Mechanism of o-Nitrophenol Reduction by Chronopotentiometry

BY A. C. TESTA AND W. H. REINMUTH

The electrochemical reduction of o-nitrophenol was studied chronopotentiometrically in a buffered ethanol–water mixture. Results obtained were consistent with the scheme: $A \xrightarrow{4e} B \xrightarrow{k} C \xrightarrow{2e} D$. Comparison of data with a theoretical equation allowed the determination of the formal pseudo-first order rate constant for the intermediate chemical reaction.
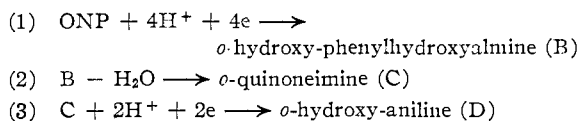
Introduction

In the polarographic reduction of o-nitrophenol the limiting current corresponds to a six electron reduction at high and low pH but shows a flat minimum value in the region of pH 6. This phenomenon has been investigated by several groups,[1-6] and two conflicting explanations have been offered.

Astle and McConnell attributed the phenomenon to intramolecular hydrogen bonding. They postulated that this interaction gave rise to an equilibrium between bonded and unbonded forms. The bonded form would undergo four electron reduction and the unbonded form six according to this scheme. This possibility seems a priori unlikely for only one well formed polarographic wave is observed and the inference would then be that the rate constants for both reductions were the same. A modification of this scheme in which only one of the two forms was reduced with slow (but not infinitely slow) interconversion to the reducible species would seem more plausible. Such a scheme can be represented as

$$\text{ONP(H-bonded)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{ONP} \xrightarrow{6e} o\text{-hydroxyaniline.}$$
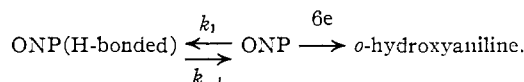
Stočesova, on the other hand, suggested that a slow chemical step interposed between two successive reductions was responsible. This scheme can be represented as

(1) $\text{ONP} + 4\text{H}^+ + 4e \longrightarrow$
                         o-hydroxy-phenylhydroxyalmine (B)

(2) $\text{B} - \text{H}_2\text{O} \longrightarrow o\text{-quinoneimine (C)}$

(3) $\text{C} + 2\text{H}^+ + 2e \longrightarrow o\text{-hydroxy-aniline (D)}$

Vertyulina and Malyugina[7] performed macroelectrolyses of ONP at pH 2.5 and found as products 5% of C and 89% of D. They interpreted this evidence as supporting Stočesova's hypothesis, but in fact it offers no basis for distinguishing between the two.

The two schemes differ importantly in that Stočesova's hypothesis requires a chemical kinetic

complication intermediate between electron transfer steps while that of Astle and McConnell requires the complication, if any, to precede electron transfer. It appeared that distinction between them could be made on the basis of the chronopotentiometric behavior of the system. The present study was undertaken with this aim.

Theoretical.—For Astle and McConnell's hypothesis, theory predicts that $i\tau^{1/2}$ should be a constant independent of the current.[8] The modification of the Astle and McConnell scheme in which an equilibrium exists between bonded and unbonded forms of o-nitrophenol, only the latter reducible, could give rise to a chemical reaction preceding electron transfer. This case has been treated previously[8] and gives rise to decreasing $i\tau^{1/2}$ for increasing current.

According to Stočesova's hypothesis, a chemical reaction occurs between two electrode processes. Rate constants for chemical reactions preceding[9] and following[10,11] electron transfer have been determined chronopotentiometrically by a number of authors, but the case of the intermediate chemical reaction has not been treated. The scheme of this latter reduction process can be represented as

$$\text{ONP} \xrightarrow{n_1} \text{B} \xrightarrow{k} \text{C} \xrightarrow{n_2} \text{D}$$
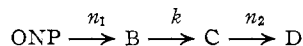
Starting with Fick's second law of diffusion with modification for kinetic effects, and appropriate boundary conditions, a useful solution can be obtained. Although the detailed solution of the boundary value problem will be presented elsewhere, the final equation is

$$i\tau_\infty^{1/2}/i\tau^{1/2} = 1 + 0.5\rho(\pi/k\tau)(\pi/k\tau)^{1/2}\,\text{erf}(k\tau)^{1/2} +$$
$$\rho^2(1 - \rho^2)^{-1/2}(k\tau)^{-1/2}\exp[k\tau(\rho^2 -$$
$$1)^{-1}]\left[\int_0^{(1-\rho^2)^{-1/2}(k\tau)^{1/2}} \exp x^2 dx + \right.$$
$$\left. \int_0^{\rho(1-\rho^2)^{-1/2}(k\tau)^{1/2}} \exp x^2 dx\right] \quad (1)$$

where $\rho = n_2/(n_1 + n_2)$ and $n_1 = 4$ electrons, $n_2 = 2$ electrons for o-nitrophenol. τ is the transition time, $i\tau_\infty^{1/2}$ represents the value to be expected for an infinite rate constant for the intermediate chemical reaction and, consequently, a six electron reduction to the aniline analog; k is the pseudo first rate constant of the dehydration of the phenylhydroxylamine to quinoneimine; erf represents the error function.

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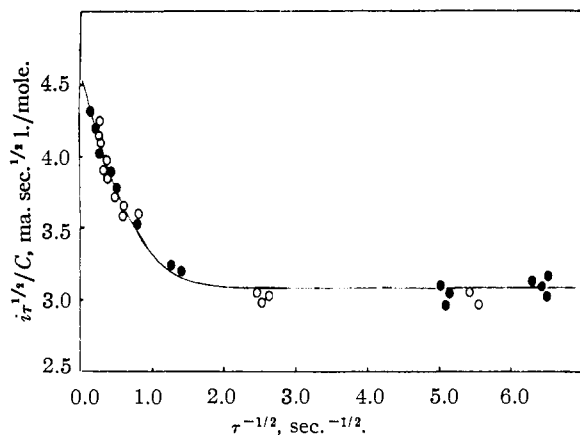
Fig. 1.—Experimental results for chronopotentiometric reduction of *o*-nitrophenol at mercury pool in 50% ethanol-water mixture in acetic acid, sodium acetate buffer (*p*H 6.2). Concentrations of *o*-nitrophenol: O = 3.00 × 10⁻³ *M*; ● = 1.50 × 10⁻³ *M*.

Experimental

The equipment used for this work has been described previously,[11] with the exception of the mercury pool used in the present work which had a projected area of 3.14 cm.[2] All measurements were made at 30.0 ± 0.1°.

Eastman *o*-nitrophenol was purified by recrystallizing three times from water–ethanol mixtures. The melting point was 46–46.5°, uncorrected. Walpole–Clark acetic acid–sodium acetate buffers were used so that the apparent *p*H's (50% ethanol–water) of the final solutions were 6.2 and 5.7 in the two cases studied. The concentrations in the higher *p*H were 0.18 *M* in sodium acetate and 0.019 *M* in acetic acid and at the lower *p*H 0.12 *M* in sodium acetate and 0.080 *M* in acetic acid. The *p*H was measured with a Beckman *p*H meter using glass and saturated calomel electrodes. Solutions studied were 1.00, 1.50 and 3.00 millimolar in *o*-nitrophenol.

Results and Discussions

Chronopotentiograms were obtained at varying currents and concentrations at apparent *p*H 6.2. The transition times observed in this study ranged from 50 seconds to 25 milliseconds. It is apparent from the results in Fig. 1 that $i\tau^{1/2}$ is not constant with varying current, thus disproving the hypothesis of Astle and McConnell. The value of $i\tau^{1/2}/C$ is independent of concentration eliminating the possibility of higher than first order kinetic complications.[11]

The theoretical equation shown above for Stočesova's scheme predicts that at high current densities $i\tau^{1/2}$ should approach a limiting value corresponding to the four electron reduction to the phenylhydroxylamine, a diffusion controlled process. As the current is decreased, the transition time becomes longer giving rise to a larger kinetic contribution and consequently an increasing $i\tau^{1/2}$. The limiting value of $i\tau^{1/2}/C$ for *o*-nitrophenol is 3.08 amp. sec.¹ᐟ² l./mole while comparable values for 4 electron reduction under the same experimental conditions are: for nitrobenzene, 3.41; and for *o*-nitrophenylacetic acid, 2.84,

The experimental results strongly favor Stočesova's hypothesis; however, the modified Astle–McConnell scheme is still not rigorously excluded by the limiting $i\tau^{1/2}/C$.

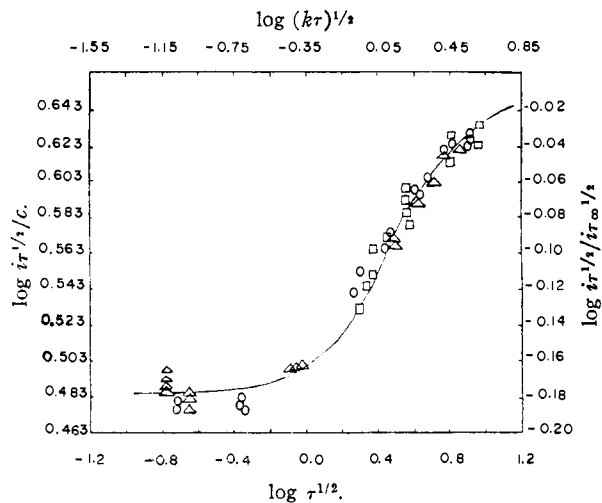In the modified Astle–McConnell scheme the limiting value of $i\tau^{1/2}/C$ at high currents would be

Fig. 2.—Variation of log ($i\tau^{1/2}/C$) with log $\tau^{1/2}$ for reduction of *o*-nitrophenol in 50% ethanol–water mixture at apparent *p*H 6.2. Concentrations of *o*-nitrophenol: O = 3.00 × 10⁻³ *M*, △ = 1.50 × 10⁻³ *M* and □ = 1.00 × 10⁻³ *M*. Coördinates given at top and right side of figure correspond to theoretical curve; at bottom and left to experimental points.

governed by the equilibrium ratio of bonded to unbonded forms of *o*-nitrophenol. With the assumption that the equilibrium constant for H-bond breakage is 2.00 the equation for this scheme would be

$$\frac{i\tau_\infty^{1/2}}{i\tau^{1/2}} = 1 + \frac{0.3618}{(k\tau)^{1/2}} \operatorname{erf}\left(1.225\, k^{1/2}\tau^{1/2}\right) \qquad (2)$$

Not only do this equation and equation 1 predict the same limiting values of $i\tau^{1/2}$ at high and low current densities but the forms of the two curves on a log-log scale (*vide infra*) are so similar that their difference lies within the experimental scatter of our data.

While the Stočesova's hypothesis would predict that the limiting value of $i\tau^{1/2}$ at high current should be a constant, in the modified Astle–McConnell scheme it would depend on the equilibrium constant.

That the constant should be 2.00 would be purely fortuitous. Moreover, because intra-molecular hydrogen bonding would be in competition with solvent interaction this formal equilibrium constant should depend on *p*H. On changing the apparent *p*H to 5.7, the limiting value of $i\tau^{1/2}$ remained the same within experimental error (3.08 amp. sec.¹ᐟ² l./mole at *p*H 6.2 *vs.* 3.11 at *p*H 5.7), while the variation of $i\tau^{1/2}/C$ with current indicated that the rate of the chemical reaction had increased. These considerations led us to the conclusion that there is indeed an intermediate chemical reaction between two electron transfers.

Having established the intermediate chemical reaction, we became interested in estimating the rate constant for the dehydration step. The complexity and transcendental nature of equation 1 do not lead to easy interpretation of experimental data. Trial and error calculations of theoretical plots of $i\tau^{1/2}$ *vs. i* to provide best fit have been employed in similar applications by other au-

thors,[12,13] but these are tedious and, in addition, insensitive to small changes in assumed parameters. The method chosen was to treat the data in log–log form as a plot of log $(i\tau^{1/2}/C)$ vs. log $\tau^{1/2}$ and to formulate the theoretical expression in an analogous form. log $(i\tau^{1/2}/i\tau_\infty^{1/2})$ vs. log $(k\tau)^{1/2}$. Superimposition of theoretical and experimental plots allowed the deduction of the rate constant—see Fig. 2.

There are two degrees of freedom in the translation of the theoretical curve to produce best fit with experimental data; one along the ordinate, the other along the abscissa. The former gives an estimate of the diffusion coefficient of the reducible species, the latter an estimate of the rate constant. The diffusion coefficient deduced from Fig. 2 is 0.82×10^{-5} cm.^{2}/sec., which is in excellent qualitative agreement with values for compounds of similar structure determined under the same conditions: nitrobenzene, 1.01×10^{-5} cm.^{2}/sec.; o-nitrophenylacetic acid, 0.70×10^{-5} cm.^{2}/sec.

The pseudo-first order rate constant deduced from Fig. 2 is 0.20 sec.$^{-1}$. Quantitative measure of the accuracy of this value was not attempted because of the large scatter in experimental data. However, a qualitative estimate based on the uncertainty in superimposition of experimental and theoretical curves is $\pm 20\%$.

Conclusions

The reduction of o-nitrophenol at high current densities proceeds with diffusion control and the transfer of four electrons, while at lower current densities up to six electrons are involved. Chronopotentiometric study of the system led to the conclusion that a slow chemical reaction is interposed between two electron transfer steps involving four and two electrons successively. Comparison of the data with exact theory allowed determination of the rate constant of the chemical step.

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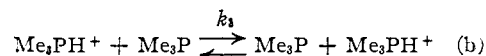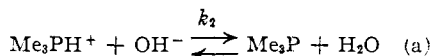# Rates and Mechanisms of Protolysis of Trimethylphosphonium Ion in Aqueous Solution Studied by Proton Magnetic Resonance

BY B. SILVER AND Z. LUZ

A kinetic analysis of the protolysis reactions of the trimethylphosphonium ion in aqueous solution has been carried out using the n.m.r technique. Two main mechanisms in the range pH 6.0 to 7.5 were found

$$Me_3PH^+ + OH^- \overset{k_2}{\underset{}{\rightleftarrows}} Me_3P + H_2O \quad (a) \qquad\qquad Me_3PH^+ + Me_3P \overset{k_3}{\underset{}{\rightleftarrows}} Me_3P + Me_3PH^+ \quad (b)$$

with second order rate constants of $4.6 \pm 0.9 \times 10^7$ and $1.2 \pm 0.6 \times 10^2$ l. mole^{-1} sec.$^{-1}$, respectively. A minor contribution comes from a pH independent exchange reaction viz., $Me_3PH^+ + H_2O \rightleftarrows Me_3P + H_3O^+$. The pseudo-first order rate constant for this reaction was found to be dependent on the Me_3PH^+ concentration and varied between 9.8 and 6.2 sec.$^{-1}$ in the concentration range 0.26 to 2.21 M.

Introduction

The nuclear magnetic resonance (n.m.r.) technique has been used recently to study a variety of proton exchange reactions which are too fast to be followed by classical methods. Quantitative studies have been carried out on the protolysis reactions of hydrogen bonded to nitrogen,[1-3] oxygen[4] and sulphur[5] in the case of amines, alcohols and thiols respectively.

The present work extends these studies to the fast protolysis reactions of hydrogen bonded to phosphorus in aqueous solutions of Me$_3$PHCl. The comparatively slow proton exchange reactions between water and phosphine,[6] hypophosphorous acid[7] and phosphorous acid[8] have previously been studied by isotopic labelling techniques.

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Experimental

Spectrometer.—The n.m.r. spectrometer used in this work was the same as that used in previous works [1-5] Cylindrical rotating glass sample holders of 3 mm. internal diameter were used. The resolution of the spectrometer was such that an effective relaxation time of about 1 sec. was measured from the decay of the 'wiggles' after fast passage through a water line. The effective T_2 of a water sample was measured before and after each record.

Preparation of Trimethylphosphonium Chloride Solutions.—Trimethylphosphine was prepared from methyl magnesium iodide[9] (from 24 g. of magnesium and 62 ml. of methyl iodide) in an atmosphere of nitrogen. Me$_3$P was distilled from the reaction vessel under nitrogen, into a solution of silver iodide (25 g.) in potassium iodide solution (100 g. in 100 ml. of water). The resulting trimethylphosphine–silver iodide complex was filtered off, washed in water and dried at 10μ pressure for several hours, in a tube with a ground-glass joint connected to a three way stopcock of a vacuum system. The tube was then gently heated to decompose the complex, the Me$_3$P formed being collected in an evacuated tube containing sodium hydroxide pellets and cooled in liquid nitrogen. After standing overnight the Me$_3$P was distilled into a tared receiver cooled in liquid nitrogen. The receiver was placed in a bath of ice-water and connected with a mercury manometer. A pressure of 15.8 cm. was recorded (quoted[10]: 15.9 and 16.1 cm. at 0°). The Me$_3$P was neutralized by adding approxi-

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