trimethylamine and 60 g. (1.9 moles) of methanol was placed in a rocking autoclave, pressurized to 160 atmospheres with carbon monoxide, and heated at 185° for 10 hours. After cooling, the reaction product was distilled and the amount of alcohol and aldehyde in the distillate determined by infrared analysis. The yield of cyclopentylcarbinol was 16.7% and that of the aldehyde 2.9%, based on the amount of cyclopentene used.

Nonyl Alcohol from Octene-1.—A mixture consisting of 66 ml. (0.42 mole) of 1-octene, 14 ml. (0.10 mole) of $Fe(CO)_5$, 18 ml. (1.0 mole) of water, 26 g. (0.44 mole) of trimethylamine and 60 g. (1.9 moles) of methanol was placed in a rocking autoclave and pressurized to 160 atmospheres with carbon monoxide. The autoclave was heated at 150–160° for 6 hours and then at 170–175° for 6 more hours. After cooling, the reaction mixture was distilled first at atmospheric pressure up to 122° and then from 90 to 120° at 2–6 mm. The amount of alcohol and aldehyde in the distillate was determined by infrared analysis and corresponded to a yield of 6% of alcohol and 0.25% of aldehyde based on the amount of olefin used. The recovered olefin consisted entirely of a mixture of 2-octene and 3-octene.

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Studies on Oxidation–Reduction Mechanism. II. The Anodic Oxidation of *p*-Aminophenol

BY WILLIAM K. SNEAD[1] AND A. EDWARD REMICK

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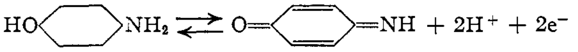
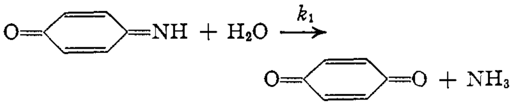
The anodic oxidation of *p*-aminophenol at *p*H 1.18 was studied by using Pt electrodes in an electrolytic cell through which flowed a small a.c. superimposed on a relatively large constant d.c. Both a.c. and d.c. voltages were obtained as functions of time by using a recording voltmeter. Theoretical mathematical equations were developed for the following possible mechanisms: (1) a reversible reaction, (2) a rate-controlling electron-transfer step, (3) a reversible electron-transfer followed by a rate-controlling hydrolysis. The experimental data were in accord with (3) but not with (1) and (2). The mathematical equations also made it possible to calculate: (1) $n = 2.0$ for the number of electrons transferred in the first step, (2) $E_0' = 0.711$ volt for the normal potential of the first step, (3) the first order rate-constant $k_1 = 0.020$ sec.$^{-1}$ for the second step, and (4) the diffusion coefficient $D_R = 0.946 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ for the participating species of the *p*-aminophenol. It was concluded that the mechanism is the same for the anodic as for the homogeneous reaction and that no mechanistic inversion occurs on lowering the *p*H to 1.18. It was emphasized that although mechanisms 2 and 3 are indistinguishable from the point of view of the theory of absolute reaction rates or experimentally by the Conant electrochemical technique, the voltammetric method used distinguishes between them in the case of the anodic reaction.

The mechanism of the oxidation of *p*-aminophenol (PAP) has been studied under a fairly wide range of conditions by several investigators. Wieland[2] suggested that quinone-imine is an intermediate in the oxidation of PAP. Since Willstätter[3] had shown that quinone-imine rapidly hydrolyzes to quinone in acid solution, Conant and Pratt[4] suggested the mechanism


(1a)


(1b)

In order to explain the observed dependence of oxidation rate on the reduction potential of the reversible oxidation–reduction system used as an oxidizing agent, they postulated that the first step is fast and reversible while the second step is slow and irreversible. They supplied evidence that quinone-imine is the intermediate in solutions of *p*H 7.8–11.3 by measuring potentiometrically the reduction potential of system 1a both by the titration method and the method of mixtures. These two methods gave concordant results within the limits of precision reasonably to be expected of such an unstable system. From the end-points of the titrations they deduced that the number of electrons involved in (1a) was $n = 2 \pm 0.2$. They also studied the rate of decay of potential in acidic solutions containing PAP and various oxidizing systems, expressing their results in terms of the "apparent oxidation potential" (A.O.P.) which was defined in terms of the reduction potential of (1a) and rate constant, k_1, of (1b). In general, neither of these quantities could be determined separately. They found that the over-all reaction rate is independent of the dilution thus showing k_1 to be a first-order rate constant.

Fieser[5] advanced Conant's work by devising his "method of discontinuous titrations." He found that potential–time plots were linear over only a limited range. Since linearity is demanded for a first order reaction, there is here clearly an implication that the kinetics of the follow-up step are complex, being first order only in the early stages. By extrapolation to zero time he was able to obtain values for the normal potential of (1a) at each *p*H (2.69 to 7.57) and very crude values for k_1.

In 1935, Bancroft and Magoffin[6] introduced their theory of the potential hump as an alternative explanation of the relation between potential (of a reagent *or an electrode*) and rate of electron transfer. They claimed that all of Conant's studies on irreversible electron transfers could be explained by their theory "if one rejects the two assumptions of a reversible electrolytic step and a practically irreversible, non-electrolytic step." This theory seems to have been in certain regards the qualitative equivalent of the theory of absolute reaction rates which

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[1] Based on the Ph.D. thesis of William K. Snead, Wayne State University, 1957.

[2] H. Wieland, *Ber.*, **43**, 718 (1910).

[3] R. Willstätter, *ibid.*, **42**, 2166 (1909).

[4] J. B. Conant and M. F. Pratt, THIS JOURNAL, **48**, 3178 (1926).

[5] L. F. Fieser, *ibid.*, **52**, 4915 (1930).

[6] W. D. Bancroft and J. E. Magoffin, *ibid.*, **57**, 2561 (1935).

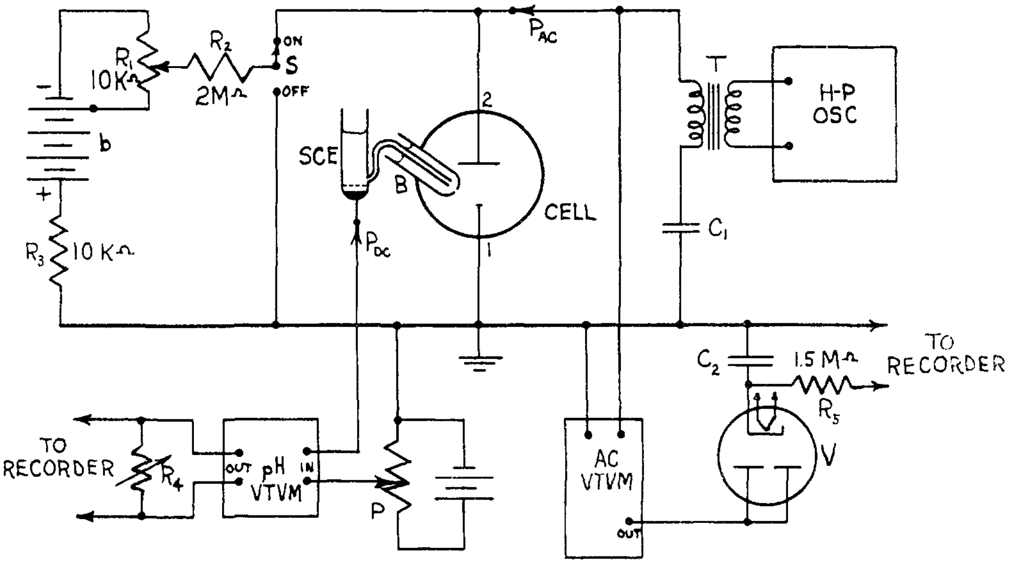

Fig. 1.—Arrangement of experimental apparatus.

was undergoing development at the same time.[7,8] Indeed, it was later pointed out by Gershinowitz[9] that both Bancroft's theory and Conant's are essentially the same and are only special cases of the more general and more rigorous theory of absolute reaction rates. He also showed that Conant's equations would obtain if electron transfer were the rate-controlling step. Gershinowitz's statement seems to be an admission that the theory of absolute reaction rates is not a sufficiently powerful tool to distinguish between these two mechanisms which differ in having as rate-controlling steps an electron-transfer and a hydrolysis, respectively.

The only work reported on the mechanism of the anodic oxidation of PAP is that of Knobloch.[10] He obtained an anodic polarographic wave at *p*H 9.2 getting a half-wave potential which corresponded to the standard potential, E_0', obtained in a potentiometric titration with ferricyanide. This indicated that the same electron-transfer step was involved at *p*H 9.2 in the anodic oxidation as in the homogeneous oxidation. His work supplied no other information about the mechanism of the anodic oxidation of PAP but he did make a more extended polarographic study of a similar compound, 2-methyl-4-aminonaphthol-1. In this case the polarographic diffusion current increased at a rate proportional to the square root of the height of mercury in the reservoir, thus establishing that diffusion was rate-controlling. Again concordance was shown between half-wave potentials and E_0' values obtained potentiometrically. Potentiometric curves showed that the ferricyanide oxidation is a two-electron process. Studies made on the rate of disappearance of the intermediate product produced by ferricyanide oxidation at *p*H 6.8 showed the follow-up step to have first order kinetics.

We have undertaken in the work presented in this article to extend the existing knowledge of the *anodic* oxidation of PAP to highly acidic solutions in which polarography is inapplicable because the dissolution potential of mercury must be exceeded and because the intermediate oxidation product undergoes further transformation too rapidly. In so doing we have measured n, k_1 and the normal potential for (1a) at *p*H 1.18 for the anodic oxidation and have been able to show that one mechanism out of three considered is in accord with our data. We hope that our work also throws some light on the problem posed by Bancroft and Magoffin and by Gershinowitz in relation to the corresponding homogeneous oxidation.

Experimental

Apparatus.—The arrangement of the apparatus used is shown schematically in Fig. 1. The electrolytic cell was a lipless 250-ml. beaker fitted with a rubber stopper which carried electrodes, 1 and 2, the salt bridge leading to a saturated calomel electrode (S.C.E.), and entrance and exit tubes for nitrogen gas purified by passing over hot copper. The working electrodes were platinum disks sealed in glass so that only one face and no edges of the disks were exposed to the electrolyte. The secondary working electrode, 2, had an area of 3.16 cm.^{2} and was platinized so that its contribution to the cell impedance was negligible. The primary working electrode, 1, was made of smooth platinum cleaned by the method of Remick and McCormick.[11] Two different primary electrodes were used. Their areas were 0.1425 and 0.0740 cm.^{2}, each being computed from the average of four diameters measured with a travelling microscope.

With the switch S in the ON position, a constant direct current flowed through the cell. The constancy of this current was assured by the high resistance of R_2 and its magnitude controlled coarsely by the taps on battery b (two Burgess No. 10308 45-volt B batteries) and precisely by rheostat R_1. The precise current magnitude was determined by measuring with a Queen potentiometer E3040 (not shown) the voltage across the precision resistor R_3. The OFF position of switch S was used in setting this potentiometer to approximately the correct value before the cell current was started. The d.c. potential of the primary working electrode, referred to the S.C.E., was measured by a *p*H vacuum tube voltmeter (*p*H VTVM) which was a Beckman industrial model M. In order to record the indication of this instrument continuously and mechanically, the circuit of the front panel indicating meter was brought to the outside of the chassis, broken at one point, and the two ends

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(7) O. K. Rice and H. Gershinowitz, *J. Chem. Phys.*, **2**, 857 (1934); **3**, 479 (1935).

(8) H. Eyring, *ibid.*, **3**, 307 (1935).

(9) H. Gershinowitz, *ibid.*, **4**, 363 (1936).

(10) I. E. Knobloch, *Coll. Czech. Chem. Communs.*, **14**, 508 (1949).

(11) A. E. Remick and H. W. McCormick, *J. Electrochem. Soc.*, **102**, 534 (1955).

connected to R_4 (a decade box). Excitation for a mechanical recorder was drawn from across this resistor. The signal was fed directly to the CURRENT jack of a Sargent model XXI polarograph which was pressed into service here merely as a recorder. The potentiometer P was used in zeroing the recorder. Calibration of the measuring circuit was effected by disconnecting the probe $P_{d.c.}$ from the point shown in Fig. 1 and connecting it to a calibrating voltage source, an accurately standardized potentiometer (not shown). A 3 megohm resistor placed in the input circuit of the VTVM during a calibration had no noticeable effect on the indications.

The a.c. circuitry is shown on the right-hand side of Fig. 1. Its purpose was to measure the small signal impedance of the electrolytic cell. Only the magnitude of this impedance could be measured because we did not have available the necessary equipment to measure continuously the time-variable phase angle. A Hewlett-Packard model 202B low frequency oscillator was employed as the a.c. source feeding through a 4:1 step-up transformer T (General Radio type 578-B), the blocking condenser C_1 and the electrolytic cell. C_1 was chosen small enough (*ca.* 0.01 μf. for 20 c.p.s.) so that the voltage drop across it was at least a hundred times that across the cell. The shunt path provided by the d.c. circuit around the cell was negligible because of the 2-megohm resistance in the d.c. circuit. A Ballentine model 310A electronic voltmeter (a.c. VTVM) was used to measure the cell a.c. voltage which, because of the above choice of C_1, was directly proportional to the cell impedance. The oscillator's output was adjusted so that the cell voltage never exceeded about 10 mv. The remaining part of the a.c. circuit (V, a 6 × 5 GT vacuum duo-diode; C_2, 0.25 μf.; and R_5, 1.5 megohms) was to furnish excitation corresponding to the voltmeter's reading to a pen and ink recorder. This system was calibrated directly in ohms of impedance by disconnecting the probe $P_{a.c.}$ and connecting it to a stepped, precision resistor. Because response to impedance was not linear, it was expedient to inscribe directly on the chart record calibration marks, stepped at 100 ohms intervals from zero to *ca.* 800 ohms. The same recorder had to be used for both the d.c. voltage and the a.c. impedance but, since it could not be used simultaneously for both purposes, two separate runs were necessary. This procedure was justified by the good reproducibility found for the electrode potential curves recorded in separate but otherwise identical runs.

The presence of a rather high concentration of supporting electrolyte minimized the *IR* drop between the working electrodes and rendered entirely negligible the much smaller *IR* drop included in the measurement of the e.m.f. of electrode 1 against the S.C.E.

All measurements were made at 30 ± 0.2°. The S.C.E. was standardized against a hydrogen electrode using four different buffer solutions, the *p*H values of which were given by Bates.[12] Its potential relative to the standard hydrogen electrode was found to be 0.2403 ± 0.0012 volt.

Materials.—One sample of the *p*-aminophenol used in this work was purified by Mr. B. Gillis of this Laboratory who sublimed it in a high vacuum at a temperature of 50–60°. The sublimate was almost pure white and melted with decomposition at 184–187°. Beilstein's "Handbuch der Organischen Chemie" lists the melting point as determined by two investigators as 184 and 186°, both with decomposition. A second sample was purified by recrystallization following a method suggested by Weygand[13] who credited it to the earlier work of Weissberger and Strasser.[14] This product was also almost white and melted over the same range as the first sample. Electrochemical data obtained using these two samples showed no significant difference.

Aqueous sulfuric acid was used as the supporting electrolyte. The solution was prepared from J. T. Baker reagent grade acid and water redistilled from permanganate and was adjusted to 0.100 *N* (*p*H 1.18). Weighed amounts of *p*-aminophenol were added to the sulfuric acid and diluted to the requisite volume to produce the electrolytic solutions used in the cell.

Procedure.—In order to get reproducible results, it proved necessary to employ the following pre-polarization scheme. Reversing battery b, a current was passed through the cell for 20 or 30 seconds in a direction making the primary electrode a cathode. The battery was then again reversed, the nitrogen flow stopped and, with the recorder "ON," switch S was thrown from OFF to ON starting the flow of current through the cell. With the current flowing and the potential automatically being recorded, the potentiometer used for current measurement was balanced; only slight deviations from constancy were ever noticed during a run. The current was cut off when the e.m.f.-time curve became steep. For a.c. measurements, the recorder was connected to receive excitation from the a.c. circuit, a calibration was made and the procedure described above was repeated in its entirety. Typical experimental curves are shown in Fig. 2. In all figures and tables one must recognize that $e_{d.c.}$ = −e.m.f. This distinction arises from a clash of conventions with regard to sign. By electrical convention potentials are referred to ground potential whereas the primary "electrode potential," $e_{d.c.}$ must be referred to the reference electrode.

Mathematical Theory

We will assume that the Conant–Pratt mechanism (equations 1a and 1b) is applicable to the anodic oxidation of PAP in acidic solution, develop the mathematical theory on that basis, and compare the derived mathematical equations with the experimental results. Equations 1a and 1b will be rewritten as

$$\mathrm{R} \rightleftarrows \mathrm{Ox} + n\mathrm{e} \qquad (2a)$$

$$\mathrm{Ox} + \mathrm{H_2O} \xrightarrow{k_1} \mathrm{Z} + \mathrm{X} \qquad (2b)$$

The concentration of each of the substances involved may be obtained mathematically as the solution to a boundary value problem in partial differential equations which simultaneously takes into account the effects of diffusion and reaction. The statement of the problem for the concentration of the reductant R starts with Fick's second diffusion law

$$\partial C_{\mathrm{R}}(x,t)/\partial t = D_{\mathrm{R}}[\partial^2 C_{\mathrm{R}}(x,t)/\partial x^2] \qquad (3)$$

where C_{R} is the molar concentration of R, D_{R} is its diffusion coefficient, x is the perpendicular distance from the anode and t is the time in seconds elapsed from the application of the e.m.f. The initial and boundary conditions are

$$C_{\mathrm{R}}(x,0) = C_{\mathrm{R}}{}^0 \qquad (4)$$

$$C_{\mathrm{R}}(x,t) \longrightarrow C_{\mathrm{R}}{}^0 \text{ as } x \longrightarrow \infty \qquad (5)$$

$$[\partial C_{\mathrm{R}}(x,t)/\partial x]_{x=0} = -i/nFD_{\mathrm{R}}A \qquad (6)$$

$C_{\mathrm{R}}{}^0$ is the initial stoichiometric concentration of R, A is the area of the anode in square centimeters, F is the faradaic constant and i is the instantaneous faradaic current, controlled for this investigation to conform to a relatively small sinusoidal a.c. superimposed on a constant d.c.

$$i = I + \hat{I} \sin \omega t \text{ when } t > 0 \qquad (7)$$

Implicit in this approach are the assumptions: (1) D_{R} is a constant, (2) in the presence of the supporting electrolyte, electrical migration of R and Ox is nil even if the participating species involved in the electron transfer are ions, (3) convection is nil and (4) the diffusion is semi-infinite and linear.

A solution of this boundary value problem was given by Rosebrugh and Lash Miller.[15] It contains a transient a.c. term which reduces to zero so rapidly that its inclusion would be of little consequence in our work. Dropping this term leaves in

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[12] R. G. Bates, "Electrometric *p*H Determinations," John Wiley and Sons, Inc., New York, N. Y., 1954.

[13] C. Weygand, "Organic Preparations," Interscience Publishers, Inc., New York, N. Y., 1945.

[14] A. Weissberger and E. Strasser, *J. prakt. Chem.*, **135**, 209 (1932).

[15] T. R. Rosebrugh and W. Lash Miller, *J. Phys. Chem.*, **14**, 816 (1910).

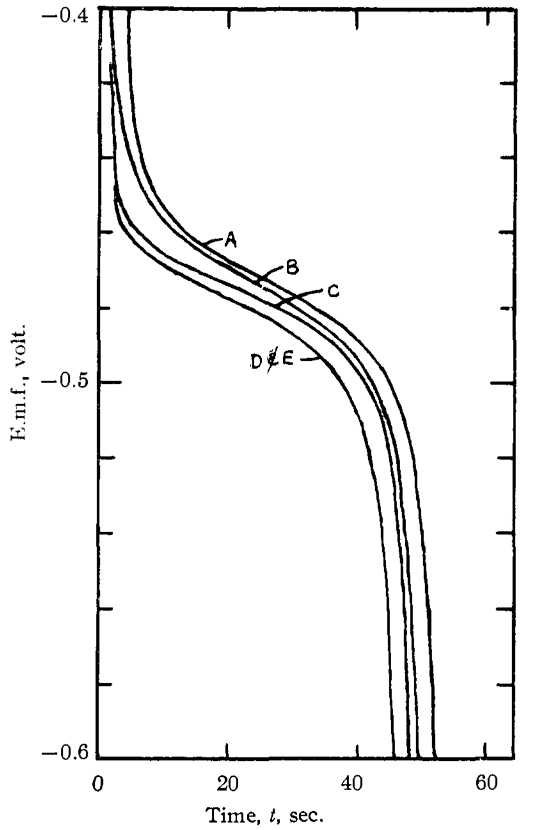

Fig. 2.—Experimental d.c. electrode potential *vs.* time curves for the anodic oxidation of *p*-aminophenol, τ constant for all curves; experimental conditions: temperature, 30°; supporting electrolyte, 0.100 *N* sulfuric acid; electrode area, *A*, 0.0740 cm.^{2}; saturated calomel reference electrode.

Curve	C_R^0, *M*	$-I$, μa.	$-I/C_R^0$, *amp. cm.*^{3} *mole*$^{-1}$
A	0.00075	4.32	5.76
B	.0015	8.65	5.76
C	.0030	17.2	5.73
D	.0050	28.6	5.73
E	.0075	42.9	5.73

the equation an a.c. term which refers to the steady state (for the a.c. component). Because of this omission the equation ostensibly does not fulfill boundary condition 4. Setting $x = 0$ in the Rosebrugh and Lash Miller equation, modified as explained, gives

$$C_R(0,t) = C_R^0 + \{2It^{1/2}/[nFA(\pi D_R)^{1/2}] + [I/nFA(\omega D_A)^{1/2}]\}\sin(\omega t - \pi/4) \quad (8)$$

where ω is the frequency of the a.c. in radians per second.

A somewhat similar boundary value problem arises in relation to the concentration of the oxidant which is supplied by diffusion and removed by the follow-up step 2b whose rate is $k_1C_{Ox}(x,t)$. The total rate of change of C_{Ox} can therefore be expressed as the difference of two terms representing diffusion and chemical reaction rate

$$\partial C_{Ox}(x,t)/\partial t = D_{Ox}[\partial^2 C_{Ox}(x,t)/\partial x^2] - k_1C_{Ox}(x,t) \quad (9)$$

The initial and boundary conditions are that $C_{Ox} = 0$ when $t = 0$ and approaches zero as x approaches infinity, since no oxidant exists initially. An additional boundary condition gives expression to the fact that the flux of oxidant at the anode's surface must be proportional to the current producing it, the proportionality factor being nFA

$$[\partial C_{Ox}(x,t)/\partial x]_{x=0} = i/nFAD_{Ox} \quad (10)$$

Equation 7 is also needed. As before, setting $x = 0$ in the solution given by Rosebrugh and Lash Miller[15] and omitting the transient a.c. term, we get

$$C_{Ox}(0,t) = \{-I/[nFA(D_{Ox}k_1)^{1/2}]\}\,\mathrm{erf}(k_1t)^{1/2} - I/[nFAD_{Ox}^{1/2}(k_1^2 + \omega^2)^{1/4}]\sin[\omega t - {}^1/_2\tan^{-1}(\omega/k_1)] \quad (11)$$

Since the electron-transfer step (equation 2a) has been assumed to be bidirectional and rapid, the Peters modification of the Nernst equation,[16] *viz.*

$$e = E_0' - (RT/nF)\ln[C_R(0,t)]/[C_{Ox}(0,t)]$$

may be used at any given *p*H value to relate the concentrations at the primary electrode to the instantaneous value, *e*, of the electrode's potential measured relative to the normal hydrogen electrode. Substitution of C_R and C_{Ox} by their values from equations 8 and 11 gives

$$e = E_0' - (RT/nF)\ln[\pi D_R/(2D_{Ox}k_1)] - (RT/nF)\ln(\tau^{1/2} - t^{1/2}) + (RT/nF)\ln\{\mathrm{erf}[(k_1t)^{1/2}]\} - \frac{RT}{nF}\ln\left[1 - \frac{\hat{I}\pi^{1/2}}{2I} \times \frac{\sin(\omega t - \pi/4)}{\omega^{1/2}(\tau^{1/2} - t^{1/2})}\right] + \frac{RT}{nF}\ln\left\{\frac{1 + \hat{I}k_1^{1/2}\sin[\omega t - {}^1/_2\tan^{-1}(\omega/k_1)]}{I(k_1^2 + \omega^2)^{1/4}\,\mathrm{erf}[(k_1t)^{1/2}]}\right\} \quad (12)$$

where the transition time, τ, is defined as[17]

$$\tau^{1/2} \equiv -nFAC_R^0(\pi D_R)^{1/2}/2I \quad (13)$$

The relations developed here are defined only for the condition: $0 < t < \tau$. Equation 8 shows that $C_R(0,t)$ becomes zero when $t = \tau$, neglecting the relatively small oscillating term. For the experimental condition of a relatively small a.c., each of the last two terms of equation 12 takes the form $(RT/nF)\ln(1 + y)$ where y is a numerically small fraction except when t is very close to τ or zero. As a first approximation we may therefore write $\ln(1 + y) = y$. Introducing this approximation and several trigonometric identities into equation 12, we get

$$e = E_0' - (RT/nF)\ln[\pi D_R/(2D_{Ox}k_1)]^{1/2} - (RT/nF)\ln(\tau^{1/2} - t^{1/2}) + (RT/nF)\ln[\mathrm{erf}(k_1t)^{1/2}] + [RT\hat{I}/(nFI)]\left\{\left[\frac{\pi^{1/2}}{2(2\omega)^{1/2}(\tau^{1/2} - t^{1/2})} + \frac{Bk_1^{1/2}}{2^{1/2}(k_1^2 + \omega^2)^{1/2}\mathrm{erf}(k_1t)^{1/2}}\right]\sin\omega t - \left[\frac{\pi^{1/2}}{2(2\omega)^{1/2}(\tau^{1/2} - t^{1/2})} + \frac{GK_1^{1/2}}{2^{1/2}(k_1^2 + \omega^2)^{1/2}\,\mathrm{erf}(k_1t)^{1/2}}\right]\cos\omega t\right\} \quad (14)$$

where $B \equiv [(k_1^2 + \omega^2)^{1/2} + k_1]^{1/2}$ and $G \equiv [(k_1^2 + \omega^2)^{1/2} - k_1]^{1/2}$. Because of the selectivity of the instruments used for measuring the d.c. electrode potential and the a.c. cell voltage, the reading on the d.c. voltmeter would be expected to be a measure of the sum of the first four terms in equa-

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(16) R. Peters, *Z. physik. Chem.*, **26**, 193 (1898).

(17) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p. 20.

tion 14; the remaining term should correspond to the reading on the a.c. meter.

$$e_{DC} = E_0' - (RT/nF) \ln (\pi D_R/2D_{Ox}k_1) - (RT/nF) \ln (\tau^{1/2} - t^{1/2}) + (RT/nF) \ln [\mathrm{erf}(k_1t)^{1/2}] \quad (15)$$

It is also necessary to consider the corresponding mathematical equations which would obtain if the Bancroft–Magoffin mechanism were operative. This mechanism, expressed in current terminology and applied to the present case, involves as a rate-determining step an irreversible electron transfer from the reductant to the electrode, proceeding *via* an activated complex. The theory of absolute reaction rates gives us the following equation[18] which we have expressed in terms of Delahay's symbols[19] and our own

$$i = nFAk^0_{f,h}C_R(0,t) \exp[\alpha nFe/RT] \quad (16)$$

where $k^0_{f,h}$ is the formal rate constant for the anodic, heterogeneous, electron-transfer reaction when $e = 0$ and α is the transfer coefficient for the anodic process. Since reductant is supplied to the electrode by diffusion as fast as it is used up by the rate-controlling oxidation, equation 8 may again be used and the value of $C_R(0,t)$ thus obtained may be substituted into equation 16. Solution of the resulting equation for e and separation into d.c. and a.c. components gives for the electrode potential

$$e_{DC} = (RT/\alpha nF) \ln (\pi D_R/2k^0_{f,h})^{1/2} - (RT/\alpha nF) \ln (\tau^{1/2} - t^{1/2}) \quad (17)$$

Results and Discussion

Equation 13 shows that for a given reductant and electrode area, τ will be constant if the ratio I/C_R^0 is constant. This is the chosen condition for Fig. 2. Equations 15 and 17 show that the d.c. electrode potential is a function of τ and t and therefore predict that all of the curves of Fig. 2 should be coincident. They obviously are not except for curves D and E which represent the two highest concentrations. However, the curves for the lower concentrations deviate by what is almost a simple translation along the t-axis. To explain this discrepancy, it is proposed that the start of the oxidation of PAP is delayed for a time which is very nearly equal to the interval of time associated with the lateral translation of the curves. From the magnitude of the delays (longer delays are associated with smaller currents) approximately the same amount of charge seems to be involved in each case. This suggests an extraneous initial process which could conceivably be connected with the charging of the double layer or the electrochemical removal of reduction products stored on the electrode during the prepolarization process. Probably curves D and E coincide because the relatively high currents there used result in such rapid initial processes that they cannot be recorded by the sluggish recorder. On the basis of these considerations we consider that curves D and E give the "best" potential–time relations; accordingly all data given in the tables to follow are taken from D and E curves.

The transition time, τ, cannot be calculated from equation 13 unless n and D_R are known, but it may be determined reasonably well from the experimental curves, such as those in Fig. 2, by using a graphical method suggested by Delahay.[20] Applied to our data, his method leads us to select as the value of τ the time at which the electrode potential curve crosses the 0.52 volt mark.

Let us define a quantity J as follows: $J \equiv -I\tau^{1/2}/AC_R^0$. Equation 13 shows that J should be constant for a given oxidation–reduction system. The data in Table I show that values of J based on experimental values of τ remain reasonably constant as I, A and C_R^0 are varied. This constancy suggests that Delahay's empirical method for determining τ is a reasonably satisfactory one for our purpose. It will be noticed that the two average values of J (each one relating to measurements made with a particular primary electrode) do not agree as well as do the individual values determined with the same electrode. This is not surprising in view of the difficulty of determining the exact macroscopic areas of disk electrodes whose edges are fused into glass and the impossibility of knowing their true areas.

TABLE I

EXPERIMENTAL VALUES OF τ AND J

C_R^0 = 0.0050 M or 0.0075 M (curves D and E)

A, cm.^{2}	$-I/C_R^0$, amp. cm.^{3} mole^{-1}	τ, sec.	J, amp. cm. sec.$^{1/2}$ mole^{-1}
0.0740	6.95	28.5	502
....	6.63	31	500
....	5.73	41.5	498
....	5.12	54	509
....	4.61	67.5	511
....	4.24	81	515
....	3.89	100.5	527
		Av.	510
0.1425	8.02	92	546
	7.14	117	543
	6.68	132	538
	6.14	156	538
	5.56	197	548
		Av.	542

TABLE II

NUMERICAL DATA TAKEN FROM D.C. ELECTRODE POTENTIAL–TIME CURVES

	−E.m.f. at the indicated fraction, f, of τ, v.					Symbol used in Fig. 4
	f = 0.1	f = 0.25	f = 0.50	f = 0.75	f = 0.90	
28.5	0.460	0.471	0.481	0.491	0.504	○
31	.461	.471	.481	.491	.503	●
41.5	.460	.469	.478	.490	.500	-○-
54	.459	.468	.477	.487	.501	-●-
67.5	.459	.466	.475	.489	.498	+
81	.457	.465	.474	.484	.495	△
100.5	.457	.464	.472	.483	.495	▲

$f = t/\tau$

The time-variation of d.c. electrode potential predicted theoretically by equations 15 and 17

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(18) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(19) Pages 34 and 186 of reference 17.

(20) Page 208 of reference 17.

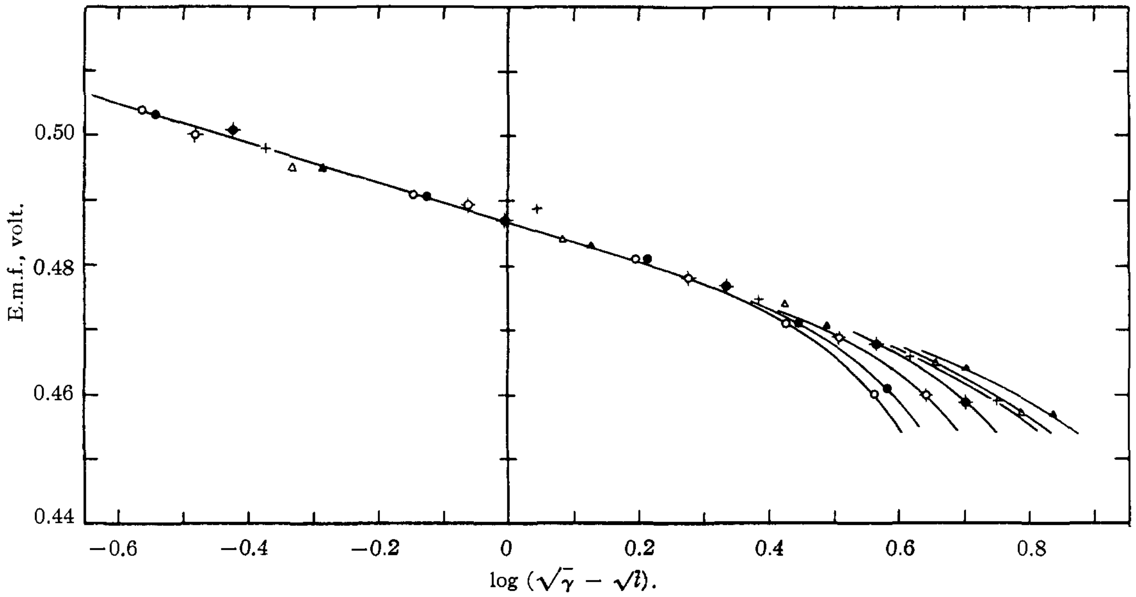

Fig. 3.—Experimental d.c. electrode potential *vs.* log ($\sqrt{\gamma} - \sqrt{l}$).

may be compared with experimental results by using the data of Table II to construct the graph shown in Fig. 3. The linear portion of the plot is predicted by both equations but the deviations from linearity at the lower end are not predicted by equation 17; they are correctly predicted by equation 15. This suggests that the Bancroft type of mechanism is not applicable to this oxidation reaction.

From the slope of the linear portion of the plot (−0.0307 volt) the value 1.965 would obtain: (1) for n, if equation 15 were used, or (2) for αn, if equation 17 were used. Since theory demands that $0 < \alpha < 1$, the value of n required by equation 17 would have to lie between 2 and ∞ with 4 as the most probable value since α usually lies close to 0.5. Neither a value of 4 for n nor a value of unity for α seem very likely. On the other hand, the value of 2 for n, as determined from equation 15, is reasonable in view of the fact that the same value has been shown to obtain for the homogeneous oxidation of PAP. Again, the results indicate that the Bancroft type of mechanism does not obtain in this case.

The diffusion coefficient, D_R, can now be calculated from equation 13 using $n = 2$ and the average value of $-I\tau^{1/2}/AC_R^0$, *viz.*, 526 amp. cm. sec.$^{1/2}$ mole^{-1}. The result is: $D_R = 0.946 \times 10^{-5}$ cm.^{2} sec.$^{-1}$.

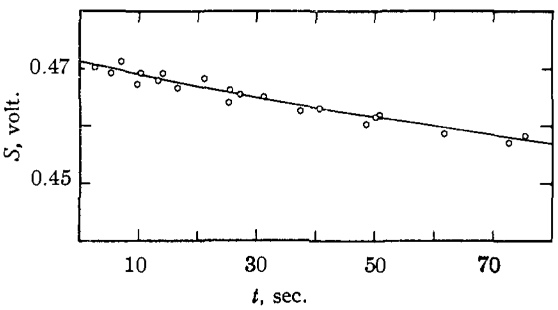

Fig. 4.—Variation of S with time.

Let us define a function S as

$$S \equiv (-\text{e.m.f.}) + (RT/2F) \ln [(\tau^{1/2}/t^{1/2}) - 1] \quad (18)$$

Equation 15 can then be written

$$S = E_0' + (RT/2F) \ln (D_R^{1/2}/D_0^{1/2}) + (RT/2F) \ln [\pi^{1/2} \text{ erf. } (k_1t)^{1/2}/2k_1t)^{1/2}] \quad (19)$$

A plot of S against t is shown in Fig. 4. For $t =$ 0, equation 19 reduces to

$$S_{t=0} = E_0' + (RT/2F) \ln (D_R/D_{ox})^{1/2} \quad (20)$$

Since the ratio of D_R/D_{ox} must be close to unity, it is clear that $S_{t=0}$ is essentially equal to E_0 which is found from Fig. 4 to be 0.471 volt referred to the S.C.E. or 0.711 volt referred to the N.H.E. This agrees very well with Fieser's value of 0.710 volt obtained by extrapolation to pH 1.18 of his data for the homogeneous oxidation of PAP.

From the intial slope of the curve of Fig. 4 and differentiation of equation 19 with respect to time it is found that

$$(dS/dt)_{t=0} = -k_1RT/6F = 20 \times 10^{-5} \text{ volt sec.}^{-1}$$

from which $k_1 = 0.020$ sec.$^{-1}$.

Equation 19 shows that, if $k_1 = 0$, S should be independent of time. Since this prediction is contrary to fact, it is clear that the data rule out a one-step, reversible electron-transfer reaction as a possible mechanism.

The a.c. impedance measurements can in principle be used to give an independent evaluation of k_1 and thus supply additional evidence by which the validity of the over-all theoretical treatment can be judged. Unfortunately the reproducibility of these measurements was not good enough to justify an attempt to correct for the charging current (which becomes appreciable in the a.c. but not in the d.c. measurements). However, plots of a.c. impedance against time gave a family of curves which were in good qualitative agreement with curves constructed from the theoretical equations. These equations were developed from equation 14 but are omitted here because they do not furnish sufficiently strong evidence for reaction mechanism.

We are now in a position to summarize the existing knowledge of the mechanism of the *anodic* oxidation of PAP. Knobloch's work showed that in basic solutions the electron-transfer step is reversible and is the same in the anodic as in the homogeneous reaction. By analogy with the similar methyl-aminonaphthol, two electrons seem to be involved. Fieser's work on the *homogeneous* oxidation of PAP showed that the range of the linear portion of the potential–time plot decreased rapidly as the *p*H was lowered to 2.69 thus suggesting that in more acidic solutions the first-order character of the follow-up step (equation 2b) might disappear altogether. General considerations also suggest the possibility that a mechanistic inversion might occur in sufficiently acidic solutions because of the possibility of the semiquinone becoming appreciably stable[21] or of the *p*-hydroxyanilinium ion becoming the participating species of the reductant. Our work at *p*H 1.18 showed no evidence of a mechanistic inversion. Our data were in accord with a mechanism of type 2a-b. The agreement between our value for E_0' and Fieser's extrapolated value together with our accurately determined value of 2 for the number of electrons transferred show that the first step (2a) of the *anodic* oxidation is the same as that of the *homogeneous* reaction. Since the second step in the *anodic* reaction involves the same transitory intermediate reactant as the *homogeneous* oxidation and since, as we showed, its initial rate constant is a first-order constant, it seems almost certain that it is identical with the second step (1b) of the homogeneous oxidation which has been established, in basic solutions, to be the hydrolysis of quinoneimine.

It is barely conceivable that there might be a change, between *p*H 2.69 and 1.18, in the participating species of the reductant when homogeneous oxidation occurs although such is not the case for the heterogeneous reaction. This is very unlikely, however. We may therefore consider that our work has extended the knowledge of the homogeneous mechanism to *p*H 1.18.

Since our data are definitely not in accord with a mechanism involving a rate-controlling electron-transfer step, our work serves to emphasize that a voltammetric technique is able to distinguish between this mechanism and the Conant–Pratt mechanism even though the two are indistinguishable from the point of view of the theory of absolute reaction rates or, in the case of homogeneous oxidation, by Conant's electrochemical (A.O.P.) technique.

DETROIT 2, MICH.

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[21] J. Weiss, *Trans. Faraday Soc.*, **42**, 116 (1946).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT CENTER OF THE ARMSTRONG CORK CO.]

The Reaction of Neutral Esters of Trivalent Phosphorus Acids with Inorganic Acid Chlorides. I. The Reaction of Trialkyl Phosphites with Sulfuryl Chloride

BY ALGIRDAS C. POSHKUS AND JOHN E. HERWEH

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The reaction of sulfuryl chloride with trialkyl phosphites has been investigated. Dialkyl phosphorochloridates, sulfur dioxide and alkyl chlorides are formed. This constitutes a useful simple synthesis of dialkyl phosphorochloridates which avoids acidic by-products.

Interest in expanded or foamed plastics has stimulated the investigation of pneumatogens, thermolabile compounds which decompose into products at least one of which is gaseous.[1a,b] Attention was directed toward the reaction of sulfuryl chloride with trialkyl phosphites[2] which was expected to proceed in a manner analogous to the Michaelis–Arbuzov reaction as applied to acid chlorides of carboxylic acids.[3a,b] Extension of Michaelis–Arbuzov reaction to compounds bearing a halogen attached to elements other than carbon has been inadequately studied.

The reaction of sulfuryl chloride with dialkyl hydrogen phosphite occurs readily at about 30–45° in the absence of solvents to give dialkyl phosphorochloridates in good yields.[4] Hydrogen chloride, one of the reaction products, has a solvolytic effect on the chloridate as well as on the dialkyl phosphite,[5a,b] thus limiting the synthetic application of this reaction.[6,7]

It has now been found that sulfuryl chloride does indeed react with trialkyl phosphites extremely vigorously even at temperatures as low as −20° in a variety of solvents at low dilution. Stable intermediates reported by Bell[2] were not found. If intermediates are formed, they are extremely labile even at 0°. Thus, in a reaction carried out at temperatures below 20°, almost a quantitative amount (>95%) of sulfur dioxide was swept out by a stream of nitrogen and absorbed in an aqueous iodine–potassium iodide solution. The reaction apparently conforms to the stoichiometry

$$(RO)_3P + SO_2Cl_2 \longrightarrow (RO)_2P(O)Cl + SO_2 + RCl$$

The order of adding the reactants did not affect the

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[1] (a) F. Lober, *Angew. Chem.*, **64**, 65 (1952); (b) R. A. Reed, *Plastics Progress*, 51 (1955).

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[3] (a) T. Reetz, D. H. Chadwick, E. E. Hardy and S. Kaufman, THIS JOURNAL, **77**, 3813 (1955); (b) T. B. Ackerman, T. A. Jordan, C. R. Eddy and D. Swern, *ibid.*, **78**, 4444 (1956); also see references cited in these papers.

[4] F. R. Atherton, H. T. Howard and A. R. Todd, *J. Chem. Soc.*, 1106 (1948).

[5] (a) W. Gerrard and E. G. G. Whitbread, *ibid.*, 914 (1952); (b) C. H. Campbell and D. H. Chadwick, THIS JOURNAL, **77**, 3379 (1955).

[6] G. W. Kenner, A. R. Todd and F. J. Weymouth, *J. Chem. Soc.*, 3675 (1952).

[7] F. R. Atherton, H. T. Openshaw and A. R. Todd, *ibid.*, 382 (1945).