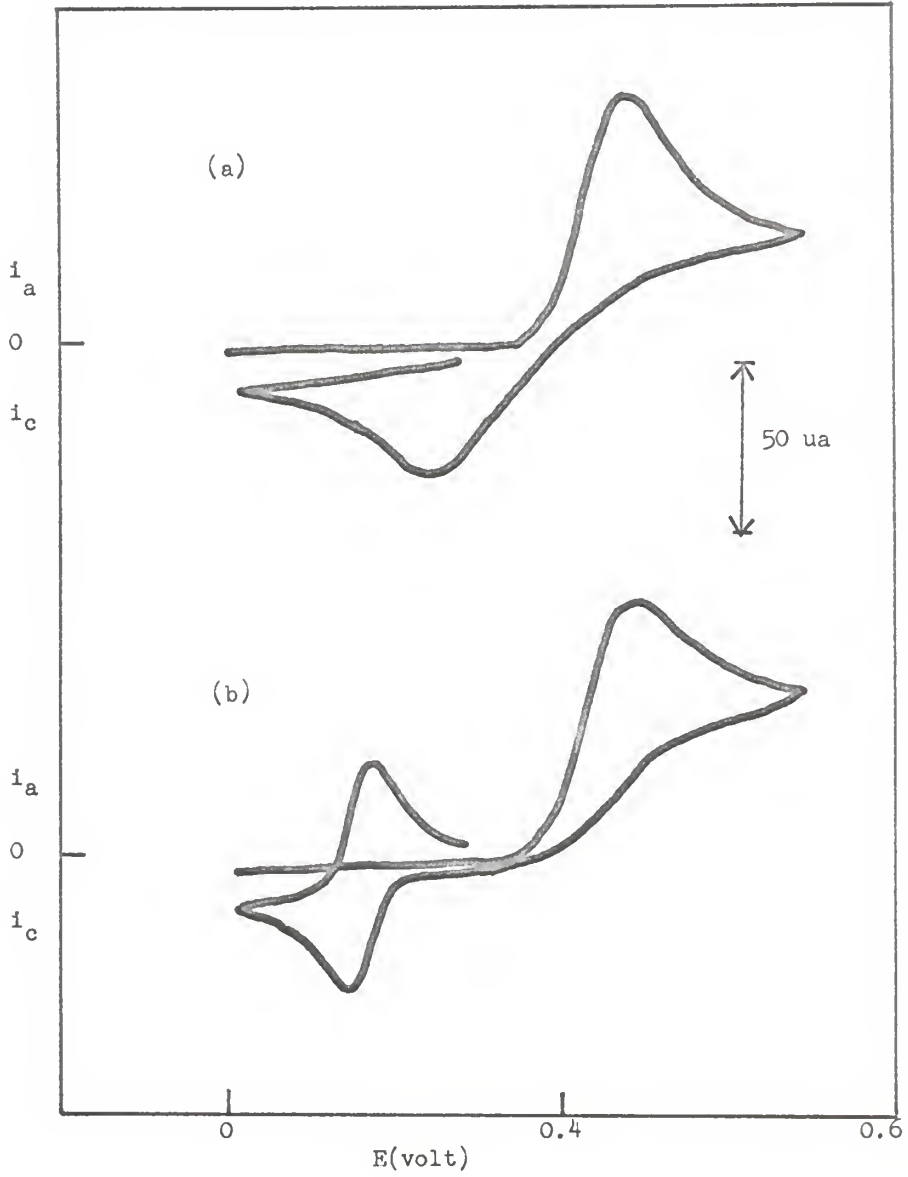
RESULTS

The cyclic voltammogram in Plate 2a is of 1×10^{-3} M 4-methylcatechol in a buffered solution of pH 2.2. On scanning in the anodic direction, a single oxidation peak corresponding to the two electron oxidation of 4-methylcatechol to 4-methyl-o-benzoquinone is seen at +0.48 volts. After reversing the scan, a single reduction peak arising from the reduction of 4-methyl-o-benzoquinone back to 4-methylcatechol is observed at +0.25 volts. No new redox processes appear on subsequent scans.

When 2.2×10^{-2} M aniline is added to the 4-methylcatechol solution, the cyclic voltammogram shown in Plate 2b is observed. The initial anodic scan shows only one oxidation peak at +0.48 volts corresponding to the oxidation of 4-methylcatechol. Upon reversing the scan, reduction of 4-methyl-o-benzoquinone is not observed but a new peak at +0.13 volts does appear. On the second anodic scan a new oxidation wave is seen at +0.17 volts. No new waves appear on the following scans over this potential range. The disappearance of the 4-methyl-o-benzoquinone reduction wave, the appearance of a new redox system at a more negative potential, and the increase in i_p/c (i_p = anodic peak current, c = concentration) for the first oxidation wave with aniline added are consistent with the ECE mechanism. The chemical and electrochemical processes responsible for this behavior have been identified previously (18,19). Following the two electron oxidation of 4-methylcatechol to 4-methyl-o-benzoquinone, 4-anilino-5-methylcatechol is formed by the 1,4-addition of aniline to 4-methyl-o-benzoquinone. The substituted catechol, being more easily oxidized than 4-methylcatechol, is oxidized either electrochemically or chemically by 4-methyl-o-benzoquinone to give 4-anilino-5-methyl-o-benzoquinone. The new oxidation wave (+0.17 volts) and reduction wave (+0.13 volts) are the result of the chemical reaction of 4-methyl-o-benzoquinone with aniline. For 1×10^{-3} M 4-methylcatechol, $it_{K=0}^{\frac{1}{2}}$ values (where $it_{K=0}^{\frac{1}{2}}$ is $it^{\frac{1}{2}}$ for

PLATE 2

- (a) Cyclic voltammogram of 1×10^{-3} M 4-methylcatechol at pH 2.2.
(b) Cyclic voltammogram of 1×10^{-3} M 4-methylcatechol at pH 2.2
in the presence of 2.2×10^{-2} M aniline.



4-methylcatechol in the absence of a chemical reaction) are constant with time ($it_{k=0}^{\frac{1}{2}} = 55.5$). When 2.2×10^{-2} M aniline is added to the solution, $it^{\frac{1}{2}}$ increases with time and at long times $it^{\frac{1}{2}}$ approaches a limiting value of twice that of $it_{k=0}^{\frac{1}{2}}$ ($it^{\frac{1}{2}} = 111$). Since aniline is electrochemically inactive in this potential region, the increase in $it^{\frac{1}{2}}$ cannot be due to the oxidation of aniline.

Table I shows the calculations of k_1 for the 1,4-addition of aniline to 4-methyl-o-benzoquinone. The numbers are taken from a typical set of chronoamperometric data for 1×10^{-3} M 4-methylcatechol and 2.2×10^{-2} M aniline at pH 6.7.

TABLE I

Calculation of k_1 .

t (sec)	i (amp x 10^{-3})	$it^{\frac{1}{2}}/c^*$	$it^{\frac{1}{2}}/it_{k=0}^{\frac{1}{2}}$ **	$k_1 t$	k_1 (sec $^{-1}$)
0.02	0.520	73.4	1.331	0.4324	21.62
0.03	0.460	79.6	1.443	0.6529	21.43
0.04	0.420	84.0	1.523	0.8524	21.31
0.05	0.385	86.3	1.566	0.9853	19.91
0.06	0.365	89.5	1.624	1.1969	19.95
0.07	0.350	92.7	1.682	1.4814	21.02
2.00	0.078	110.0	1.996		
3.00	0.065	110.2	2.000		
4.00	0.055	110.0	1.996		

* c = concentration of 4-methylcatechol (1×10^{-3} M)

** $it_{k=0}^{\frac{1}{2}} = 55.1$

Since values of $it^{\frac{1}{2}}$ for 4-methylcatechol were constant, the electrode surfaces were reproducible and no effects due to electrode roughness or size variation were apparent. Upon the addition of aniline to the 4-methylcatechol solution, current-time curves were

observed to vary more than when aniline was not present. Therefore, six repetitions of each chronoamperometric experiment were made and the three or four curves in closest agreement were used to calculate k_1 . These values were then used to calculate an average value for the second order rate constant, k_2 . The slight variation of results from one electrode to the next is attributed to adsorption and/or extraction of aniline by the carbon paste electrode. The variance in k_1 decreases as the concentration of unprotonated aniline decreases. Thus, as the pH decreases the reproducibility becomes better. Typical data can be illustrated by the k_2 values obtained at pH 5.9 where k_2 varied from 9.5×10^2 to 1.0×10^3 .

The plot of $\log k_2$ as a function of pH (Plate 3) shows that k_2 increases linearly with an increase in hydrogen ion concentration below pH 3. Above pH 3 k_2 is independent of pH. From Plate 3 it is apparent that that specific acid catalysis is observed for the 1,4-addition of aniline to 4-methyl-o-benzoquinone. A plot of $\log k_2$ vs. the Hammett acidity function, H_0 , gives a straight line with a slope of -0.78. This indicates that the mono-protonated 4-methyl-o-benzoquinone is the reactive quinone in strong acid solutions.

General acid catalysis was investigated by varying the concentration of a monochloroacetic acid - acetate buffer from 0.1 M to 1.0 M and observing the rate constants while keeping the pH constant (Table II). Although slight variations in the rate constants were observed, no significant changes occurred. Thus no general acid catalysis was observed.

PLATE 3

Log k_2 vs. pH and log k_2 vs. H_0 , the Hammett acidity function, for
the 1,4-addition of aniline to 4-methyl-o-benzoquinone.

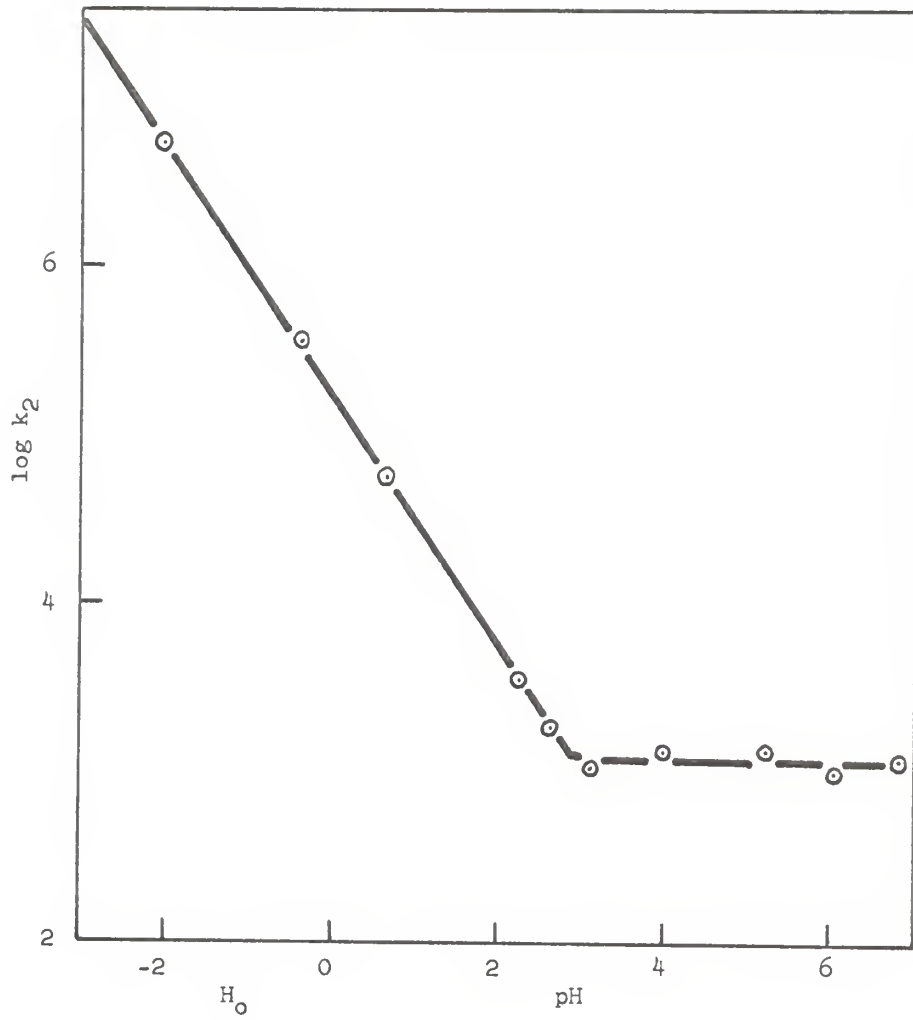


TABLE II

Data for general acid catalysis.

analytical concentration of buffer	k_1 (sec^{-1})	k_2 (liters/mole sec)
0.1 M	0.154	1.89×10^3
0.5 M	0.152	1.87×10^3
1.0 M	0.148	1.82×10^3

Data are from $5 \times 10^{-4} \text{M}$ 4-methylcatechol and $1.1 \times 10^{-2} \text{M}$ aniline at pH 2.2.

Cyclic voltammetry was used to obtain the oxidation peak potential of 4-methylcatechol at several pH values over a pH range of 2-7. A plot of the oxidation peak potential as a function of pH (Plate 4) gives a straight line with a slope of -0.058 volts/pH unit. This result is anticipated from the Nernst equation for a two-electron, two-proton process:

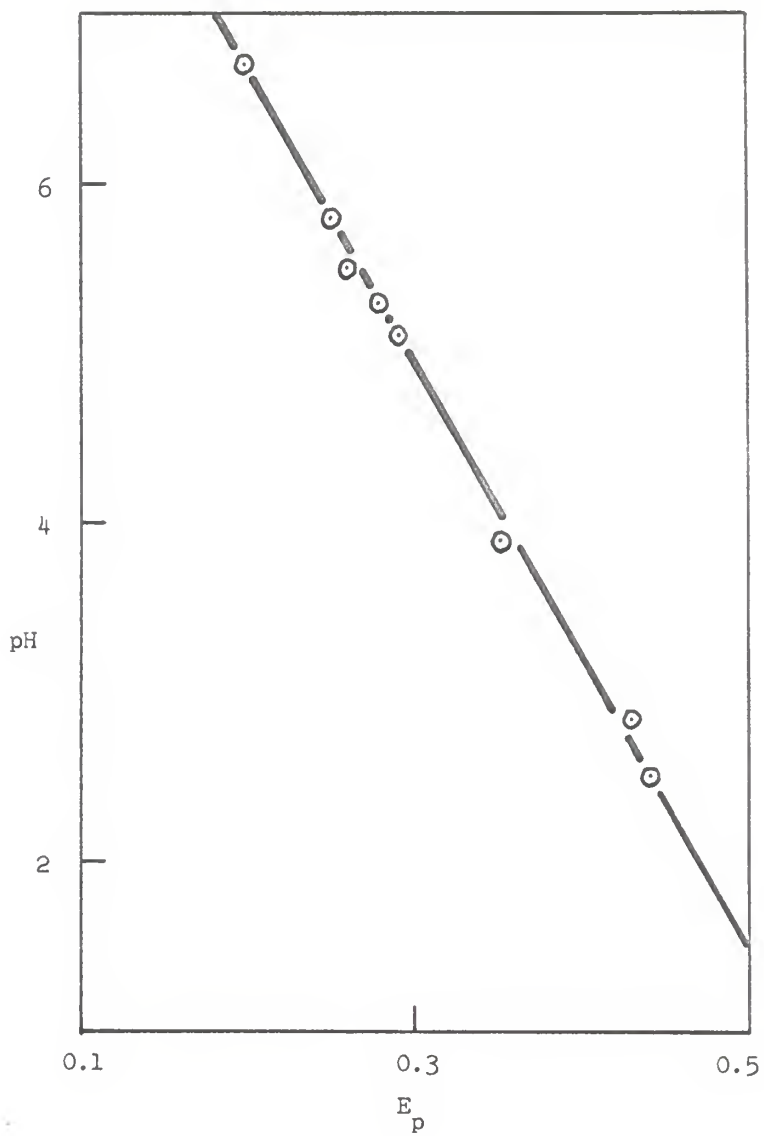
$$E = E^{\circ} + \frac{RT}{2F} \ln \frac{[\text{quinone}][\text{H}^+]^2}{[\text{hydroquinone}]} \quad (19)$$

In general a similar plot (parallel to that for 4-methyl-o-benzoquinone) will be obtained for any other quinone undergoing a two-electron, two-proton process.

While the cyclic voltammogram of 4-methylcatechol and 4-aminoacetophenone was similar to that of 4-methylcatechol and aniline, chronoamperometric and coulometric data showed complications. Repetitive runs of chronoamperometry on the same carbon paste electrode showed a decrease in $it^{\frac{1}{2}}$. Since the solution was stirred between each run, this decrease cannot be attributed to a decrease in the concentration of reactants at the electrode surface. Therefore, the product of the 1,4-addition of 4-aminoacetophenone to 4-methyl-o-benzoquinone was either adsorbed by the carbon paste or

PLATE 4

E_p , oxidation peak potential, vs. pH for 4-methylcatechol.



or formed a precipitate on the electrode surface. Chronocoulometry, a technique frequently used to determine the adsorption of reactants and products (20-23), also showed product adsorption was occurring. Because of this, the rate of this reaction was not studied further.

The reaction of 4-methyl-o-benzoquinone with a twenty-fold excess of sodium thiosulfate was also studied. The cyclic voltammogram of 4-methylcatechol in a buffered solution of pH 3.8 is similar to that observed for 4-methylcatechol at pH 2.2 (Plate 2a) although a cathodic shift of potentials has occurred due to an increase in pH. The cyclic voltammogram of 4-methylcatechol and sodium thiosulfate (Plate 5) shows an oxidation peak at +0.38 volts and another at +0.53 volts. The peak at +0.38 volts is not due entirely to the oxidation of 4-methylcatechol since the anodic current observed is approximately twice that observed for 4-methylcatechol in the absence of sodium thiosulfate. This indicates that some product is oxidized at nearly the same potential as 4-methylcatechol. The anodic peak at +0.53 volts is due to the oxidation of one or more additional products and suggests that more than one thiosulfate ion adds per molecule of 4-methylcatechol. The absence of a well-defined reduction peak also indicates a solution redox reaction is occurring. A substituted 4-methyl-o-benzoquinone of higher redox potential than 4-methylcatechol oxidizes the 4-methylcatechol to give 4-methyl-o-benzoquinone and a substituted 4-methylcatechol. Since the addition of thiosulfate is very rapid, as observed from chronoamperometric data, the reduction of 4-methyl-o-benzoquinone is not observed. Chronoamperometric data also show that the number of electrons involved, eight, corresponds to three moles of thiosulfate adding per mole of 4-methylcatechol. Constant-potential coulometric data also indicate that three moles of thiosulfate add per mole of 4-methylcatechol.

The cyclic voltammogram of p-hydroquinone at pH 5 is seen in Plate 6. The increase in the anodic peak height for p-hydroquinone in the presence of thiosulfate (Plate 6b) indicates a reaction

PLATE 5

Cyclic voltammogram of 1×10^{-3} M 4-methylcatechol and 2.2×10^{-2}
M thiosulfate at pH 3.8.

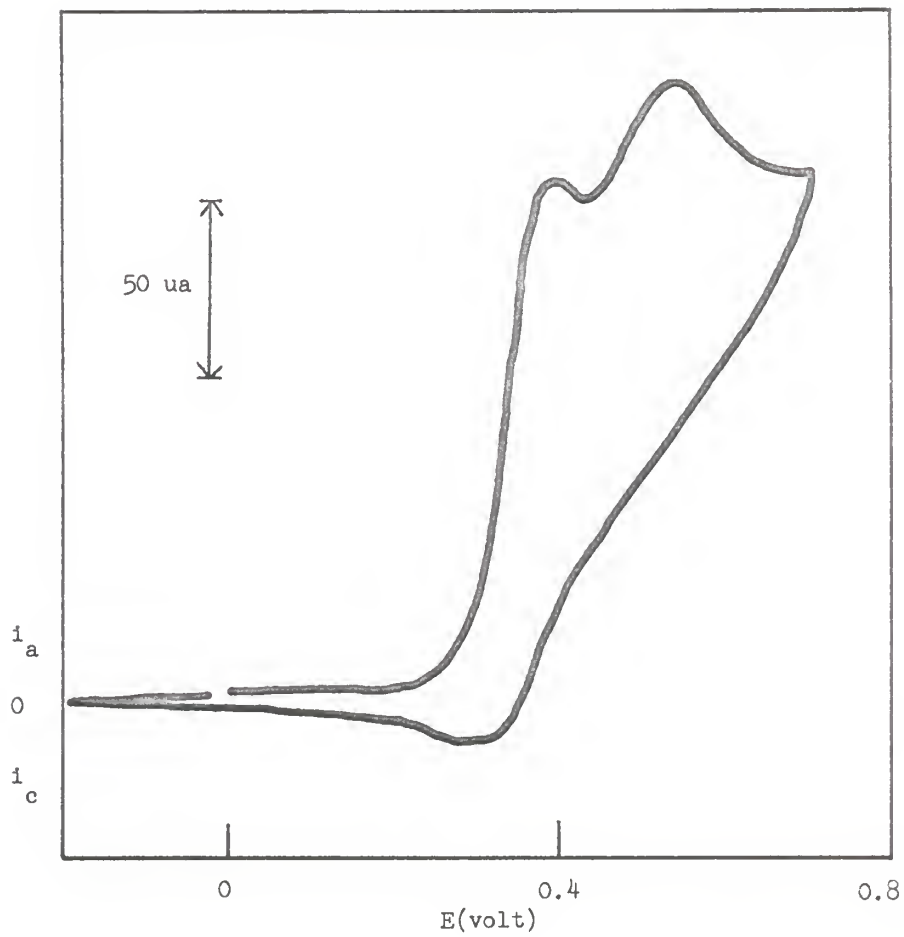
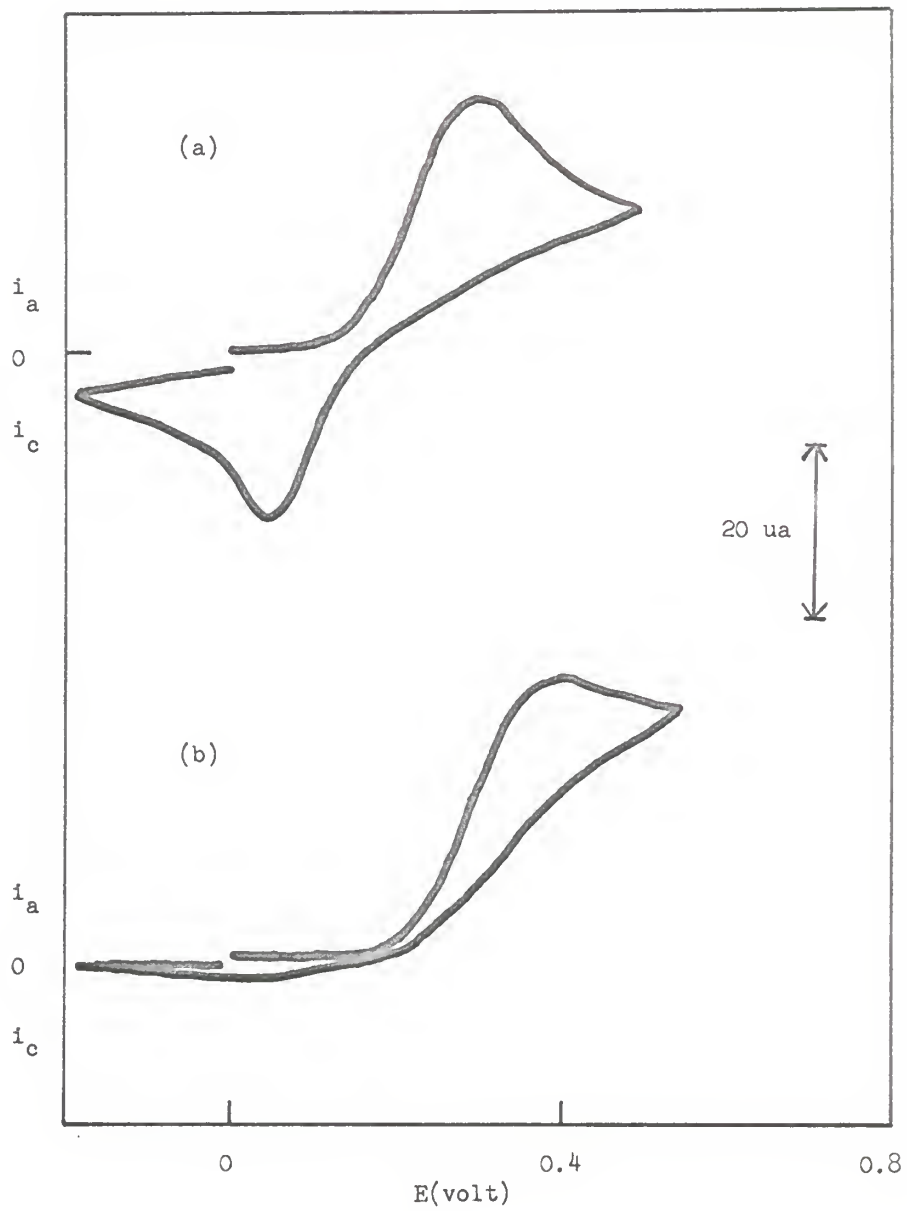


PLATE 6

- (a) Cyclic voltammogram of 5×10^{-4} M p-hydroquinone at pH 5.1.
(b) Cyclic voltammogram of 5×10^{-4} M p-hydroquinone at pH 5.1
in the presence of 1×10^{-2} M thiosulfate.



is occurring. However, since the cyclic voltammogram of p-hydroquinone and thiosulfate shows only one oxidation peak, and since the oxidation peak height is greater than that of p-hydroquinone, the product is oxidized at the same potential as p-hydroquinone. A comparison of the oxidation peak heights of 4-methylcatechol and thiosulfate (Plate 5b) and p-hydroquinone and thiosulfate (Plate 6b) shows the latter is a slower reaction. The absence of a reduction wave indicates a rapid follow-up reaction is occurring. Chronoamperometric data show that the number of apparent electrons that have reacted at 3.2 seconds is four. The value of $it^{1/2}/c$ continues to increase smoothly, indicating that more than one mole of sodium thiosulfate adds per mole of p-hydroquinone.

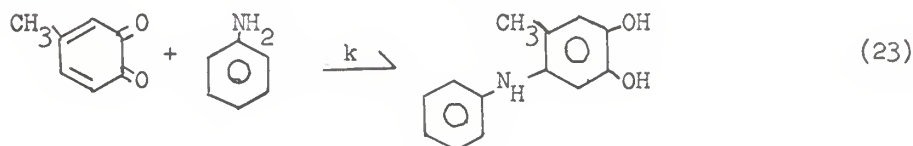
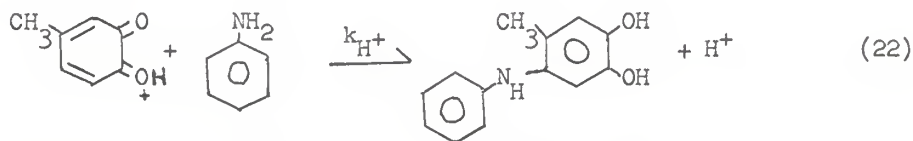
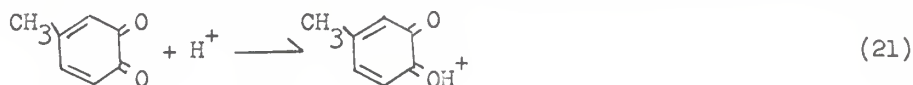
Because thiosulfate added to more than one position, trimethylhydroquinone was used to limit the number of reactive sites on the quinone to only one position. Since preliminary experiments at an unshielded carbon paste electrode indicated a very slow addition of thiosulfate to trimethyl-p-benzoquinone, this was studied at a semi-infinite-linear-diffusion (SILD) electrode. The SILD electrode eliminates diffusion to the electrode from the sides and accurate chronoamperometric data can be taken at times up to five minutes. Values of $it^{1/2}$ for trimethylhydroquinone were constant for times from one to five minutes. The addition of sodium thiosulfate, however, still caused less than a 10% increase in $it^{1/2}$ for times up to five minutes. Since the variation of $it^{1/2}/it_{k=0}^{1/2}$ is not sufficiently large to permit calculation of rate constants, chronoamperometry cannot be used to study the addition of thiosulfate to trimethylhydroquinone.

DISCUSSION

The rate data shown in Plate 3 suggest an acid catalyzed pathway in addition to the uncatalyzed pathway. The acid catalyzed pathway probably involves protonation of the quinone prior to the rate determining addition of aniline to 4-methyl-o-benzoquinone. The rate of the reactions shown in equations 21-23 can be given by the following rate law:

$$\text{rate} = (k_{H^+}[H^+] + k) C_Q[\text{An}] \quad (20)$$

where $\log k_{H^+} = 5.25$, $\log k = 3.15$, C_Q = analytical concentration of quinone, and $[\text{An}]$ = equilibrium concentration of unprotonated aniline.



While the data in Table I show unequivocally that only one mole of aniline adds per mole of 4-methyl-o-benzoquinone, the data in Tables III and IV indicate that multiple addition to p-benzoquinone and 4-methyl-o-benzoquinone is occurring in the case of thiosulfate. Comparison of the rates of thiosulfate addition shows that the reaction is more rapid for 4-methyl-o-benzoquinone than for p-benzoquinone. This result is anticipated because of the more positive standard reduction potential for 4-methyl-o-benzoquinone: 0.753 volts vs. 0.700 volts for p-benzoquinone (24). Both potentials are vs. the standard hydrogen electrode. Although the standard

TABLE III

Calculation of $it^{\frac{1}{2}}/it_{k=0}^{\frac{1}{2}}$ for 4-methyl-o-benzoquinone and thiosulfate.

t (sec)	i (amp x 10 ⁻³)	$it^{\frac{1}{2}}/c$	$it^{\frac{1}{2}}/it_{k=0}^{\frac{1}{2}}$
1	0.214	214.0	3.86
2	0.159	224.0	4.04
3	0.135	234.0	4.22
4	0.119	238.0	4.27
5	0.105	236.0	4.25
6	0.096	236.0	4.25
7	0.090	238.0	4.27

Data are for 1×10^{-3} M 4-methylcatechol and 2×10^{-2} M sodium thiosulfate at pH 3.8.

TABLE IV

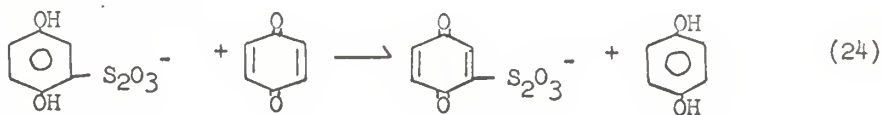
Calculation of $it^{\frac{1}{2}}/it_{k=0}^{\frac{1}{2}}$ for p-benzoquinone and thiosulfate.

t (sec)	i (amp x 10 ⁻³)	$it^{\frac{1}{2}}/c$	$it^{\frac{1}{2}}/it_{k=0}^{\frac{1}{2}}$
1	0.0369	184.5	1.42
2	0.0316	222.5	1.71
3	0.0294	255.0	1.96
4	0.0281	280.5	2.16
5	0.0270	303.0	2.33
6	0.0264	323.0	2.49
7	0.0254	337.5	2.60
8	0.0250	354.0	2.72
9	0.0244	365.0	2.81

Data are for 5×10^{-4} M p-hydroquinone and 1×10^{-2} M sodium thiosulfate at pH 5.1.

reduction potentials for the thiosulfate-substituted p-hydroquinone and for the thiosulfate-substituted 4-methylcatechol are not known with certainty, cyclic voltammetry indicates that all thiosulfate-substituted species are oxidized either concurrently or at slightly more anodic potentials than the corresponding unsubstituted species. Since the reactivity of the substituted and unsubstituted quinones should be nearly equal, substitution is expected to continue until all sites are reacted. In contrast, 4-anilino-5-methylcatechol is much more readily oxidized than 4-methylcatechol. From the dependence noted above on the standard reduction potential of the quinone, further addition of aniline is not to be expected. No addition to trimethylhydroquinone is observed for thiosulfate and aniline, a result which should also be anticipated in view of its low standard reduction potential of 0.525 volts vs. standard hydrogen electrode (24).

While the data substantiate the reports (1-5) of a dependence of the rate upon the standard reduction potentials for several quinones, no evidence was found here to support the argument of rate dependence upon the formal reduction potential of a specific quinone. Assuming that 4-methyl-o-benzoquinone and aniline behave analogously to p-benzoquinone and thiosulfate, the claim of Ogata and co-workers (6) of a dependence of the rate constant upon the formal reduction potential appears to be in error. They assumed a single mole of thiosulfate adds per mole of p-benzoquinone. As observed previously, however, the product of the addition of thiosulfate at pH 5 is oxidized concurrently with hydroquinone. Hence, unreacted quinone should be expected to oxidize the thiosulfate-substituted hydroquinone (eq. 24).



AN ELECTROCHEMICAL STUDY OF THE KINETICS
OF THE ADDITION OF
AROMATIC AMINES TO 4-METHYL-O-BENZOQUINONE

by

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ABSTRACT

The addition reaction of aniline and thiosulfate to 4-methyl-o-benzoquinone and the addition reaction of thiosulfate to p-benzoquinone have been studied by cyclic voltammetry and chronoamperometry. The rate of addition of aniline to 4-methyl-o-benzoquinone has been found to obey the rate law: $\text{rate} = (k_{H^+}[H^+] + k) C_Q[An]$, where C_Q is the analytical concentration of quinone and $[An]$ is the equilibrium concentration of unprotonated aniline. The value of k_{H^+} is 1.8×10^5 and the value of k is 1.4×10^3 . The slope (-0.78) of the plot of the log of the second order rate constant vs. the Hammett acidity function, H_0 , suggests protonation of the quinone prior to the rate determining addition of aniline. General acid catalysis was not observed. As stated by the rate law, the second order rate constant is independent of pH in the pH range 3-7.

The products of the thiosulfate addition to both 4-methyl-o-benzoquinone and p-benzoquinone were found to be oxidized either concurrently or at slightly more positive potentials than 4-methyl-o-benzoquinone and p-benzoquinone. Multiple addition of thiosulfate was observed for both quinones. The order of addition to 4-methyl-o-benzoquinone and p-benzoquinone was in the order of their standard reduction potentials: 4-methyl-o-benzoquinone = 0.753 volts vs. 0.700 volts = p-benzoquinone. Both potentials are vs. Standard Hydrogen Electrode. As predicted for a two-electron, two-proton process, the formal reduction potential for 4-methyl-o-benzoquinone decreased by 0.059 volts per unit increase in pH.

These results are consistent with a dependence of rate upon the standard reduction potential but not upon the formal reduction potential of a specific quinone. The previous report of rate dependence of thiosulfate addition to p-benzoquinone upon the formal reduction potential appears to be in error and is the result of multiple addition of thiosulfate to the quinone.