Electrochemical Oxidation of a Quinol Phosphate[1]

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Abstract: The oxidation of 2-methyl-1,4-naphthoquinol 1-phosphate at solid electrodes is characterized in aqueous solutions using cyclic and linear potential sweep voltammetry, potentiostatic techniques, and esr spectroscopy. An oxidation scheme is postulated in which chemical reactions coupled to the electron-transfer steps play an important role. In alkaline media the oxidation proceeds through a one-electron intermediate, the 2-methyl-1,4-naphthosemiquinone radical, which can either undergo hydrolysis or be further oxidized. This hydrolysis rate is estimated and the resulting rate expression indicates that the intermediate can function as a phosphorylating agent.

The electrochemical oxidation in aqueous media of 2-methyl-1,4-naphthoquinol 1-phosphate (I) is characterized in this paper. In the range from 1 *M* sulfuric acid to pH 12, the over-all process proceeds by an irreversible two-electron oxidation to 2-methyl-1,4-naphthoquinone (II). However, the detailed oxidation mechanism is markedly dependent on pH and exhibits complications due to several coupled chemical reactions.

Quinol phosphates possess the potential of being phosphorylating agents and have been suggested as being agents for oxidative phosphorylation in biological systems.[2] Their oxidation has been studied in aqueous solutions by Clark, *et al.*,[3] and Lapidot and Samuel.[4] The latter work indicated that the oxidation proceeds by two pathways: P–O and C–O bond fission. A dual pathway has also been found for the oxidation in dry dimethylformamide.[5] The oxidation pathway of biological interest involves fission of the P–O bond to produce a metaphosphate intermediate, the phosphorylating agent. The oxidation has been shown to take this path to the extent of 30% in aqueous solution (pH 4)[4] or dimethylformamide[5] when bromine is the oxidant. Electron spin resonance (esr) spectra of semiquinone phosphate radicals have been observed by Allen and Bond.[6] These radicals were produced by permanganate oxidation of the quinol phosphates in alkaline solution. These observations are correlated in this study, and a detailed mechanism is proposed for the oxidation of this biologically important molecule.

The over-all products of the electrode reactions were established by esr and cyclic voltammetry. Linear potential sweep voltammetry was ideally suited to the study of this oxidation process and was used to obtain both qualitative and quantitative information. The diagnostic criteria for elucidation of the effects of chemical reactions coupled to electron-transfer steps, derived by Nicholson and Shain,[7,8] were used throughout this investigation. The simplicity and power of these criteria are demonstrated by the results.

Experimental Section

The apparatus for the cyclic voltammetric and potentiostatic experiments has been described;[9] the apparatus for the chronopotentiometric experiments was conventional. In most of the experiments the detector was a Moseley Model 135A X-Y recorder. In a few experiments a Hewlett-Packard Model 202A signal generator was used in conjunction with a Tetronix Model 531A oscilloscope to record the current-potential curves. The esr spectra were obtained using a Varian Model V4500 X-band spectrometer employing 100-kc field modulation. A Gilmont ultramicroburet with a 0.1-ml capacity was used for the acid-base titrations. A Leeds and Northrup Model 7664 pH meter, and a "black dot" glass electrode were used to measure pH.

Carbon paste electrodes (Nujol)[10,11] were used throughout this study. The electrode well was machined from Teflon and had a geometric area of 0.713 cm^2. A heavy circular wire made contact with the paste *ca.* 1 mm from the electrode surface. On occasion the electrical resistance of an electrode was measured; in all cases it was less than 8 ohms. Seldom were currents greater than 250 μa obtained in these studies; hence uncompensated *iR* was less than *ca.* 2 mv.

The carbon paste ring-disk electrode was based on a design of Galus, *et al.*;[12] it had dimensions of 0.305, 0.385, and 0.485 in., for the disk diameter, the ring i.d., and the ring o.d., respectively.

The preparation of the electrodes varied in two respects from the methods in the literature. First, a very dry paste was used. The ratio of grams of graphite to grams of Nujol was 1.92. The second difference concerned the preparation of the electrode surface. It was found that slight but real variations in current-potential curves for charge-transfer controlled processes could be caused by changing the surface on which the carbon paste surface was smoothed. Unless otherwise noted, the electrode surfaces used in this study were prepared on the surface of parchment paper which was covered with a thin layer of carbon paste. With use this surface would become "slick," and a fresh piece of parchment paper would be used. This method of electrode surface preparation gave the "most reversible" current-potential curves which were reproducible from day to day. Typically, peak currents and half-peak potentials were within ranges of ±2% and ±2 mv, respectively, except in the more basic solutions where the potentials became less reproducible.

The 2-methyl-1,4-naphthoquinol 1-phosphate (monotriethylammonium salt), obtained as a generous gift from Hoffman LaRoche Inc., was used without further purification. A titration with acid indicated that the sample was 99+% pure. The 2-methyl-1,4-naphthoquinone was Eastman White Label and was used without further purification.

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[1] Part of this work was presented at the Winter Meeting of the American Chemical Society, Phoenix, Ariz., Jan 16–21, 1966.

[2] V. M. Clark, G. W. Kirby, and A. R. Todd, *Nature*, **181**, 1650 (1958).

[3] V. M. Clark, D. W. Hutchinson, G. W. Kirby, and A. Todd, *J. Chem. Soc.*, 715 (1961).

[4] A. Lapidot and D. Samuel, *Biochem. Biophys. Acta*, **65**, 164 (1962).

[5] A. Lapidot and D. Samuel, *J. Am. Chem. Soc.*, **86**, 1886 (1964).

[6] B. T. Allen and A. Bond, *J. Phys. Chem.*, **68**, 2439 (1964).

[7] R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

[8] R. S. Nicholson and I. Shain, *ibid.*, **37**, 178 (1965).

[9] J. R. Alden, J. Q. Chambers, and R. N. Adams, *J. Electroanal. Chem.*, **5**, 152 (1963).

[10] R. N. Adams, *Anal. Chem.*, **30**, 1576 (1958).

[11] C. Olson and R. N. Adams, *Anal. Chem. Acta*, **22**, 582 (1960).

[12] Z. Galus, C. Olson, H. Y. Lee, and R. N. Adams, *Anal. Chem.*, **34**, 164 (1962).

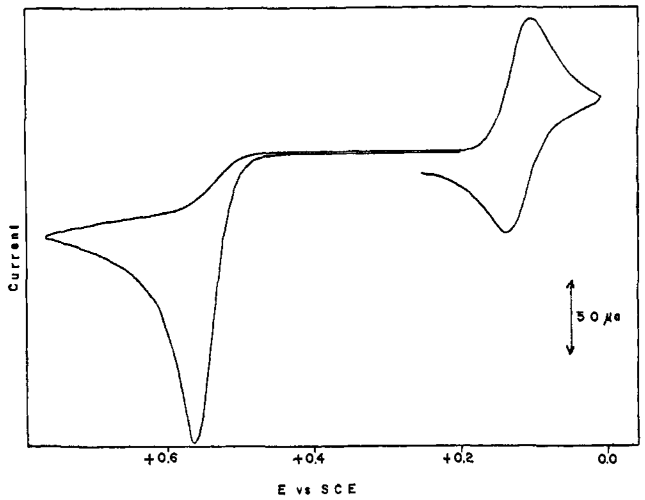

Figure 1. Cyclic voltammogram of 0.535 × 10^{-3} *M* I, 1 *M* H_2SO_4, 60 mv/sec.

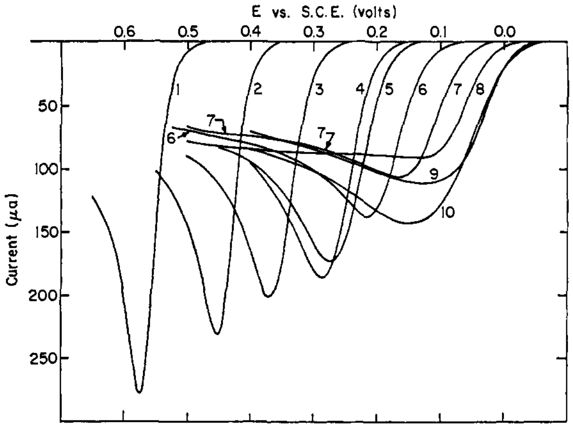

Figure 2. Single sweep voltammograms of I, 60 mv/sec. All currents have been "normalized" to 0.755 × 10^{-3} *M*: (1) 1 *M* H_2SO_4, (2) pH 2.50, (3) pH 4.04, (4) pH 5.63, (5) pH 6.32, (6) pH 7.44, (7) pH 8.38, (8) pH 9.27, (9) pH 11.18, (10) pH 11.87.

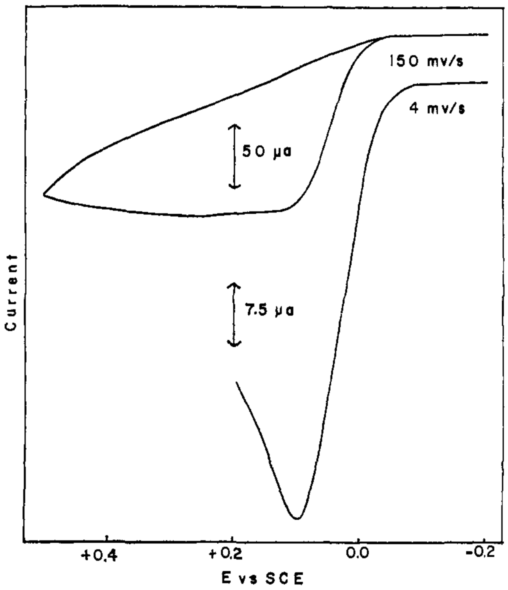

Figure 3. Single and cyclic voltammograms of 0.879 × 10^{-3} *M* I, pH 10.39.

The buffers used in this study were prepared from 0.02 *M* acetic, phosphoric, and boric acids unless noted otherwise; 0.5 *M* Na_2SO_4 was added to maintain constant ionic strength. Sodium sulfate was also added to the sulfuric acid solutions (except to the 1 *M* solution) to maintain the sulfate ion concentration constant at 0.5 *M*. Laboratory distilled water which had been distilled from permanganate solution and redistilled was used to prepare all solutions. For the experiments with II, acetonitrile which had been rapidly distilled over P_2O_5 (twice) was added to dissolve the quinone.

All solutions were 0.5 to 1.0 m*M* in I and were prepared immediately before use with a weighed amount of I and 50 ml of a well-deaerated buffer solution. All experiments were carried out at room temperature (297 ± 1°K). Current-potential curves were recorded at different sweep rates in a random order, and a fresh electrode surface was prepared for each curve. Prepurified nitrogen which had been saturated with water was passed over the solution at all times. At least two and usually three current-potential curves were recorded at each sweep rate. Potentiostatic current-time curves were recorded either at the end of the run or intermittently in solutions of high pH in which I tended to be unstable. The potentials for the potentiostatic experiments were selected *ca.* 0.2 v anodic of the peak potential of any faradaic process for I and before the oxidation of triethylammonium ion.

A potentiostatic procedure was used to obtain the current-potential curves on the ring-disk electrode. The disk potential was stepped into the oxidation wave from a point cathodic of the wave; the currents were measured two seconds after application of the potential step. A given electrode was used for two or three potential steps, and then new surfaces were prepared.

The electrochemical and esr procedures for the *in situ* electrolysis have been described.[13]

Results and Discussion

Cyclic and single sweep voltammograms representative of each pH region are shown in Figures 1 to 3. In sulfuric acid (Figure 1), the current-potential (*i-E*) curve displayed a narrow two-electron oxidation wave at *ca.* 600 mv *vs.* a saturated calomel electrode (sce). As the pH was raised, the wave shifted cathodically 60 mv per pH unit and broadened out, and the peak current decreased (Figure 2). There was no sign of a cathodic process that corresponded to a *reversible* reduction of an oxidation product at any pH or sweep rate. At pH values greater than 7, the values of $i_p/ACv^{1/2}$ (where i_p is the peak current, *A* is the electrode area, *C* is the concentration of I, and *v* is the sweep rate) could not be explained on the basis of a two-electron transfer and were dependent on sweep rate. The effect of pH on the *i-E* curves is shown in Figure 2, in which single sweep voltammograms at constant sweep rate (60 mv/sec) have been "normalized" to a given concentration to facilitate comparison. At pH 9.27 (curve 8, Figure 2) essentially no peak was observed in the *i-E* curve, and the maximum value of the current was less than one-third of the current in strong acid. At even higher pH (curves 9 and 10, Figure 2) the peak current increased, and the half-peak potential became essentially independent of pH. In these solutions the peak current was strongly dependent on sweep rate; typical *i-E* curves at pH 10.39 are shown in Figure 3.

Although the peak current varied markedly with pH, the value of $it^{1/2}$ obtained from potentiostatic current-time curves varied only slightly with pH. The diffusion coefficient calculated from the Cottrell equation (assuming a two-electron transfer) was 6.3 × 10^{-6} cm²/sec in 1 *M* H_2SO_4, decreased to 4.5 × 10^{-6} at pH 9, and then increased slightly as the pH approached 12. At all pH values the value of $it^{1/2}$ was constant to at least 2% for times from 1 to 15 sec. This result indicates that the assumption of semiinfinite linear diffusion, which was used throughout this work, was valid.

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[13] R. N. Adams, *J. Electroanal. Chem.*, 8, 151 (1964).

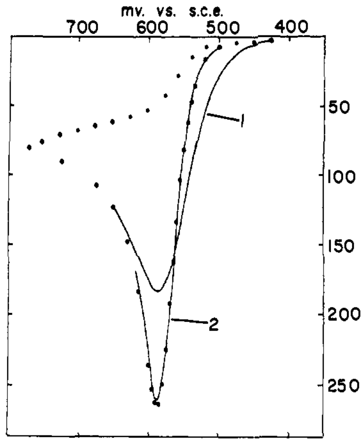

Figure 4. Comparison of a single sweep voltammogram in 1 *M* H_2SO_4, 100 mv/sec, with two models for the electrode process: (1) an irreversible two-electron transfer, $\beta n_a = 1$; (2) a reversible two-electron transfer followed by an infinitely fast chemical reaction. The points are experimental values.

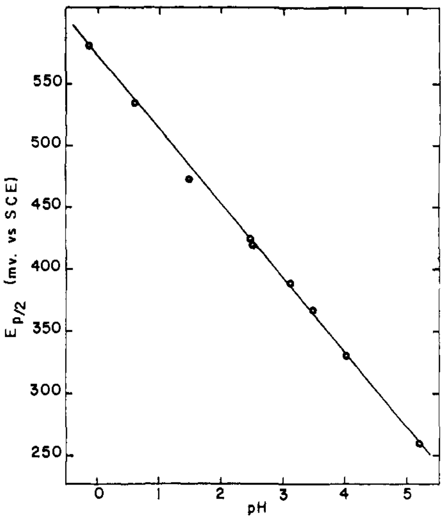

Figure 5. pH dependence of $E_{p/2}$ at 60 mv/sec. The solid line has a slope of 60 mv per pH unit.

The over-all product of the electrode reaction was II at all pH values. This was established by cyclic voltammetry and oxidation at constant potential, followed by examination of the electrode products by esr. A small volume of a solution of I in 1 *M* H_2SO_4 was oxidized at a carbon paste electrode for several hours, the acid neutralized, acetonitrile added, and the acetonitrile layer which contained the colored electrolysis products examined by esr. For the pH 9.65 solution the oxidation at constant potential was carried out *in situ* at a platinum electrode in an esr electrolysis cell, and the products were detected by subsequent reduction at the platinum electrode. The results are given in Table I; the product was II in both cases. The oxidation–reduction couple of II was evident in the cyclic voltammograms of I. Authentic samples of II (in 20% acetonitrile) were reduced at carbon paste electrodes, and the $E_{p/2}$ values compared with those from the cyclic voltammograms of I at several pH values. Excellent agreement (within 10 mv) was obtained over a wide range of sweep rates.

Table I. Product Identification by Esr

Electrolysis solution	Coupling constants, gauss[a]		
		II	Product
1 *M* H_2SO_4[b]	$a_H^{(1,3,3,1)}$	2.91	2.88
	$a_H^{(1,1)}$	2.39	2.38
	$a_H^{(1,2,1)}$	0.68	0.69
	$a_H^{(1,2,1)}$	0.52	0.50
pH 9.65[c]	$a_H^{(1,3,3,1)}$	2.96	2.94
	$a_H^{(1,1)}$	2.29	2.29
	$a_H^{(1,4,6,4,1)}$	0.64	0.64

[a] The precision was ±0.02 gauss. [b] The esr spectra were obtained in acetonitrile–water mixtures; see text for details. [c] The spectrum of II was obtained in 20% acetonitrile.

Evident from Figures 1 to 3 is the marked pH dependence of the oxidation mechanism. As the pH is increased, a one-electron intermediate and the chemical reactions which it can undergo characterize the oxidation. The detailed results and discussions for each pH region are given below.

Acidic Solutions. In acid the oxidation process is characterized by a two-electron transfer followed by a very fast chemical reaction. In Figure 4, an oxidation wave obtained in 1 *M* H_2SO_4 is compared to two models for the electrode process. The points are the experimental values and the curves 1 and 2 were calculated from the data given by Nicholson and Shain[7] using the geometrical electrode area and a diffusion coefficient of 6.3×10^{-6} cm²/sec. This diffusion coefficient was obtained from both the potentiostatic $it^{1/2}$ constants and the chronopotentiometric transition times. Curve 1 corresponds to the case of an irreversible two-electron charge transfer with a βn_a value of unity, where β is the anodic transfer coefficient and n_a is the number of electrons in the charge-transfer step. Curve 2 was calculated assuming a reversible two-electron charge transfer followed by a very fast chemical reaction. The potential scales were arbitrarily adjusted to give the best fit. It can be seen that a reversible two-electron transfer followed by a fast chemical reaction correctly predicts both the height and the "thinness" of the peak voltammogram. This model further predicts that the value of $E_{p/2}$ will shift 14.5 mv anodic per decade increase in the sweep rate; a value of 15.5 mv was found. This wave shape remains qualitatively unchanged at sweep rates up to *ca.* 10 v/sec. From the lack of a reverse wave at these sweep rates, a lower limit of 10^3 sec^{-1} can be set on the rate of the follow-up reaction. The reversible charge transfer is further supported by the independence of the peak potential on the method of electrode surface preparation in the strong acid solutions.

A mechanism for the oxidation of I in 1 *M* H_2SO_4 is postulated in the oxidation scheme (eq 1, Scheme I). The follow-up reaction probably involves attack of a water molecule, since it has been shown by O^{18} tracer studies that the oxidation proceeds *via* fission of the C–O bond in 1 *M* $HClO_4$.[14]

The effect on the wave shape and half-peak potential of increasing the pH is shown in Table II and Figure 5.

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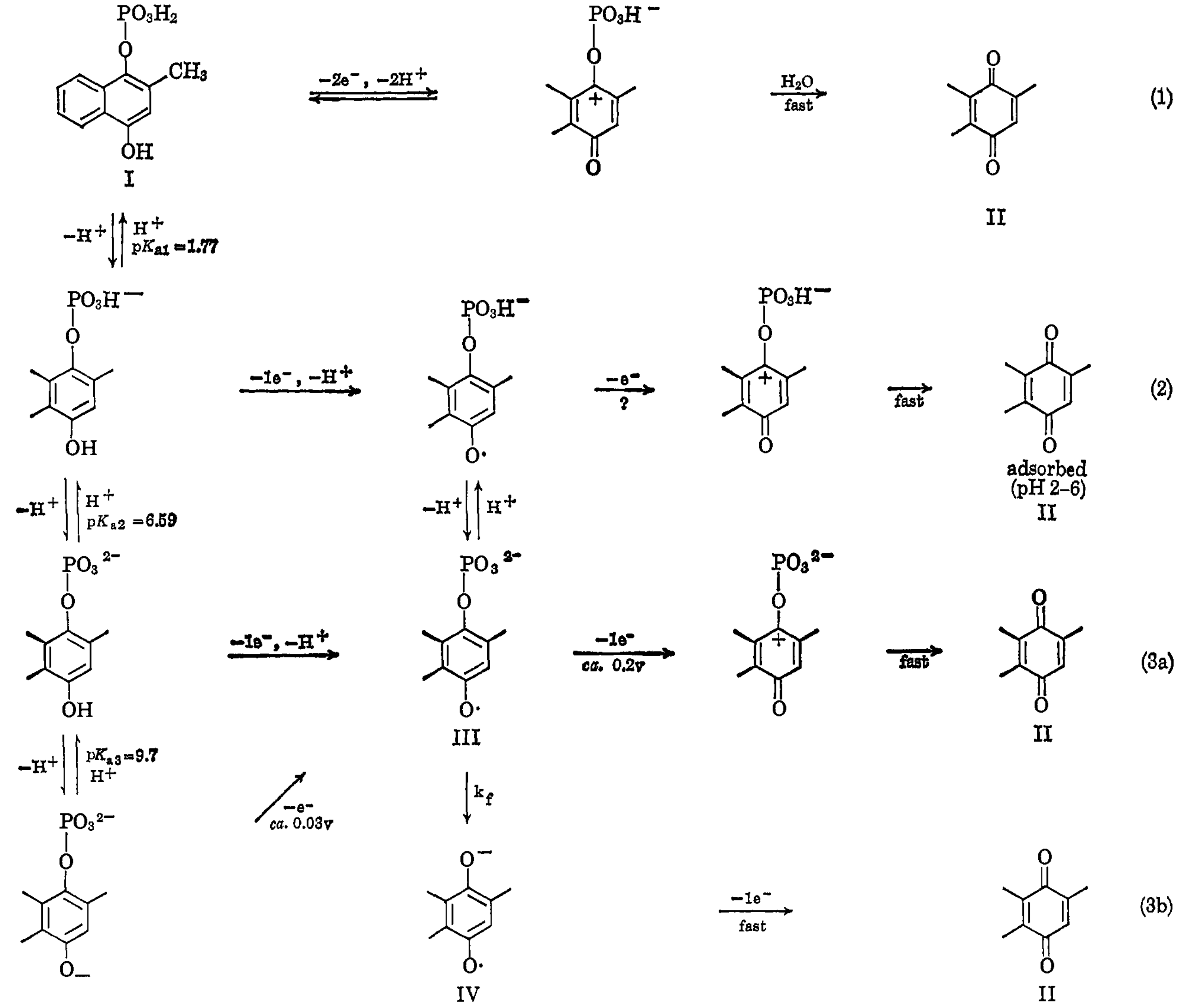
[14] Since the rate of hydrolysis of the two-electron intermediate was not measured and since no attempt was made to analyze for condensed phosphates, the fate of the phosphate entity is neglected in this oxidation scheme. This aspect of the oxidation is discussed for alkaline solutions below.

Scheme I



In addition, the value of $i_p/ACv^{1/2}$ decreased and became dependent on sweep rate. These effects are attributed to an increase in charge-transfer control as the pH is increased. The value of $E_p - E_{p/2}$ increased from a value close to that predicted for a reversible two-electron transfer to that predicted for an irreversible two-electron transfer with a transfer coefficient of 0.5. In these solutions the apparent βn_a value, calculated from either eq 4 or 5,[7,15] combined with the equation for an irreversible electron transfer (eq 6),[7,15] predicted

$$E_p - E_{p/2} = 47.7/\beta n_a \text{ (mv)} \qquad (4)$$

$$\frac{dE_{p/2}}{(d \log v)} = 29.5/\beta n_a \text{ (mv)} \qquad (5)$$

the experimental peak currents at the fastest sweep rates employed. Typical behavior in this pH region is

$$\frac{i_p}{ACv^{1/2}} = 298n(\beta n_a)^{1/2}D^{1/2} \qquad (6)$$

shown in Figure 6. In this figure the circles are the experimental values, the X's were calculated from the value of $E_p - E_{p/2}$ at each sweep rate and eq 4 and 6, and the dashed line was calculated from $dE_{p/2}/(d \log v)$ and eq 5 and 6. The diffusion coefficient was again obtained from the potentiostatic $it^{1/2}$ value.

Thus, to accommodate this behavior, the electrode reaction is pictured as containing an electron-transfer process which decreases and becomes rate controlling as the pH is increased. Similar behavior could be caused by a chemical step preceding the electron-transfer process. For this oxidation, however, such a

Table II. Peak Voltammogram Parameters in Acidic Solutions[a]

Solution, pH	$E_p - E_{p/2}$, mv	$i_p/ACv^{1/2}$, (amp)(cm^{-2}) M^{-1} (v/sec)$^{-1/2}$
0.59 (1 M H_2SO_4)[b]	26.5	2.18
1.44 (0.1 M H_2SO_4, 0.4 M Na_2SO_4)[b]	30.5	1.89
2.50	30	1.84
3.48	36	1.68
4.04	40	1.55
4.48	46	1.38
5.63	49	1.41
6.32	55	1.35

[a] Sweep rate 100 mv/sec. [b] The pH of these solutions was calculated using the activity coefficient data in H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold Publishing Corp., New York, N. Y., 1958, pp 576, 594.

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(15) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p 125.

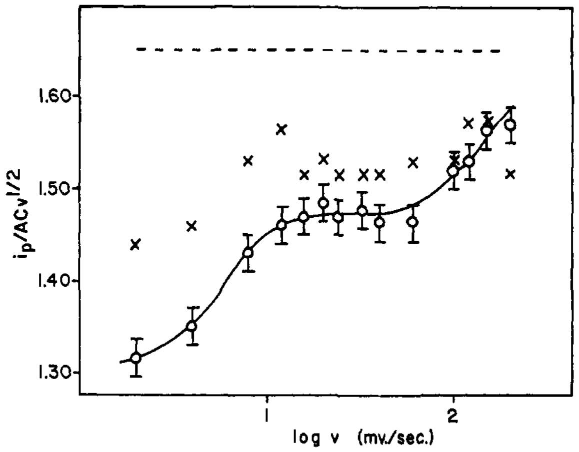

Figure 6. Peak current variation with sweep rate for 0.586×10^{-3} *M* I, pH 4.04. The solid line is experimental; the ×'s and dashed line are calculated. See text for details.

kinetic complication is not consistent with the over-all pH dependence of the *i–E* curves or the constancy of the potentiostatic $it^{1/2}$ values.

The increase of $i_p/ACv^{1/2}$ with sweep rate, which was general in the pH range 2–6, is difficult to explain. This increase was not observed at other pH values. One complicating feature of the electrode process which might be associated with this behavior is the fact that the naphthoquinone (II) was definitely adsorbed at the electrode surface during the course of the *i–E* curves. This was demonstrated by the following experiment. A peak voltammogram was run on a solution of I (pH 3.67); the electrode was removed from the solution, washed with water for 30 sec, and immersed in background solution; and a cathodic potential sweep was initiated. The resulting cyclic voltammogram was readily identified with that of II. The peak currents of this cyclic voltammogram did not decrease with successive scans, indicating that II remained at the electrode surface. Further work is required and in progress on this aspect of the oxidation.

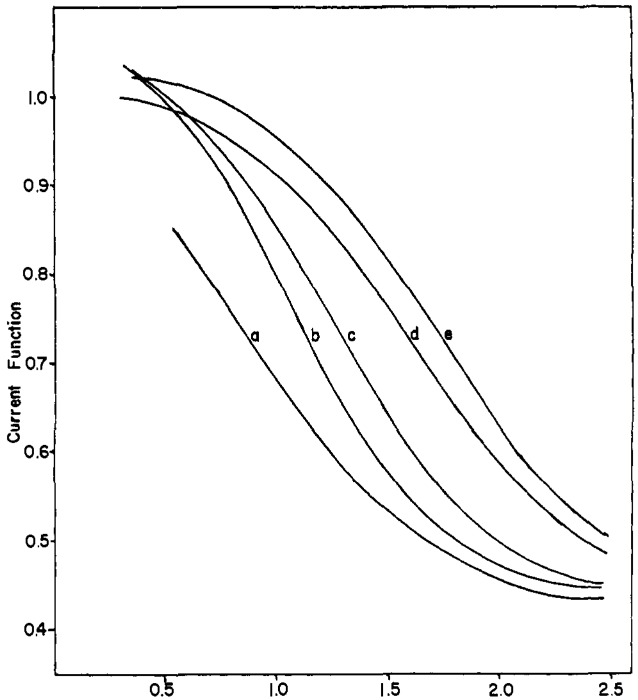

Figure 7. Peak current variation with sweep rate in alkaline media. The current function is given by $i_p/602D^{1/2}ACv^{1/2}$. (a) pH 9.53, (b) pH 9.90, (c) pH 10.40, (d) pH 11.18, (e) pH 11.59.

Basic Solutions. In this region a distinct one-electron oxidation wave could be detected and the dependence of the peak currents on sweep rate became more interesting. At fast sweep rates two drawn out irreversible oxidation waves were present, while at slow sweep rates only one peak-shaped wave was present. This behavior is shown in Figure 3. The peak current value corresponded to an *n* value of 1 at fast sweep rates and to an *n* value of 2 at slow sweep rates. However, the value of the potentiostatic $it^{1/2}$ constant, obtained by applying a potential +0.5–0.6 v *vs.* sce, still corresponded to an *n* value of 2 and a diffusion coefficient (calculated using the Cottrell equation) of *ca.* 5×10^{-6} cm²/sec. No waves other than ones that could be assigned to the quinone or a background process[16] were detectable on the cathodic segment of the cyclic voltammograms. The peak current dependence on sweep rate, shown in Figure 7, is typical of a mechanism in which a chemical step occurs between two one-electron steps (ece mechanism).[8] A scheme of the form

$$\begin{tikzcd}
\mathrm{I}^{-3} \arrow[r, "-e"] & \mathrm{III} \arrow[r, "-e"] \arrow[d, "k_f"] & \lbrack \arrow[d] \\
 & \mathrm{IV} \arrow[r, "-e", "\text{fast}"'] & \mathrm{II}
\end{tikzcd} \qquad (7)$$

is proposed in the oxidation scheme (eq 3). At slow sweep rates the oxidation proceeds *via* hydrolysis of the one-electron intermediate oxidation product, the semiquinone phosphate radical (species III). No waves corresponding to the reversible reduction of the one-electron intermediate were detected on the cathodic segments of the cyclic voltammograms at sweep times much shorter than the estimated lifetime of III. Thus the initial oxidation is written as an irreversible electron-transfer process. At fast sweep rates the current function tended to 0.44 which, according to eq 6, corresponds to a βn_a value of 0.79.

The results obtained with a rotating ring-disk electrode[17,18] are in accord with this oxidation scheme (see Figure 8). In this experiment the ring potential was maintained at −0.2 v *vs.* sce, which was *ca.* 0.2 v cathodic of the oxidation of I and anodic of any background reduction process or the reduction of the naphthoquinone (II). When the disk potential was stepped into the oxidation wave, a small (note the different current scales in Figure 8) cathodic ring current resulted. This current, which was dependent on the ring potential, evidently arose from the irreversible reduction of III formed at the disk and swept out to the ring. The ratio of ring-to-disk current decreased as the disk

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(16) We were unable to eliminate a background process at the carbon paste electrode from the cathodic segment of the *i–E* curves in alkaline solutions. This process distorted the quinone wave at these concentration levels.

(17) A Frumkin, L. Nekrasov, B. Levich, and J. Ivanov, *J. Electroanal. Chem.*, 1, 84 (1959).

(18) V. G. Levich, "Physicochemical Hydrodynamics," translated from the Russian, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.

potential was increased. This is consistent with the above scheme in which, at high potentials, the intermediate is removed by the reaction sequence, III $(-e) \rightarrow [\ ] \rightarrow$ II. This leads to a product, II, not reducible at the ring potential.

In further support of this mechanism is the fact that Allen and Bond obtained the semiquinone phosphate radical (III) esr spectrum at pH 11.7 by permanganate oxidation in a flow apparatus.[6] We have been unable to detect a spectrum which could be assigned to III by oxidation at a platinum electrode, although low intensity signals which could not be resolved were obtained.

The presence of the second wave negates the use of methods based on controlled current to study this mechanism. If a constant current is applied, the rate of the electron transfer cannot be increased to a point at which it is no longer the controlling step without reaching a potential such that the second electron transfer occurs. Thus chronopotentiograms of I at this pH were drawn out and no break corresponding to the first process could be measured.

Estimation of k_f from the curves of Figure 7 is complicated by several aspects of the oxidation mechanism. First is the irreversibility of the initial electron transfer. Second, the reaction

$$\text{III} + \text{IV} \rightleftarrows \text{I} + \text{II} \qquad (8)$$

which is thermodynamically favorable might effect the *i–E* curves. The importance of this reaction has been pointed out by Hawley and Feldberg[19] who considered the potentiostatic case. Other complications are that the peak currents might include a contribution from the second electron transfer and that, in the solutions of higher pH, a limiting value of the current could not be attained at the fastest sweeps allowed by the X–Y recorder.

Accommodation of reaction 8 into a treatment describing this oxidation scheme was not attempted. To estimate k_f several assumptions were made. First, the treatment of Nicholson and Shain[8] for a reversible electron transfer was used, and, second, the effect of the bimolecular reaction was ignored. The ratios of observed peak current to peak current in the absence of kinetic complications (i_k/i_d) were calculated for different values of k_f/v and r (which equals $(D_{II}/D_I)^{1/2}$) using eq 9. This equation was obtained from ref 8 and takes into account the difference between the diffusion coefficients of I and IV.

$$\frac{i_k}{i_d} = \frac{[\pi^{1/2}\chi(at) + r\pi^{1/2}\phi(at)]_{\max}}{0.446} \qquad (9)$$

The notation is the same as that of ref 8, and the values of $\pi^{1/2}\chi(at)$ and $\pi^{1/2}\phi(at)$, which are proportional to the fluxes of I and IV, respectively, were obtained from Tables III and IV of this reference. The diffusion coefficients of I and II were determined from potentiostatic *i–t* curves and differ by a sizable amount. The agreement of predicted values of i_k/i_d with experimental values was improved markedly, over 2 decades of sweep rate, by accounting for the difference in diffusion coefficients in this manner. The data were consistent with the following rate expression for the intermediate chemical step.

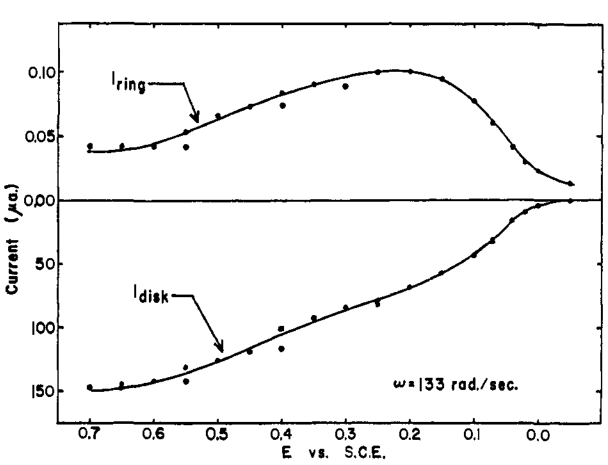

Figure 8. Current–potential curves obtained at a carbon paste ring-disk electrode: 0.423×10^{-3} *M* I, pH 10.10, rotation rate 133 radians/sec.

$$k_f = k_1 + k_2[\text{OH}^-]$$
$$k_1 = 0.2 \pm 0.1 \text{ sec}^{-1} \qquad (10)$$
$$k_2 = 700 \pm 400 \text{ l. mole}^{-1}\text{ sec}^{-1}$$

In the pH 7–9 region the *i–E* curves are drawn out and exhibit two or three waves, depending on sweep rate. The position and appearance of these waves were not dependent on the supporting electrolyte or buffer components. For example, essentially the same cyclic voltammograms were obtained in 1 *M* NaClO_4 using tris(hydroxymethylaminomethane) as a buffer component.

These results are best explained by considering the results at pH values below and above this region. At slow sweep rates the oxidation wave definitely consists of two distinct processes. The second process can be assigned to the oxidation of III by following the transition from neutral to basic solutions. The hydrolysis of this species is slow enough in neutral solutions that its oxidation can be detected at slow sweep rates. The assignment of a third wave at *ca.* 400 mv *vs.* sce is more difficult and has not definitely been made. It must be due to a follow-up reaction of some kind since it becomes more prominent at slow sweep rates. It first becomes apparent in the voltammograms at pH *ca.* 6 as a small wave just anodic of the main process and is present until hydrolysis of III becomes appreciable (pH *ca.* 9.5). A tempting assignment would be that this wave is due to oxidation of the protonated semiquinone phosphate. However, the deprotonation would be too fast for this to be a reasonable hypothesis, unless this species is a very weak acid ($\text{p}K > ca.\ 10$).

The conclusions of this study are best summarized by the oxidation scheme. The most important result is that in alkaline media the oxidation proceeds by hydrolysis of the one-electron intermediate. This was established using relatively slow linear potential sweep voltammetry which allowed the oxidation process to take place by the lowest energy route and gave the

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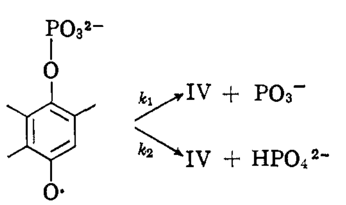
[19] D. M. Hawley and S. W. Feldberg, presented before the Division of Analytical Chemistry, Winter Meeting of American Chemical Society, Phoenix, Ariz., Jan 1966, Paper No. 26.



(11)

(12)

best separation between the two successive charge-transfer controlled steps. The rate data suggest the following pathways for the hydrolysis (eq 11 and 12), one independent of and one dependent on pH. The pH-independent pathway might produce a metaphosphate intermediate; hence the possible phosphorylating agent of biological interest is the semiquinone phosphate radical.

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Examination of Phosphorus Hyperfine Coupling Constants in Nitroaromatic Anion Radicals[1a]

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Abstract: The electron spin resonance spectra of the anion radicals produced by electrochemical reduction of diethyl 4-nitrophenyl phosphate (**1**), O,O-diethyl O-4-nitrophenyl thiophosphate (**2**), diethyl 4-nitrobenzyl phosphonate (**3**), diphenyl 4-nitrophenyl phosphate (**4**), diphenyl 2,6-dimethyl-4-nitrophenyl phosphate (**5**), di(4-methylphenyl) 4-nitrophenyl phosphate (**6**), and di(2-methylphenyl) 4-nitrophenyl phosphate (**7**) have been examined. In every case, unequivocal assignment of a ^{31}P hyperfine coupling constant, a_P, was possible. The magnitude of a_P varied from 7.05 gauss for the radical derived from **1** in acetonitrile to 17.51 gauss for the radical derived from **3** in dimethylformamide. In all cases the values of the nitrogen and nitrophenyl ring proton coupling constants remained closely similar to those observed for nitrobenzene anion. The variation in values of a_P suggests that steric effects as well as inductive effects influence the ^{31}P coupling constant in these radicals and that at least some contribution of a hyperconjugative mechanism is likely for transmission of unpaired spin to the phosphorus atom.

Even superficial inspection of the recent chemical literature shows the rapid development of organophosphorus chemistry. Organophosphorus compounds have become increasingly important as intermediates in organic synthesis and as ligands in coordination chemistry. The central role of phosphate groups in photosynthesis, in nucleic acids, and in the energy-transfer processes of metabolism is well established.[2] Other phosphates are some of the most virulent poisons known. Some fluorinated phosphates are nerve gases and other phosphate and thiophosphate esters are widely used as pesticides.

Despite the fact that free-radical intermediates have frequently been postulated for organophosphorus reactions, comparatively few phosphorus-containing radicals have been prepared in solution under conditions which permitted their study in detail. Many of these radicals are apparently highly reactive and cannot be obtained in concentrations sufficient for characterization. Thus, in 1953, Hein[3] noted that the reaction of alkali metals with phosphine oxides led to colored, paramagnetic solutions, but he reported no specific data. Ramirez[4] observed electron spin resonance (esr) signals from intermediates in the reaction of triphenylphosphine with chloranil, but was able to report only that the radical species had a g factor close to 2. Other workers have reported phosphorus-containing radicals in irradiated solids[5–7] and at liquid nitrogen temperatures.[8]

Considerable attention has been devoted to attempts to prepare the anion radical of triphenylphosphine. Two reports of esr spectra resulting from alkali metal reduction of triphenylphosphine in tetrahydrofuran exist in the literature.[9,10] Assignments of these spectra to the triphenylphosphine anion did not, however, appear unequivocal since Chapman[11] had found only signals which he attributed to the biphenyl anion when triphenylphosphine was reduced with sodium–potassium alloy in dimethoxyethane. Recently Britt and Kaiser[12] have shown that the reaction of alkali metals with triphenylphosphine in tetrahydrofuran proceeds in two steps. In the first step a phenyl group is cleaved yielding a metal phenide and a metal diphenyl phosphide. Further reduction of the metal diphenyl

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