In Situ Electrochemical Electron Spin Resonance

The Catalytic (EC') Mechanism

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The oxidation of the acetate anion mediated by tris(4-bromophenyl)ammoniumyl, electrogenerated from the parent amine, has been investigated using ESR with an *in situ* channel electrode flow cell. In the absence of acetate, the oxidation of tris(4-bromophenyl)amine (TBA) is a reversible one-electron process which forms the corresponding radical cation, tris(4-bromophenyl)ammoniumyl (TBA⁺⁺). In the presence of acetate the process takes on the characteristics of the catalytic (EC') mechanism. Analysis of the diffusion-limited current/electrolyte flow rate behaviour allows the precise mechanism to be deduced. This is shown to be an EC' pre-equilibrium mechanism:

TBA – e → TBA⁺
TBA⁺ + CH₃CO₂⁻
$$\rightleftharpoons$$
 TBA + CH₃CO₂⁻
CH₃CO₂⁻ → CH₃⁻ + CO₂

with rate-determining electron transfer between the amine radical cation and the acetate anion.

In a previous paper¹ we described a flow cell suitable for simultaneous electrochemical/ESR measurements. It was seen that a silica cell, in the shape of a laminar-flow channel electrode, could be located at the centre of the ESR cavity with negligible perturbation of the ESR sensitivity. This allowed the identification of radical species formed in electrode reactions. Furthermore, the known pattern of flow in the channel electrode facilitated the calculation of the spatial concentration distributions of electrogenerated radicals for the case of stable radicals¹ and those decaying by first-order kinetics.² Such calculations allowed the steady-state ESR signal to be related to the generating current, the electrolyte flow rate and the geometry of the channel. Variation of the rate of mass transport, through control of the electrolyte flow rate, was thus shown to provide a probe of the lifetimes of the radical intermediates. The channel electrode cell has been demonstrated to be suitable for its application to the study of a wide range of electrode reaction mechanisms. Electrode mechanisms studied include ECE^{2,3} and DISP⁴ processes, as well as more complicated mechanisms.^{5,6} More recently photoelectrochemical reactions have been studied. The photoreduction of crystal violet⁷ was seen to have the characteristics of an EC mechanism, and the photoreduction of fluorescein at high pH⁸ was found to follow a 'photo-DISP2' mechanism.

In this paper we continue with our examination of the diverse range of possible electrode mechanisms open to study at the channel electrode, and investigate the use of *in situ* electrochemical ESR measurements in the study of catalytic (EC') mechanisms. In particular we consider the mediated oxidation of the acetate anion by the electrogenerated radical cation (TBA⁺⁺) of tris(4-bromophenyl)amine (TBA).

The use of the radical cation (TBA^{+}) for a wide range of homogeneous oxidations is well established,⁹⁻¹⁵ and it has been shown to oxidise carboxylate anions.^{16,17} The mechanism of this process has been proposed to be an electron-transfer process:¹⁷

$$TBA^{+} + CH_{3}CO_{2}^{-} \rightleftharpoons TBA + CH_{3}CO_{2}^{-}$$
(1)

$$CH_3CO_2 \rightarrow products.$$
 (2)

In the case that TBA⁺⁺ was electrogenerated the reaction has been demonstrated to have the characteristics of a catalytic (EC') mechanism.^{18–21} In this paper we show that *in situ* elec-

trochemical ESR measurements are consistent with this suggestion. The nature of the precise mechanism and its kinetic parameters are deduced.

Theory

A schematic diagram of the channel electrode can be seen in fig. 1. It consists of an electrode embedded in the wall of a rectangular duct through which solution flows. Under laminar flow conditions, and with a sufficiently long 'lead-in' length such that the solution flowing over the electrode is characterised by a parabolic velocity profile, then the components of the solution velocity in the three cartesian directions are:²²

$$v_x = v_0(1 - y'^2/h^2); \quad v_{y'} = v_z = 0$$
 (3)

where v_0 is the solution velocity in the centre of the channel, h is the half-height of the channel and y' is as defined in fig. 1.

Under conditions where (i) edge effects are negligible, (ii) $h \ll d$, and (iii) axial diffusion may be neglected, it has been established^{22,23} that the appropriate steady-state convective-diffusion equation is

$$0 = D \,\partial^2 c / \partial y^2 - v_x \,\partial c / \partial x \tag{4}$$

where c is the concentration of the species of interest (C) and D is its diffusion coefficient.

The EC' mechanism of interest is defined by the following general kinetic scheme:

$$\mathbf{A} \pm \mathbf{e} \rightleftharpoons \mathbf{B} \tag{5}$$

$$\mathbf{B} + \mathbf{P} \xrightarrow{\mathbf{A}_6} \mathbf{A} + \mathbf{Q} \tag{6}$$

$$Q \longrightarrow \text{products.}$$
 (7)

(This mechanism has been more rigorously classified as an EC' pre-equilibrium mechanism,²¹ and this notation is henceforth adopted.) In order to describe the behaviour of this mechanism the steady-state convective-diffusion equation [eqn (4)] has to be modified so that it contains terms relating the loss of material through kinetic decay. The relevant

k7



Table 1. Values for the matrix element d_1



 $g^{A,B,P}$ represents the normalised concentration of A, B, P.

Table 2. Values for the matrix element d_i

species	<i>d</i> _j
А	$g_{j,k}^{\mathrm{A}} + \left(\Delta y^2 / D_{\mathrm{A}} \lambda_j k_7 K_6 \frac{g_{j,k}^{\mathrm{B}} g_{j,k}^{\mathrm{P}}}{g_{j,k}^{\mathrm{A}}} \frac{p^*}{a^*} \right)$
В	$g_{j,k}^{\rm B} - \left(\Delta y^2 / D_{\rm B} \lambda_j k_7 K_6 \frac{g_{j,k}^{\rm B} g_{j,k}^{\rm P}}{g_{j,k}^{\rm A}} \frac{p^*}{a^*} \right)$
Р	$g_{j,k}^{P} - \left(\Delta y^2 / D_{P} \lambda_j k_7 K_6 \frac{g_{j,k}^{B} g_{j,k}^{P}}{g_{j,k}^{A}} \frac{p^*}{a^*} \right)$

Table 3. Values for the matrix elements b, a and c

species	b_1	bj
Α	$1+2\lambda_1$	$1+2\lambda_i$
В	$1 + \lambda_1$	$1+2\dot{\lambda_i}$
Р	$1 + \lambda_1$	$1 + 2\lambda_i$
	$a_j = -\lambda_j$ $j = 2, \ldots, J-1$,
	$c_j = -\lambda_j$ $j = 1, \ldots, J-2$	

Under conditions where the Leveque approximation is valid^{22,23} the current is a unique function of K^* . The observed behaviour is best expressed in terms of the effective number of electrons transferred, $N_{\rm eff}$. Fig. 2 shows how this depends upon K^* for various values of p^*/a^* in the EC' (pre-



Fig. 2. Working curves showing the effective number of electrons transferred, $N_{\rm eff}$, as a function of the normalised rate constant, K^* , for the EC' (pre-eqm) mechanism, using various ratios of p^*/a^* : (a) 0, (b) 1, (c) 2.5, (d) 5, (e) 10.



Fig. 1. A schematic diagram of a channel electrode, with the coordinate system defining the location of the channel electrode in the ESR cavity.

coupled transport equations for the EC' (pre-eqm) mechanism can be delineated as follows:

$$0 = D \ \partial^2 a / \partial y^2 - v_x \ \partial a / \partial x + k_7 K_6 \frac{bp}{a}$$
(8)

$$0 = D \ \partial^2 b / \partial y^2 - v_x \ \partial b / \partial x - k_7 K_6 \frac{bp}{a}$$
(9)

$$0 = D \ \partial^2 p / \partial y^2 - v_x \ \partial p / \partial x - k_7 K_6 \frac{bp}{a}$$
(10)

The appropriate boundary conditions for the transportlimited case are

$$x = 0; p = 1; a = 1; b = 0$$
 (11)

$$x > 0, y = 0: dp/dy = 0; a = 0; db/dy = -da/dy$$
 (12)

$$x > 0, y = 2h: dp/dy = 0; da/dy = 0; db/dy = 0.$$
 (13)

In the above equations a, b and p represent the concentrations of species A, B and P, and $k_{\pm n}$ and K_n are the forward and backward rate constants and the equilibrium constant for the appropriate reaction (n) as defined above. In writing the kinetic terms in eqn (8)-(10) we have assumed that $k_{-6}[A] \gg k_7$.

We have demonstrated elsewhere²³ how the general coupled equations such as (8)-(10), may be solved under the boundary conditions pertinent to the channel geometry by use of a computational procedure, namely the backward implicit (BI) method. This involves the calculation of vectors, that describe the concentrations in the y direction for different values of x. The calculation proceeds 'downstream', each vector enabling the calculation of the next, starting from the boundary conditions specified for upstream of the electrode. The methodology and the advantages of this approach have been well documented.^{8,23} The finite-difference equivalents of the above steady-state transport equations and the relevant boundary conditions are used to construct matrix equations for A, B and P. The matrix elements unique to the EC' (preeqm) mechanism are given in tables 1-3; the other matrix elements are unchanged from those pertaining to the calculation of the transport-limited current for a simple electron transfer.23

Using these matrix equations the BI method was applied to the problem under investigation here to determine the diffusion-limited current at the channel electrode under conditions where an EC' (pre-eqm) mechanism operates. Convergence of the limiting-current data was found with J = 2000, K = 200, where J and K, respectively, represent the number of grid points in the y and x directions, for the vector calculations in the BI method. The results were expressed in terms of the normalised rate constant:

$$K^* = k_7 K_6 \frac{p^*}{a^*} (h^2 x_{\rm E}^2 / 4v_0^2)^{1/3}$$
(14)

where p^* and a^* are the bulk concentrations of P and A.

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eqm) mechanism. These figures were calculated for a channel electrode of dimensions 2h = 0.04 cm, d = 0.6 cm, $x_{\rm E} = 0.4$ cm, w = 0.4 cm, $D = 2.0 \times 10^{-5}$ cm² s⁻¹ and volume flow rate $V_f = 10^{-3}$ cm³ s⁻¹.

The ESR signal behaviour was deduced from the BI calculation of the concentration distribution of B (which corresponds to TBA'+ in the system examined) both adjacent to and downstream of the electrode. The ESR signal was calculated from the equation⁸

$$S = S_0 w \int_0^{x_d} \cos^2[(x - 0.5x_E)/(x_d - 0.5x_E)\pi/2] \int_0^{2h} [B] dy' dx$$
(15)

where S_0 is the ESR signal due to 1 mol of radicals located at the cavity centre, and the \cos^2 function denotes the spatial dependence of the sensitivity of the ESR cavity.²⁴ In the form written above this equation relates to an electrode located centrally perpendicular to the modulation coils of the ESR cavity. It has been shown⁸ that the integrals in eqn (15) can be evaluated from weighted summations using the distribution of [B] generated from the BI calculation. From this method the ESR signal behaviour was analysed in terms of the variation of $S/I_{\rm lim}$ with the electrolyte flow rate, where $I_{\rm lim}$ was found from the Levich equation²² and $N_{\rm eff}$ values were obtained from working curves as shown in fig. 2.

Experimental

The basic apparatus and experimental techniques have been described previously.^{1,7} The silica channel electrode unit was 30 mm long and had approximate cross-sectional dimensions of 0.4 mm × 6.0 mm. Platinum electrodes, of dimensions 4.0 $mm \times 4.0$ mm, were cemented to the silica cover plate and then carefully polished before use, with successive grades of diamond lapping compounds down to 0.25 µm. The ESR spectrometer employed in this work was a Bruker ER200D, fitted with a 9 in† magnet.

Electrochemical measurements were carried out using an Oxford Electrodes potentiostat modified to boost the counter-electrode voltage.²⁵ A reference electrode was located in the flow system upstream of the ESR cavity. This was a silver wire pseudo-reference electrode. A platinum gauze counter-electrode was located downstream of the working electrode, outside the ESR cavity. Flow rates in the range 10^{-4} -10⁻¹ cm³ s⁻¹ were employed.

Acetonitrile (Fisons, dried distilled) was refluxed with calcium hydride and then fractionally distilled. Tetrabutylammonium perchlorate, TBAP (Fluka, purum) was recrystallised once from a mixture of ethanol and petroleum ether. Tris(4-bromophenyl)amine, TBA, (Aldrich, 99%) and tetrabutylammonium acetate (Fluka, >95%) were used as received, as was acetic acid (BDH AnalaR).

Supporting theory was generated from programs written in FORTRAN 77 on a VAX 11/785 mainframe computer, using NAG 11 library routines.

Results and Discussion

We consider first the oxidation of TBA in acetonitrile, in the absence of acetate anion, at the platinum channel electrode. Current vs. voltage curves were recorded as a function of the electrolyte flow rate. It was deduced that $E^0 = +1.20$ V vs. SCE, in agreement with previously reported values.¹² Tafel analysis of the current vs. voltage curves (a plot of E vs.

 $+ 1 \text{ in} = 2.54 \times 10^{-2} \text{ m}.$

10 G

from 2.74 mmol dm⁻³ TBA in acetonitrile.

in agreement with that expected for a reversible one-electron electrode process.²⁶ Analysis of the flow rate dependence of the limiting current revealed a cube-root dependence, as is predicted by the Levich equation:²²

coefficient calculated from these data was found to be 1.89×10^{-5} cm² s⁻¹, in good agreement with the literature value.20

In situ electrochemical ESR experiments were performed at potentials corresponding to the oxidation of TBA to TBA^{**} and revealed the ESR spectrum, shown in fig. 3. This spectrum consists of a single line of peak-to-peak linewidth ca. 70 G, in agreement with previous observations.^{27,28}

We have shown previously¹ that for a stable radical

$$S = \text{constant} \times I_{\text{lim}} / V_{\text{f}}^{-2/3}.$$
 (17)

Fig. 4 shows a plot of $\log(S/I_{\lim})$ vs. $\log(V_f)$, with the line drawn through the points having the gradient of -2/3 as required by eqn (17) for a stable radical.

The oxidation of TBA can on the basis of the electrochemical and ESR measurements fit the category of a one-electron reversible process. Addition of acetate anion, however, produces behaviour typical of an EC' process.²⁰ Fig. 5 shows the limiting current vs. electrolyte flow rate behaviour obtained in the absence and presence of acetate. The currents observed in the presence of acetate are greater than those predicted for



Fig. 4. The variation of $(S/I_{\rm lim})$ with electrolyte flow rate $(V_{\rm f})$ for the radical cation TBA⁺⁺, electrogenerated from 2.74 mmol dm⁻³ TBA

in acetonitrile.



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Fig. 5. The flow rate (V_i) dependence of the diffusion-limited current at the channel electrode for the oxidation of TBA (2.49 mmol dm⁻³) in the presence of no acetate (\bigcirc) and 10.6 mmol dm⁻³ acetate (\bigcirc).

the one-electron process, and the effective number of electrons, N_{eff} , transferred increases as the flow rate is decreased. Analysis of the N_{eff} vs. flow rate behaviour, in terms of an EC' (pre-eqm) mechanism, using working curves similar to those produced in fig. 2 was carried out. This facilitated the deduction of the normalised rate constant K* as a function of flow rate. In fig. 6 this quantity is plotted against $V_f^{-2/3}$, as suggested by eqn (14), for different ratios of [TBA]/[acetate]. For the two ratios investigated good straight lines were obtained, from which was deduced the value of the product



Fig. 6. Values of K^* deduced from the measured N_{eff} values and the relevant working curves plotted against $V_f^{-2/3}$. [acetate]/[TBA]: \bigcirc , 4.25; \bigoplus , 1.13.



Fig. 7. ESR spectrum of the radical cation TBA'⁺, electrogenerated from TBA (2.49 mmol dm⁻³) in the presence of 10.6 mmol dm⁻³ acetate anion.

 $k_7 K_6$. This was found to be $0.7 \pm 0.2 \text{ s}^{-1}$, in good agreement with that obtained from rotating disc electrode studies.¹⁸

The BI method was then used to model the ESR signal $S-I_{lim}-V_f$ behaviour for TBA⁺⁺ in the EC' (pre-eqm) mechanism, using the value of the product $k_7 K_6$ found from the channel electrode data. The ESR spectra observed in the presence of acetate require some comment. For ratios of [acetate]/[TBA] < ca. 4 the single broad-line spectrum of TBA'+ was observed resembling that as shown in fig. 3. However, for [acetate]/[TBA] > ca. 4, a second set of ESR signals was observed superimposed upon those due to TBA⁺⁺, as shown in fig. 7. These were interpreted as being due to an as yet unidentified species formed via reaction of methyl radicals produced in step (2) in the scheme above. Support for this conjecture was found in experiments undertaken with [acetate]/[TBA] > 25, where the spectra were found to consist solely of the products of the methyl radicals with no evidence of TBA⁺, as shown in fig. 8.

Fig. 9 shows the theoretically predicted $S-I_{lim}-V_f$ behaviour for TBA⁺⁺, both in the absence and presence of the acetate anion, compared with experiment for the pertinent value of the normalised rate constant. Excellent agreement is found between theory and experiment, which can be taken as



Fig. 8. ESR spectrum produced from the electrogeneration of TBA⁺⁺, from TBA (1.04 mmol dm⁻³) in the presence of 26.7 mmol dm⁻³ acetate anion.



Fig. 9. The variation of $(S/I_{\rm lim})$ with electrolyte flow rate (V_t) for the radical cation TBA⁺⁺ (2.49 mmol dm⁻³), in the absence (\bigcirc) and presence (\bigcirc) of acetate (10.6 mmol dm⁻³). The broken line represents the slope of -2/3 expected for a stable radical, and the solid line that calculated theoretically assuming an EC' (pre-eqm) mechanism with the product $k_7 K_6 = 0.70 \text{ s}^{-1}$.

an independent confirmation that the EC' (pre-eqm) mechanism, shown below, operates in this electrode reaction.

$$TBA - e \rightarrow TBA^{+}$$
 (18)

 $TBA^{+} + CH_{3}CO_{2}^{-} \rightleftharpoons TBA + CH_{3}CO_{2}^{-}$ (19)

$$CH_3CO_2^{\cdot} \rightarrow CH_3^{\cdot} + CO_2 \tag{20}$$

Conclusions

The oxidation of tris(4-bromophenyl)amine (TBA) in acetonitrile is a reversible one-electron process which generates the corresponding radical cation (TBA⁺⁺). In the presence of acetate direct electron transfer appears to occur between TBA⁺⁺ and acetate and the reaction may be shown to have the characteristics of an EC' (pre-eqm) mechanism. The benefit of the use of combined electrochemical and spectroscopic techniques in the elucidation of the mechanism of a disputed electrode reaction is demonstrated once more.²⁹ We thank the S.E.R.C. for a PDRA for A.M.W., the S.E.R.C. and Ohmeda for a CASE studentship for R.J.N., and Dr Mark Laing for helpful discussions.

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