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Carbon electrodes*: Part 2. The anodic oxidation of N-propylamine

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The anodic oxidation of a primary aliphatic amine, n-propylamine, has been studied at electrodes of vitreous carbon and pyrolytic graphite. The electrode reaction has been found to differ greatly for the two materials, as evidenced by the voltammetric behaviour at rotating disc electrodes and the results of preparative electrolyses. The observations at the vitreous carbon electrode are in agreement with the mechanism proposed by Mann and Barnes for the oxidation of propylamine at a stationary platinum electrode. A novel mechanism is proposed for the oxidation at a pyrolytic graphite anode.

1. Introduction

Relatively few studies have been made of the anodic oxidation of primary amines, mainly owing to the lack of synthetic applications. Recently Masui [1] and co-workers reported an unsuccessful attempt to oxidize n-propylamine in aqueous solution at a vitreous carbon electrode. No oxidation waves were found in the pH range 2–12. Hampson [2, 3] has been able to oxidize several primary amines at a silver anode using the same conditions, the oxidation process in this case involving reaction of the amine with a film of silver oxide on the electrode surface.

Primary amines have been successfully oxidized in non-aqueous solvents, though again relatively little work has been published. Mann and Barnes [4, 5] studied the oxidation of several primary amines at a platinum anode in acetonitrile and proposed reaction mechanisms involving the initial formation of a cation radical. This could either split into a carbonium ion and amidogen radical, or undergo deprotonation and further electron transfer to yield an iminium ion. The second alternative pathway was held to be favoured at high anodic potentials. The overall mechanism was considerably complicated by the further reaction of decomposition products, particularly ammonia. Mann's work was performed at a stationary platinum anode, and it was thought that further insight into the electrode process might be gained by studying the effect of changing the electrode material. In particular the importance of adsorbed intermediates would be indicated. The oxidation of n-propylamine was therefore studied at vitreous carbon and pyrolytic graphite electrodes using the same solvent, supporting electrolyte and reference electrode as used by Mann. Both voltammetric and preparative studies were carried out.

2. Experimental

2.1. *Apparatus*

The acetonitrile was purified by the method of O'Donnell *et al.* [6]. Sodium perchlorate (Analar) was used as supporting electrolyte.

The small rotating disc electrodes used in the voltammetric studies have been described else-

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[*] Part 1 M. P. J. Brennan and O. R. Brown, *J. Appl. Electrochem.*, 2 (1972) 43.

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where [7]. The electrodes used for preparative electrolyses were discs of vitreous carbon (Vitreous Carbons Ltd.) and pyrolytic graphite (Le Carbone Ltd.) of diameter 2·5 cm mounted in P.T.F.E. holders (Fig. 1). The pyrolytic graphite disc had a cleavage plane as the working surface. Vitreous carbon electrodes were prepared by polishing with fine carborundum paper and 'gamma' grade alumina polishing powder. The pyrolytic graphite face electrodes were prepared by removing a thin flake with a razor blade, and the edge electrodes by cutting with a fine hacksaw followed by light polishing on carborundum paper to remove saw marks. All the electrodes were washed thoroughly in acetonitrile before being introduced into the cells.

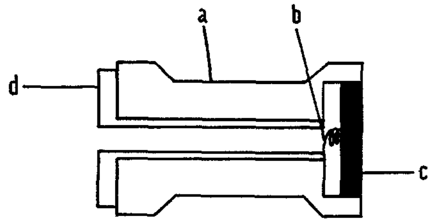


Fig. 1. Preparative R.D.E. (a) P.T.F.E.; (b) phosphor-bronze spring; (c) vitreous carbon or pyrolytic graphite; (d) brass.

A divided cell of 150 ml capacity was used for voltammetric studies with a platinum plate of area 2 cm^2 as counter electrode. The cell used for preparative studies was also divided and of 400 ml capacity, incorporating a jacket for coolant water (Fig. 2). The counter electrode was a mercury pool of area 24 cm^2. A system of cooled traps could be attached to the cell to collect volatile products. The reference electrode used was a silver wire in 0·01 M silver perchlorate in acetonitrile.

Polarization curves were recorded on a Bryans 26000 X-Y recorder, and current-time curves on a TOA EPR-2T recorder. The potentiostat and function generator have been described previously [8, 9].

Potentiometric titrations were performed in a cell incorporating a liquid seal tap to separate the calomel reference electrode from the non-aqueous titrant, in conjunction with a Radiometer 4 pH meter. Gas chromatographic analyses were carried out on an F and M model 810 chromatograph fitted with a flame ionization detector.

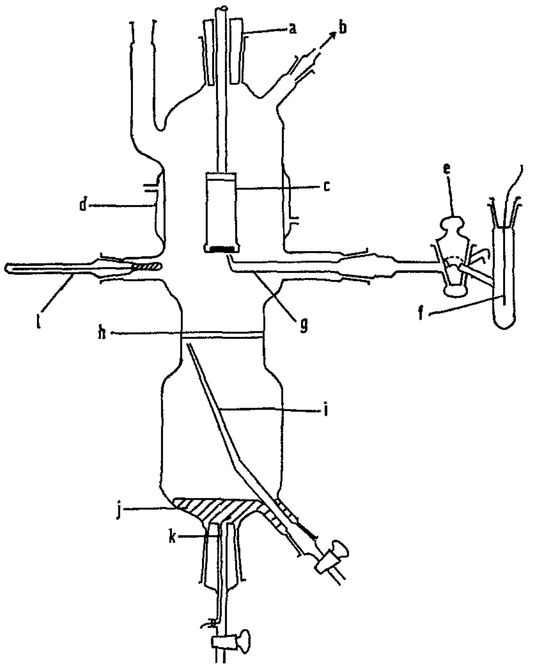


Fig. 2. Preparative cell. (a) P.T.F.E. cone; (b) to cooled traps; (c) R.D.E.; (d) water jacket; (e) liquid seal tap; (f) silver reference electrode; (g) Luggin capillary; (h) glass sinter; (i) gas bleed tube; (j) mercury pool counter electrode; (k) platinum contact; (l) thermometer.

2.2 *Procedure*

Polarization curves were obtained by linear potential scans over the range 0 to +2·1 V, and the effects of varying the electrode rotation speed and amine concentration studied. The apparent order of reaction with respect to amine was determined by varying the bulk concentration at constant potential and electrode rotation speed. Sodium perchlorate concentrations of 0·1 M to 0·5 M were employed, and amine concentrations of 0·002 M to 0·3 M.

Preparative electrolyses were carried out at potentials of +2·0 V and +1·4 V with amine concentrations of 0·47 M and 0·21 M respectively. A stream of helium was passed over the electrolyte surface to flush volatile products into a system of traps cooled in liquid nitrogen. At various stages the effect of electrode rotation speed was studied, the electrolyses being performed at a rotation speed of 50 rad s^{-1}. The orange-coloured anolyte obtained at the end of a run was analysed as follows:

(1) A sample of anolyte in dimethyl sulphoxide (DMSO) was titrated potentiometrically with standardized potassium methoxide in anhydrous methanol, to estimate the total concentration of ammonium plus n-propylammonium ions.

(2) A sample of anolyte was shaken with solid sodium hydroxide to release propylamine from its salt and was analysed by g.l.c. to determine the concentration of free amine.

The results permitted calculation of the amount of amine consumed during the electrolysis (and therefore the mean coulometric number), and the amount of hydrogen ion generated.

(3) The anolyte was then evaporated to remove excess acetonitrile and poured into water, from which organic materials were extracted with ethyl acetate. The extracts were dried over anhydrous sodium sulphate, and examined by g.l.c. on an Apiezon L column at 100°C.

(4) The material condensed in the cooled traps was allowed to evaporate and samples were examined by g.l.c. on a Porapak Q column and compared with standards of methane, ethane, ethylene and propane. A small amount of propylamine had also condensed in the trap. This was removed and estimated as in step [3].

The potentiometric titrations to determine the total amount of ammonium and n-propylammonium ion formed during the electrolysis were carried out in DMSO as recommended by Barnes and Mann [10]. The hydroxide ion in aqueous medium is an insufficiently strong base to liberate propylamine from its hydrogen perchlorate salt. g.l.c. quantitative analyses of propylamine concentrations were performed on a column of Carbowax 20 M, modified by the addition of 10% sodium hydroxide [11].

3. Results

3.1. *Voltammetric studies*

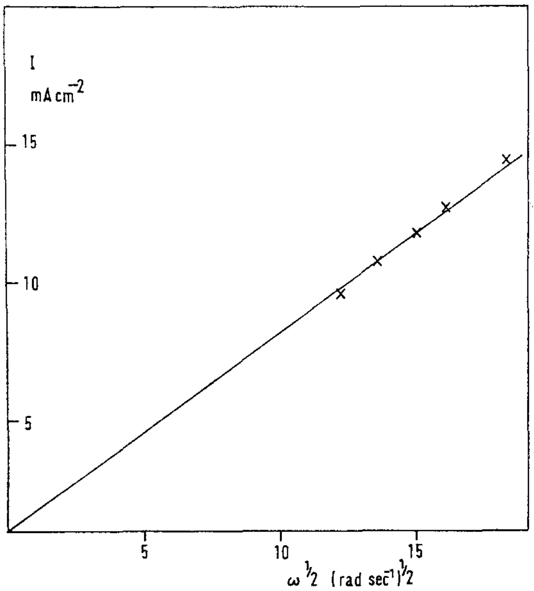


Fig. 3. Limiting currents at the rotating vitreous carbon disc. ($PrNH_2$ concentration 0·01 M, sweep rate 0·09 V s^{-1}, $NaClO_4$, 0·2 M.)

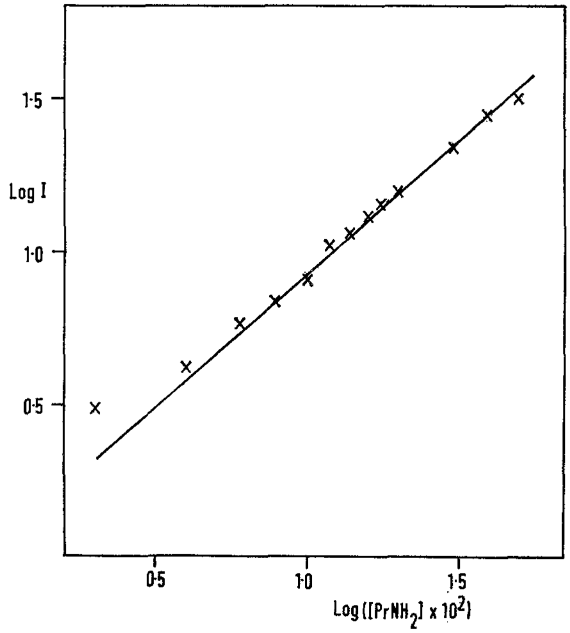


Fig. 4. Apparent reaction order plot (vitreous carbon; $E = 1{\cdot}5$ V; electrode area 0·19 cm^2).

The polarization curves recorded at the vitreous carbon electrode gave drawn-out waves, with a Tafel slope of approximately 250 mV and $E_{1/2} = +1{\cdot}5$ V. A plot of limiting current versus (rotation speed)$^{1/2}$ gave a linear plot passing through the origin (Fig. 3), indicating that the current-limiting process was reactant diffusion to the electrode. The effect of varying the bulk amine concentration was plotted in the form log *i* versus log [$PrNH_2$], the currents obtained at +1·5 V being used. The resulting straight line had a gradient of 0·87, indicating a reaction order of approximately unity (Fig. 4). The effect of increasing the electrode rotation speed, ω, at high amine concentrations (0·3 M) was to cause the current to increase to a maximum value, and then steadily decrease as the rotation speed grew larger. The value of ω corresponding to the maximum current increased as the potential was set more anodic (Figs. 5 and 6). This decrease of current with increasing rotation speed was also observed during the preparative electrolyses at vitreous carbon.

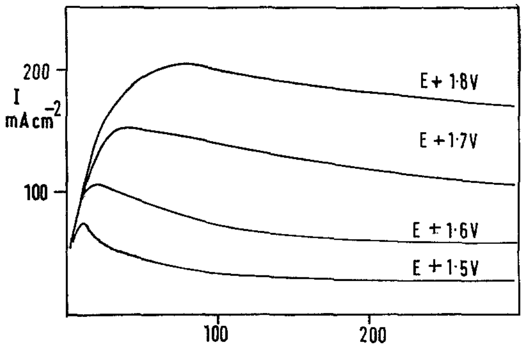


Fig. 5.

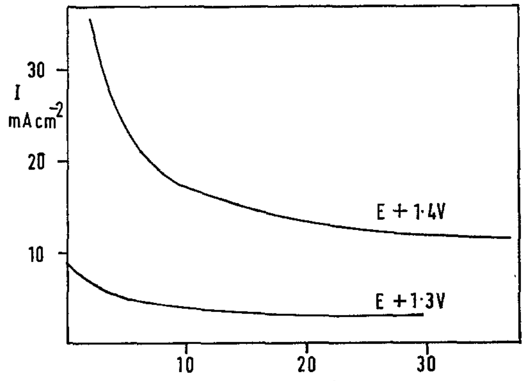


Fig. 6.

Figs. 5 and 6. The effect of electrode rotation speed upon the current obtained at a rotating vitreous carbon disc electrode. ($PrNH_2$, 0·2 M; $NaClO_4$, 0·5 M.)

The polarization range available on both pyrolytic graphite electrodes was limited to 0 to +1·5 V by a process in the supporting electrolyte believed to be due to the formation of an interlamellar graphite compound. Fig. 7 shows a typical background polarization curve to +2·0 V which illustrates the quasi-reversibility of the process. The limiting currents were unaffected by changes in electrode rotation speed. On the addition of amine a further wave appeared with an approximate half-wave potential of +1·0 V (Fig. 8). A plot of limiting current versus $\omega^{1/2}$ for this wave gave a linear plot passing through the origin. (Fig. 9). The effect of varying the amine concentration on the current at +1·04 V was plotted in the form ·log i versus log[$PrNH_2$]. The gradient of the resulting straight line was 0·86, indicating an apparent reaction order of approximately unity (Fig. 10). At an amine concentration of 0·3 M there was only a slight increase in current upon increasing the rotation speed from 10 rad s^{-1} to 400 rad s^{-1}. No current maxima or regions of current diminishing with increasing rotation speed were observed, on either the face or the edge electrode.

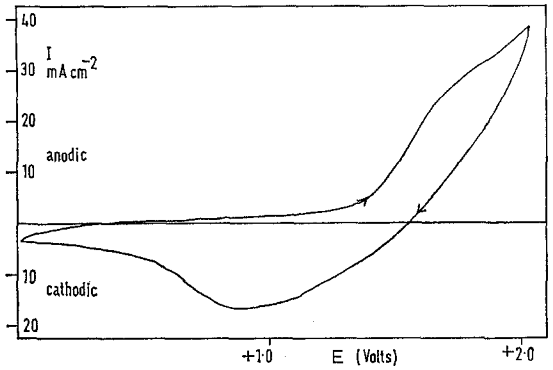


Fig. 7. Background polarization curve at a rotating pyrolytic graphite (face) electrode. (Sweep rate 0·1 V s^{-1}; $NaClO_4$, 0·2 M.)

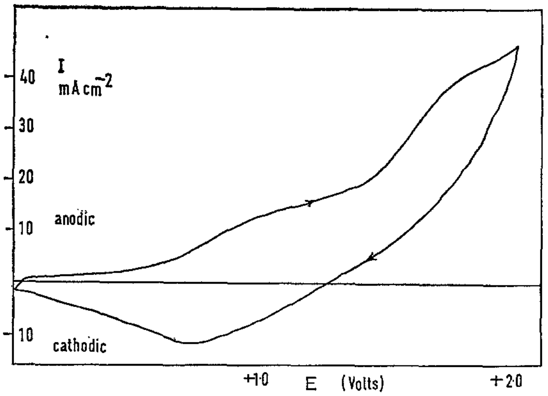


Fig. 8. Amine oxidation wave at the pyrolytic graphite (face) electrode. ($PrNH_2$ 0·01 M; sweep rate 0·1 V s^{-1}; $NaClO_4$, 0·2 M.)

Table 1

	$E = +2{\cdot}0$ V			$E = +1{\cdot}4$ V		
	n	$H^+/PrNH_2$	c.d. mA cm^{-2}	n	$H^+/PrNH_2$	c.d. mA cm^{-2}
Vitreous carbon	1·2	0·8	40	0·95	0·8	8·7
Pyrolytic graphite	1·8	1·4	109	1·5	1·2	40

3.2. *Preparative electrolyses*

The coulometric number, n, for the consumption of amine, the ratio moles H^+ generated/moles $PrNH_2$ consumed, and the initial current densities for the electrolyses are listed in Table 1. Here the vitreous carbon electrode is compared only with a pyrolytic graphite face since it was not possible to obtain pyrolytic graphite in sufficient thickness for the construction of a large rotating disc with the edge orientation.

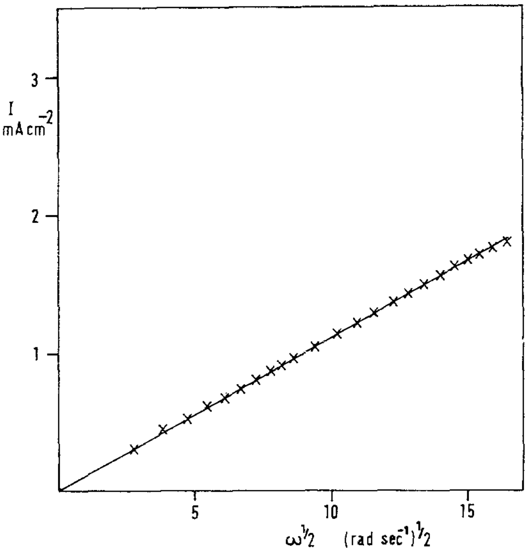


Fig. 9. Rotation speed dependence of limiting currents at a pyrolytic graphite (face) electrode. ($PrNH_2$, 0·002 M; $NaClO_4$, 0·2 M; sweep rate 0·09 V s^{-1}.)

At the pyrolytic face electrode the current fell continuously with time throughout the course of the electrolysis. At the commencement of an experiment the current was insensitive to electrode rotation speed, displaying a normal $i \propto \omega^{1/2}$ behaviour near completion. At the vitreous carbon anode, however, the current rose initially, reaching a peak at ~150% of its

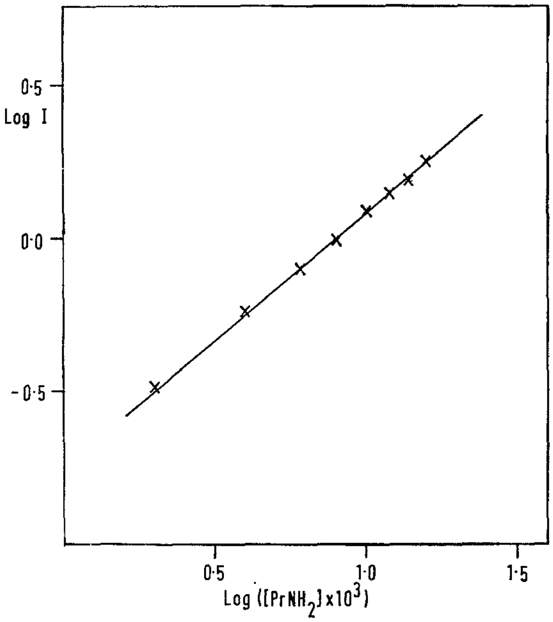


Fig. 10. Apparent reaction order plot. (Pyrolytic graphite face; $E = 1{\cdot}04$ V, electrode area 0·44 cm^2.)

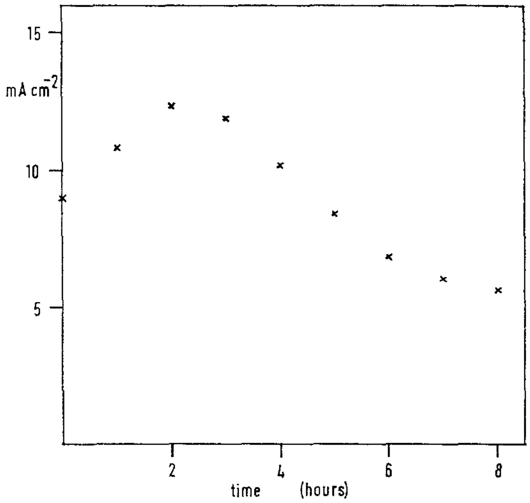


Fig. 11. The current-time maximum observed during preparative electrolysis at a vitreous carbon electrode. ($PrNH_2$, 0·21 M; $NaClO_4$, 0·5 M.)

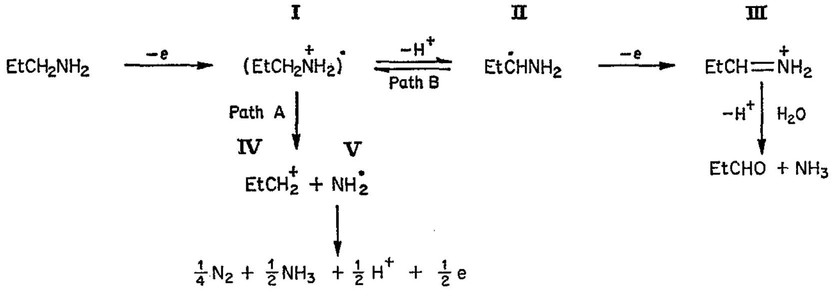
starting value before gradually falling. Fig. 11 shows a typical *i-t* curve. In addition the current showed an inverse relationship with rotation speed at the commencement of electrolysis, similar to the behaviour observed on the kinetic electrode in 0·3 M amine solution. Near the termination of the experiment the current increased with increasing rotation speed.

The pyrolytic face electrode was destroyed by electrolysis at +2·0 V, confirming the belief that an interlamellar graphite compound is formed at these potentials. The appearance of the electrode after the experiment was consistent with this view, an attack having been made on the edges of the disc which had the effect of raising the surface. At +1·4 V the electrode was not attacked.

The volatile product material condensed during all the electrolyses was shown by g.l.c. to contain trace amounts of ethylene, propane and ethane, increasing in that order. The non-volatile product material on g.l.c. showed 23 major components plus several minor ones, indicating the complexity of the follow-up reactions to electron transfer. The g.l.c. trace was similar for all the electrolyses, no substantial potential or electrode material effects on the retention times being observed.

4. Discussion

The results obtained on the vitreous carbon electrode correspond in general with the observations of Barnes and Mann for the oxidation of propylamine at a platinum anode, and agree with the reaction scheme they proposed on the basis of their results. This scheme, which accounts for the oxidation of propylamine via two parallel E.C.E. mechanisms is reproduced in part below.



The ammonia produced in pathway B and the amidogen radical produced in pathway A are assumed to be further oxidized directly or otherwise to nitrogen and hydrogen ion at the (relatively) high potentials employed for the oxidation of propylamine.

The relationship between current and electrode rotation speed which might be expected for an E.C.E. process has been considered by Adams [12], Karp [13] and Filinovskii [14]. These treatments envisage a simple single E.C.E. process $A\xrightarrow{e}B\xrightarrow{k}C\xrightarrow{e}D$. In the mechanism proposed by Mann for amine oxidation both pathways consist of several electrochemical and chemical steps in parallel and consequently the simple treatment cannot strictly be applied. We can, however, neglect the contribution to the current from the oxidation of ammonia produced by the reaction of the iminium ion III with water, since the rate of this reaction will certainly permit the diffusion of III or its derived imine away from the electrode surface in the solutions used. Hence in the time scale of a voltammetric measurement very little of the ammonia produced by this means will be capable of diffusing back to the electrode. Mann claimed that pathway A dominated on platinum at low potentials, and in particular that more than 90% of propylamine reacted via this pathway at +1·2 V. If the predominance of this pathway at low potentials also occurs on vitreous carbon then analysis of the $i-\omega$ relationships observed at low potential might be possible. Pathway A, from amine right through to completion, strictly speaking consists of several successive E.C. steps. It is anticipated, however, that the oxidation of $NH_2^{\cdot}$ to N_2 and H^+ will be very fast compared with the other steps and will be completed without escape of the intermediate stages from the electrode surface. The pathway can therefore be treated as a single E.C.E. step.

$$EtCH_2NH_2 \xrightarrow{-e} EtCH_2^+NH_2^- \xrightarrow{k} EtCH_2^+ +$$

$$NH_2^- \xrightarrow{-2e} \tfrac{1}{2}\,N_2 + 2H^+$$

Analysis of the $i-\omega$ curves obtained at low potentials in terms of this model was carried out according to the treatments of Karp, Filinovskii and Adams.

All three authors consider the reaction:

$$A \xrightarrow{n_1 e} B \xrightarrow{k} C \xrightarrow{n_2 e} D$$

The assumption is made that the concentration of C at the electrode surface is zero. Each molecule of B formed can either be lost to the bulk or converted by chemical reaction to C with subsequent oxidation to D. As both the chemical step and diffusion are first order, the fraction of B molecules to undergo further reduction does not depend upon the concentration of B at the electrode surface and hence is not affected by the rate of conversion of A to B (i_1). Therefore, the treatments of Filinovskii, Karp and Adams which include the boundary condition $[A]_s = 0$ can be adapted to cases in which $[A]_s \neq 0$.

Their results can be expressed in the following form:

$$\frac{i_L}{i_{L,A}} = F\left(\frac{\delta^2 k}{D}\right)$$

$i_{L,A}$ is the limiting diffusion current due to A when the second oxidation step occurs to a negligible extent ($\omega \rightarrow \infty$), i_L is more generally the limiting diffusion current when $\omega < \infty$. Now $i_{L,A}$ can be replaced by i_1 the limiting current in the first step. Hence we can write

$$\frac{i}{i_1} = F\left(\frac{\delta^2 k}{D}\right),$$

i_1 can be related to $i_{\omega=\infty}$ by the following relationship:

$$i_1^{-1} = i_{\omega=\infty}^{-1} + (0{\cdot}62\ n_1\ FAC_A\ D^{\frac{2}{3}}\nu^{-\frac{1}{6}}\omega^{\frac{1}{2}})^{-1},$$

to allow for rate control by diffusion of reactant to the surface.

Hence

$$\frac{i}{i_1} = \frac{i}{i_{\omega=\infty}} + \frac{i}{K\omega^{\frac{1}{2}}}$$

Where $K = 0{\cdot}62 n_1 FAC_A D^{\frac{2}{3}}\nu^{-\frac{1}{6}}$. ν = kinematic viscosity, D = diffusion coefficient, A = electrode area, C_A = concentration of A. This constant must be calculated using suitable values for D and ν. Taking $D = 10^{-5}$ cm^2 s^{-1} and $\nu = 10^{-2}$ cm^2 s^{-1} a value of K was obtained for the system studied as $3{\cdot}51 \times 10^{-3}$ A s$^{-\frac{1}{2}}$.

Theoretical plots of $F(x)$ versus log (x) were constructed using the functions given by the three authors, making the assumption $n_1 = n_2$ (Fig. 12).

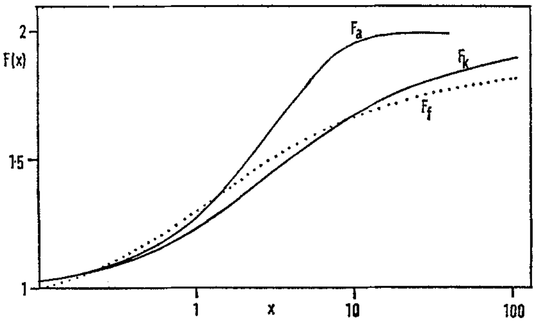


Fig. 12. Theoretical curves for an E.C.E. process at a rotating disc electrode. F_a [12]; F_K [13]; F_F [14].

Adams: $$F_A(x) = \left(\frac{n_1+n_2}{n_1}\right) - \frac{n_2}{n_1}\exp\left(\frac{-x}{\pi}\right)$$

Karp: $$F_k(x) = \left(\frac{n_1+n_2}{n_1}\right) - \frac{n_2}{n_1}\cdot\frac{\tanh(x)^{\frac{1}{2}}}{x^{\frac{1}{2}}}$$

Filinovskii: $F_F(x)$ =

$$0{\cdot}94\left[1+\frac{n_2}{n_1}\left(1-\frac{(1+0{\cdot}526x)^{\frac{1}{2}}}{1+x}\right)\right]$$

Plots of i/i_1 versus log (ω^{-1}) were constructed on the same scale and the ordinate adjusted by a factor n_1/n_2 where n_1 was assumed to be 1

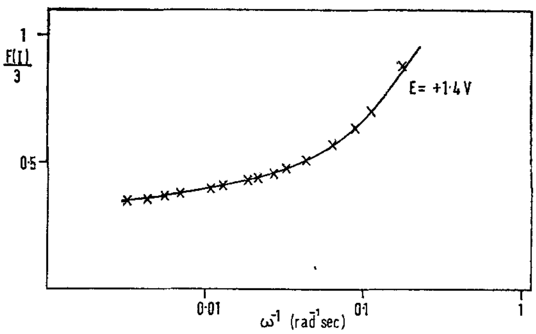


Fig. 13. Experimental data for the vitreous carbon electrode. ($PrNH_2$, 0·2 M; $NaClO_4$, 0·5 M; $E = +1{\cdot}4$ V.)

and n_2 was 1, 2 and 3. The data recorded at $+1 \cdot 4$ V when plotted in this form gave a reasonable fit to the function $F_A(x)$ and the value of k, the chemical rate constant in the E.C.E. process, was calculated to be $0 \cdot 045 s^{-1}$ (Fig. 13). The fit was obtained with $n_2 = 3$. This strongly suggests that the amidogen radical in the scheme considered performs a rapid hydrogen abstraction from other species present ($PrNH_2$, MeCN) before undergoing further oxidation. This is in agreement with the observed maximum value of $i_{max}/i_{\omega \to \infty}$ of 4 shown in Fig. 6. The overall process implied by this analysis is:

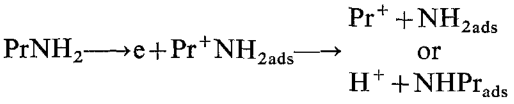
$$EtCH_2NH_2 \xrightarrow{-e} EtCH_2N^+H_2^{\cdot} \xrightarrow{k_1} EtCH_2^+ + NH_2^{\cdot} \xrightarrow{k_2(\geqslant k_1)} NH_3 \xrightarrow{-3e} \tfrac{1}{2}N_2 + 3H^+ \qquad (1)$$

This is in agreement with the explanation proposed by Mann for the observed current-time peaks in the exhaustive electrolysis of propylamine at platinum. He attributed them to the oxidation of ammonia produced by the slow decomposition of the cation radical I. The value of the chemical rate constant indicated by the above analysis is in agreement with the requirements of a slow decomposition. Current-time peaks similar to those described by Mann were observed in the preparative electrolyses at vitreous carbon.

The proposed scheme (Equation 1) predicts values of 4 for n and of 3 for ($H^+/PrNH_2$) respectively which contrast with those observed (Table 1). This probably arises because further molecules of propylamine are involved in the chemical follow-up reactions of the reactive intermediates.

The process at the pyrolytic face electrodes exhibits quite different characteristics, suggesting that the mechanism is different from that discussed for vitreous carbon. The following observations lead to the conclusion that the process of propylamine oxidation to nitrogen, hydrogen ion and propyl cation is completed in a single approach to the electrode, and that no intermediates are formed which are capable of escape to the bulk of the solution: (1) The phenomenon of current decrease with increasing rotation speed in 0·3 M solutions was not observed; (2) There were no current-time maxima in the preparative electrolyses; (3) The values of the coulometric number and the ratio moles H^+ produced/moles $PrNH_2$ consumed were higher than for the vitreous carbon electrode; (4) The current densities at a given potential were higher than for vitreous carbon.

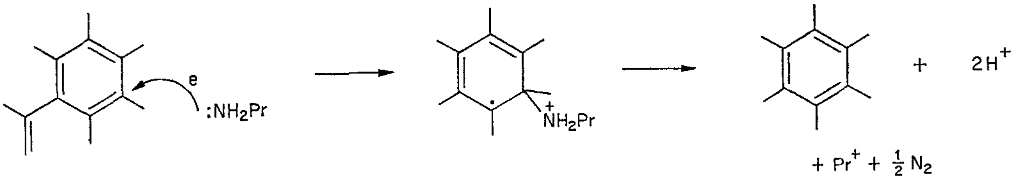
These facts are consistent with a more efficient process of ammonia or amidogen radical oxidation at the pyrolytic face electrode. There are two possible explanations; either the cation radical $PrNH_2^{\dotplus}$ is not formed at this electrode, or it is unable to escape after formation. The latter explanation is unsatisfactory since it requires the postulation of cation-radical adsorption on the electrode surface, or, alternatively, invoking a much higher rate of decomposition of the cation radical to Pr^+ and $NH_2^{\cdot}$ so that the rotating disc was incapable of detecting the process. Additionally one must consider the observation that the oxidation process commences at a much less anodic potential than on the vitreous carbon anode. It is suggested therefore that in this case there is a single step mechanism involving electron transfer and an adsorbed nitrogen species.



$$PrNH_2 \longrightarrow e + Pr^+NH_{2ads} \longrightarrow \begin{matrix} Pr^+ + NH_{2ads} \\ \text{or} \\ H^+ + NHPr_{ads} \end{matrix}$$

The adsorbed amine group is then further oxidized without leaving the electrode surface. It remains to be explained, however, why this does not occur at the vitreous carbon electrode. Clearly the reactive sites for this process cannot simply be unsatisfied valences at the carbon surface since previous work [7, 15] has shown that the density of this type of site is much higher on vitreous carbon. Furthermore one would then expect a much higher reactivity at the pyrolytic edge than at the face, which was not observed. The activity of the pyrolytic graphite electrodes must therefore be connected with the aromatic nature of this material, suggesting a scheme such as the that shown at the top of page 217.

The initial step may be a potential-assisted nucleophilic attack upon the electrode followed by loss of hydrogen ion. Alternatively the propyl cation may be lost first. The effect of the potential applied to the electrode is to act as an electron-withdrawing substituent upon the C_6 nucleus. The overall process involves three



electrons and produces two protons. However, since the propyl cation can react further with other amine molecules the theoretical coulomb number 3 is not observed.

Acknowledgements

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