The Application of Electrochemical Techniques to the Study of Homogeneous Chemical Reactions

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1 Introduction

All instrumental techniques require a number of years development before commercial apparatus is available and the theoretical background is thoroughly understood. Happily a number of electrochemical techniques have reached this state of maturity and are now well suited to the investigation of the homogeneous chemical reactions of inorganic, organic, organometallic, and biochemical species.

Indeed, polarography, cyclic voltammetry, potential step methods, rotating-disc and ring-disc electrode techniques, coulometry, product isolation techniques, and spectroelectrochemical methods may together be adapted to allow the study of reaction mechanisms, the identification of intermediates, and the measurement of rate constants for their chemical processes. These intermediates may be either relatively stable or rather shortlived, and in general electrochemical techniques can cover a range of half lives between 0.1 ms and 10^4 s. Electrochemical techniques are particularly well suited to the study of intermediates which may be produced by fast one-electron transfer processes, and hence it is not surprising that electrochemistry has made a significant contribution to the understanding of radical ion chemistry.

The study of homogeneous chemical reactions by electrochemical techniques is dependent on one of two concepts. Either a system may be designed where the chemical reaction of interest controls the rate of production of an electroactive species, or the species whose chemistry is to be studied may be produced by an electrode reaction. In the latter case the overall electrochemical experiment effectively consists of two parts; in the first the species is generated and in the second the electrode system is used to analyse for the species remaining in solution after a time lapse. This concept has very general application since a very wide range of species may be produced at electrodes (*e.g.* carbanions, radicals, carbonium ions, dications, ion radicals, metal ions in unusual oxidation states, halogens, organometallic species).

This review sets out to describe the most important electrochemical methods used in the study of homogeneous chemical reactions and to illustrate their use with examples taken from the whole of chemistry. The first section, however, discusses the basic principles of electrode processes essential to the understanding of these techniques.

2 Fundamental Concepts of Electrode Processes

The electrochemical experiments to be discussed in this review always consist of an investigation of the relationship between the current flowing through the system and the electrode potential (*versus* a reference electrode) and the dependence of this *i–E* relationship on experimental parameters such as the time-scale on which the observation is made, the nature of the solution environment, and the effect of convection.

Even the simplest electrode process (adsorbed intermediates and surface reactions will not be discussed) is, however, a sequence of several events; for example, the conversion of the solution-free species A into the solution-free product B is a three-step process

$$\mathrm{A_{soln}} \xrightarrow{\text{mass transport}} \mathrm{A_{surface}} \tag{1}$$

$$\mathrm{A_{surface}} \pm n\mathrm{e} \xrightarrow{\text{electron transfer}} \mathrm{B_{surface}} \tag{2}$$

$$\mathrm{B_{surface}} \xrightarrow{\text{mass transport}} \mathrm{B_{soln}} \tag{3}$$

The current is determined by the overall rate of this sequence and therefore by the slowest of the three steps. Thus an understanding of any electrochemical experiment requires a consideration of both the heterogeneous electron-transfer process and mass transport.

The Heterogeneous Electron-transfer Process.—It is the electrode potential which determines whether sufficient energy is being supplied for the electron transfer to occur. The standard electrode potential, $E^{\ominus}$, for the reaction

$$\mathrm{A} \pm n\mathrm{e} \rightleftharpoons \mathrm{B} \tag{4}$$

versus a reference electrode, for example a hydrogen electrode, is related to the standard free energy, $\Delta G^{\ominus}$, of the overall cell reaction *e.g.*

$$\mathrm{A} \pm n\mathrm{H}^{+} \rightleftharpoons \mathrm{B} \pm \frac{n}{2}\,\mathrm{H_2} \tag{5}$$

by the equation

$$\Delta G^{\ominus} = -nFE^{\ominus} \tag{6}$$

Certain electron-transfer processes are fast at the standard potential ($k^{\ominus} > 10^{-2}$ cm s^{-1}, see later) and in most experiments with such electrode processes it appears that the electron-transfer process at the electrode surface remains in equilibrium. Under these circumstances the shape of the rising portion of the *i–E* curve can be derived by calculating the surface concentrations of the reactant and product, C_{A}^{σ} and C_{B}^{σ}, respectively, from the Nernst equation

$$E = E^{\ominus} \pm 2.3\,\frac{RT}{nF}\log C_{\mathrm{A}}^{\sigma}/C_{\mathrm{B}}^{\sigma} \tag{7}$$

a purely thermodynamic equation. Such systems are known as reversible.

Conversely, irreversible electrode processes are those where some consideration must be given to the kinetics, as well as the thermodynamics of the reaction in order to deduce the relationship between current and potential. Such electrode reactions occur only at a low rate at the reversible potential, and in order to obtain a measurable current it is necessary to apply an overpotential. The equation relating current and potential for irreversible reactions has been derived elsewhere[1-4]

$$i = nFA\,k^{\ominus}\left[C_{\mathrm{A}}^{\sigma} \exp\left[-\frac{\alpha nF}{RT}(E - E^{\ominus})\right] - C_{\mathrm{B}}^{\sigma} \exp\left[\frac{(1-\alpha)nF}{RT}(E - E^{\ominus})\right]\right] \tag{8}$$

where $k^{\ominus}$ is the standard rate constant, α the transfer coefficient, and A is the surface area. The former is a measure of the rate at the standard electrode potential. Under normal experimental conditions, one of the exponential terms in equation (8) is usually negligibly small and the equation becomes of the type

$$\log i = \log nFAC_{\mathrm{A}}^{\sigma}k^{\ominus} - \frac{RT}{2.3\alpha nF}(E - E^{\ominus}) \tag{9}$$

Irreversible electrode processes give rise to *i–E* curves which are more drawn out and displaced along the potential axis when compared with those for a reversible system.

Mass Transport.—In general three types of mass transfer must be considered: migration, diffusion, and convection. They arise from the movement of a species under the influence of, respectively, a potential field, a concentration gradient, and an external mechanical force. In kinetic experiments, the contribution of migration is usually suppressed by addition of an excess of an inert electrolyte, and it is normal to carry out experiments under conditions where either it is necessary to consider only diffusion, *i.e.* the system is unstirred, protected from temperature gradients, *etc.*, or the solution is stirred in a defined manner. It is then necessary to consider both diffusion and convection.

The rate of mass transport is dependent on the geometry of the electrode system, but most electrochemical experiments on a timescale of seconds or less and in unstirred solution are well approximated by one-dimensional equations, *i.e.* by linear diffusion to a plane electrode. Diffusion is then described by Fick's laws in the form

$$\mathrm{flux}_i = -D_i\frac{\mathrm{d}C_i}{\mathrm{d}x} \tag{10}$$

and

$$\frac{\partial C_i}{\partial t} = D_i\frac{\partial^2 C_i}{\partial x^2} \tag{11}$$

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[1] J. O'M. Bockris and A. K. N. Reddy, 'Modern Electrochemistry—Volume II', Plenum Press, New York, 1970.

[2] B. E. Conway, 'Theory and Principles of Electrode Processes', Ronald Press, New York, 1965.

[3] K. J. Vetter, 'Electrochemical Kinetics', Academic Press, New York, 1967.

[4] J. Koryta, J. Dvořak, and V. Boháčková, 'Electrochemistry', Methuen, London, 1970.

The first law describes the flux of a species through a plane normal to the electrode in terms of the concentration gradient at that plane in space and a diffusion coefficient, D. The second relates to non-steady state conditions and describes the change in the concentration with time of a species due to diffusion alone.

In stirred solutions where both diffusion and convection must be considered, the mass-transport equation will be of the type

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - V_x \frac{\partial C_i}{\partial x} \tag{12}$$

where V_x is the velocity of solution movement in the x direction. Convective diffusion is, of course, dependent on the electrode geometry and the mode of stirring and it is usually necessary to write the equation in three-dimensional co-ordinates. Generally

$$\frac{\partial C_i}{\partial t} = D_i \Delta^2 C_i - V \operatorname{grad} C_i \tag{13}$$

The breakdown of an electrode process into the sequence (1)—(3) readily explains the familiar S-shape of a steady-state *i–E* curve. At low potentials, it is the electron-transfer process which is the slowest step, and the rate of this process increases exponentially with potential [see equations (7) and (9)]. Eventually step (2) becomes fast compared with (1) and mass transport becomes the rate-determining step; hence a plateau is observed on the *i–E* plot since the rate of mass transport does not depend on potential.

In the potential region of this mass-transport limited current, the electroactive species will undergo the electron-transfer reaction as soon as it reaches the electrode surface so that at the surface its concentration will be zero.

In experiments designed to study homogeneous chemical reactions, wherever possible the potential is chosen so that the electrode reaction is mass-transport controlled. Under these circumstances it is not necessary to consider the electron transfer process in any detail and no information about the kinetics of this process is required.

3 Formulation of Theory

In order to obtain quantitative kinetic data for a homogeneous chemical reaction from an electrochemical experiment it is necessary to formulate a theoretical description of the experiment and to solve the resulting partial differential equations. The solution required will describe the dependence of the *i*, *E*, *t* behaviour on the rate constant for the chemical reaction.

The experiment may be described completely by a set of partial differential equations together with their initial and boundary conditions. For each species in the system, it is possible to write down a partial differential equation which describes how its concentration within the diffusion layer close to the electrode surface varies with time and distance from the electrode surface. In general this equation will have terms which describe the change in concentration with time due to diffusion, convection, and chemical reactions, *e.g.* for a one-dimensional mass-transport situation

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - V_x \frac{\partial C_i}{\partial x} \pm k\, C_i^{\nu} C_j^{\mu} \tag{14}$$

where k is the rate constant for the chemical reaction and ν and μ are the order of reaction with respect to the species i and j, respectively. Integration of any such set of equations will require (i) information about the concentration of all species at one particular time, normally at the start of the experiment, $t = 0$, where the concentrations of all species are uniform at all points in space and determined only by the preparation of the solutions for the experiment, and (ii) information concerning the concentrations at two points in space. These are normally at the electrode surface, $x = 0$, and at an infinite distance from the electrode; the former are determined by the nature of the electrochemical experiment and in some cases will depend on time, while the latter again depend only on the solutions prepared for the experiment.

In such general terms the situation sounds somewhat complex and is perhaps best simplified by some particular examples. Figure 1 shows the differential equations, initial and boundary conditions for two chemical systems and three electrochemical experiments carried out at stationary electrodes in unstirred solution (*i.e.* convection need not be considered).

The solution of such sets of equations is seldom trivial and usually requires the use of the Laplace Transformation, conversion to integral equations followed by numerical integration or, more recently, simulation techniques. Such techniques are beyond the scope of this review and the interested reader is referred elsewhere.[5,6] Fortunately a complete solution is not always required since the current is given by

$$i = -nFAD \left(\frac{\partial C_A}{\partial x}\right)_{x=0} \tag{15}$$

where C_A is the concentration of the electroactive species. Hence only the evaluation of $\frac{\partial C_A}{\partial x}$ at $x = 0$ is necessary in order to determine the current. Of course, $\left(\frac{\partial C_A}{\partial x}\right)_{x=0}$ is commonly a function of time.

The complete solutions of the differential equations describe how the concentration of each species in the system varies as a function of time and distance from the electrode surface. These are known as concentration profiles and a qualitative consideration of their time evolution during an experiment is often

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[5] W. H. Reinmuth, *Analyt. Chem.*, 1962, **34**, 1446.

[6] S. Feldberg, *Electroanalyt. Chem.*, 1969, **3**, 199.

extremely instructive (see, for example, Figure 2) and allows qualitative predictions concerning the results of the experiment.

Systems

(*a*) $A + e \rightleftharpoons B$

$B \xrightarrow{k} P$

(*b*) $A + e \rightleftharpoons B$

$2B \xrightarrow{k} A + P$

Differential equations

(*a*) $$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2}$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} - kC_B$$

(*b*) $$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} + kC_B^2$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} - 2kC_B^2$$

Initial Conditions

$t = 0, \quad x \geqslant 0 \quad C_A = C_A^\infty$ and $C_B = 0$

Boundary Conditions

$t > 0, \quad x = \infty \quad C_A = C_A^\infty$ and $C_B = 0$

$t > 0, \quad x = 0$

(i) Potential step experiment to a potential on the limiting current plateau:

$$C_A^\sigma = 0 \text{ and } D_A \left(\frac{\partial C_A}{\partial x}\right)_{x=0} = -D_B \left(\frac{\partial C_B}{\partial x}\right)_{x=0}$$

(ii) Double potential step. First pulse, τ s, as (i). Second pulse at a potential where $B - e \rightarrow A$ is diffusion controlled.

$$t < \tau \quad C_A^\sigma = 0 \text{ and } D_A \left(\frac{\partial C_A}{\partial x}\right)_{x=0} = -D_B \left(\frac{\partial C_B}{\partial x}\right)_{x=0}$$

$$t > \tau \quad C_B^\sigma = 0 \text{ and } D_A \left(\frac{\partial C_A}{\partial x}\right)_{x=0} = -D_B \left(\frac{\partial C_B}{\partial x}\right)_{x=0}$$

(iii) Linear potential sweep, scan rate ν V s^{-1}

$$E = E_i + \nu t$$

$$\frac{C_A^\sigma}{C_B^\sigma} = \exp\left[\frac{RT}{F}(E - E^{\ominus})\right] \text{ and}$$

$$D_A \left(\frac{\partial C_A}{\partial x}\right)_{x=0} = -D_B \left(\frac{\partial C_B}{\partial x}\right)_{x=0}$$

Figure 1 *Differential equations, initial and boundary conditions for potential step and linear potential sweep experiments designed to study the kinetics of two types of homogeneous chemical reaction* (a) *first-order decay and* (b) *disproportionation, where the reactive species is produced in an electrode reaction*

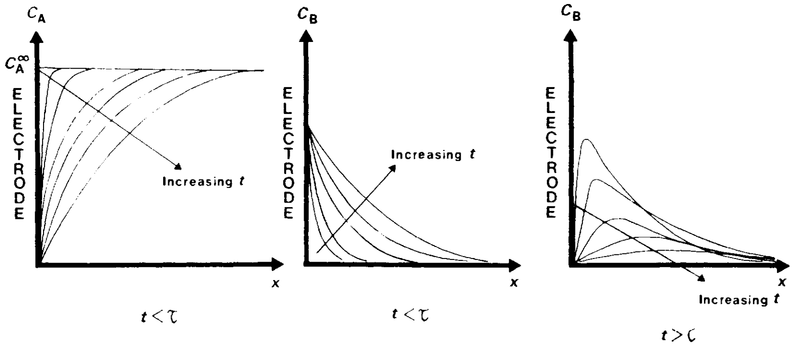

Figure 2 *The evolution with time of the concentration profiles for species* A *and* B *during a double potential step experiment as Figure* 1, a(ii), *for a particular value of k. Length of* A *pulse* τ s.

4 Polarography

In classical polarography,[7-11] an *i–E* curve is recorded by varying the potential of a dropping mercury electrode slowly in a linear manner (*ca.* 0.1 V $\min^{-1}$). Polarography was the first instrumental electrochemical method to be developed and its popularity over many years may be attributed to the simple equipment required and the high degree of reproducibility which may be attained. It has, however, recently become less fashionable largely because the timescale on which chemical reactions are observed, essentially the drop time of the mercury electrode, is much more restricted than with the techniques described later. Systems for study are, of course, limited to those with an electroactive species within the potential range of mercury.

The polarogram for each electron-transfer process has a characteristic S-shape (see Figure 3) and the experimental measurables are: (i) the current on the limiting current plateau; (ii) the half-wave potential, $E_{\frac{1}{2}}$, *i.e.* the potential where the current is half the limiting value; (iii) the slope of the *i–E* curve in the region where the current changes with potential – this is commonly determined by measuring $E_{\frac{3}{4}} - E_{\frac{1}{4}}$.

Although the limiting current for many electrode reactions is determined by the rate of diffusion of the electroactive species, it is not uncommon for it to be determined by the rate of a homogeneous chemical reaction.[7-13] Kinetic waves

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[7] L. Meites, 'Polarographic Techniques', Interscience, New York, 1965.

[8] P. Zuman, 'The Elucidation of Organic Electrode Processes', Academic Press, New York, 1969.

[9] J. Heyrovsky and J. Kuta, 'Principles of Polarography', Publishing House of the Czech. Academy of Science, Prague, 1965.

[10] H. Strehlow, in 'Techniques of Organic Chemistry—Volume VIII', ed. A. Weissberger, Interscience, New York, 1963.

[11] 'Physical Methods of Chemistry, Part IIa, Electrochemical Methods', ed. A. Weissberger and B. W. Rossiter, Wiley-Interscience, New York, 1971.

[12] R. Guidelli, *Electroanalyt. Chem.*, 1971, **5**, 149.

[13] P. Zuman, *Progr. Phys. Org. Chem.*, 1967, **5**, 81.

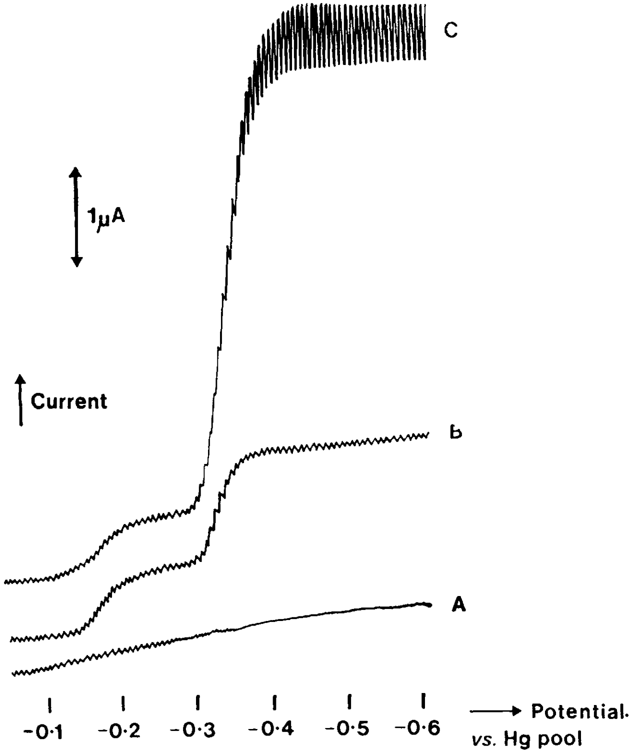

Figure 3 *D.c. polarograms for* (A) 0.1M-H_2SO_4; (B) 0.1M-H_2SO_4 + 10^{-4}M *sodium molybdate*; (C) 0.1M-H_2SO_4 + 10^{-4}M *sodium molybdate* + 0.4M *sodium perchlorate. The limiting current on the plateau of curve* C *would allow the estimation of the rate constant for the* Mo^{III} + ClO_4^- *reaction*

arise when the rate at which the electroactive species is produced at the electrode surface is determined by a chemical reaction, *i.e.*

$$A \overset{k}{\rightleftharpoons} O \xrightarrow{+ne} R \qquad (16)$$

Where the equilibrium in the bulk solution away from the electrode lies to the left, A is not electroactive and the rate of conversion is slow; the limiting current for the electrode reaction will be small compared with the expected diffusion current if A were reduced directly, and the kinetics of the chemical reaction may be determined directly from a measurement of the limiting current. This method has been widely employed, for example to study the dehydration of diols to aldehydes and slow protonation reactions.[7,8,9,13]

When the product of the primary electron-transfer reaction is unstable in the solution environment and the product of the chemical reaction is electroactive, the limiting current will again contain a kinetic component.[7-13] There are two principal types of system where such behaviour occurs

$$\mathrm{O} \xrightarrow{+ne} \mathrm{R} \xrightarrow{k} \mathrm{O'} \xrightarrow{+me} \mathrm{R'} \tag{17}$$

$$\mathrm{O} \xrightarrow{ne} \mathrm{R} \xrightarrow[+\ \text{reactant}]{k} \mathrm{O} + \text{product} \tag{18}$$

In the former case, the polarographic wave will in the limit change from an *n*e wave when the chemical reaction is slow to an (*n* + *m*)e wave when it is fast. In the intermediate situation the wave height will be between these extreme values and will be a function of the rate constant, *k*. An example of this situation is the reduction of aromatic hydrocarbons in the presence of low concentrations of a proton donor[14]

$$\mathrm{Ph} + \mathrm{e} \rightleftharpoons \mathrm{Ph}^{\cdot -} \tag{19}$$

$$\mathrm{Ph}^{\cdot -} + \mathrm{BH} \xrightarrow{k} \mathrm{B}^- + \mathrm{PhH}^{\cdot} \xrightarrow{+\mathrm{e}} \mathrm{PhH}^- \tag{20}$$

In the latter case, the polarographic wave, known as a catalytic wave, can be many times the height of the diffusion controlled current for a simple reduction of O and this catalytic current may be shown to be dependent on the rate constant for the chemical step. The system

$$\mathrm{Mo^{V}} + 2\mathrm{e} \rightarrow \mathrm{Mo^{III}} \tag{21}$$

$$\mathrm{Mo^{III}} + \mathrm{ClO_4^-} \rightarrow \mathrm{Mo^{V}} + \mathrm{Cl^-} \tag{22}$$

is representative of such systems[15] and Figure 3 shows the polarograms for reduction of molybdate in the presence and absence of perchlorate ion. In the sulphate medium, molybdate reduces in the two steps

$$\mathrm{Mo^{VI}} \xrightarrow{+\mathrm{e}} \mathrm{Mo^{V}} \xrightarrow{2\mathrm{e}} \mathrm{Mo^{III}} \tag{23}$$

as can be seen by the waves $E_{\frac{1}{2}} = -0.14$ and -0.32 V, respectively, and the fact that the second is twice the height of the first. Both are diffusion controlled. The simple test for diffusion control is to examine the limiting current as a function of the head of mercury above the capillary, h; i_d is proportional to $\sqrt{h}$. In the presence of perchlorate ion the first wave is unchanged but the second at $E_{\frac{1}{2}} = -0.32$ V is greatly enhanced in height since it is now a catalytic wave.

The shift in half-wave potential with change in the solution environment has been widely employed to study solution equilibria. In particular the variation of $E_{\frac{1}{2}}$ with pH and the concentration of complexing agents has been used to study the protonation equilibria of organic molecules and the complexation of metal ions respectively. In both cases it is possible to ascertain both the stoicheiometry of the equilibrium and the equilibrium constant. Indeed polarographic studies

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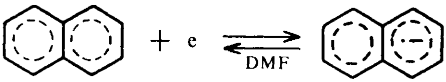
[14] M. Peover, *Electroanalyt. Chem.*, 1967, **2**, 1.
[15] I. M. Kolthoff and W. Hodara, *J. Electroanalyt. Chem.*, 1963, **5**, 2.

have contributed substantially to our knowledge of pK_A values and stability constants.[7–10,13]

Reversible one-electron transfer processes give rise to a wave with a slope $[E_{\frac{3}{4}} - E_{\frac{1}{4}}] = 56$ mV. Hence although further corroborative evidence is essential, the observation of a polarographic wave with such a slope is strong evidence that the electrode process involves the transfer of one electron and produces an intermediate stable on the timescale of the droptime of the electrode. Indeed such polarographic results provided the first electrochemical evidence for stable anion radicals[14] and for transition metal ions in unusual oxidation states,[16] *e.g.*



(24)

$$\mathrm{Sm}^{3} + e \xrightleftharpoons[\mathrm{MeCN}]{} \mathrm{Sm}^{2+} \tag{25}$$

Polarography is an excellent technique for analysis and hence may readily be used to follow slow chemical reactions ($\tau_{\frac{1}{2}}$ > mins) provided one of the reactants or products is electroactive. For example the reaction

$$\mathrm{MeCOCO_2H} + \mathrm{NADH} \xrightarrow[\text{buffer}]{\text{phosphate}} \mathrm{MeCHOHCO_2H} + \mathrm{NAD^+} \tag{26}$$

which is catalysed by the enzyme lactate dehydrogenase, may be followed by monitoring the limiting current for the polarographic reduction of the nicotinamide-adenine dinucleotide (NAD$^+$).[17]

5 Linear Sweep and Cyclic Voltammetry

In linear sweep voltammetry[11,18,19] the potential of a stationary electrode (a hanging or sitting drop mercury or micro solid electrode) is varied rather rapidly (0.1—1000 V s^{-1}) and linearly with time between two fixed potentials E_i and E_f and the resulting current response is recorded. In such experiments the rapid change in potential requires that non-steady state diffusion must be taken into account, and as a result the *i–E* curve for a simple electrode process shows a marked current peak instead of the smooth S-shape for a steady-state technique. In addition the current density for the electrode reaction will be considerably higher and time dependent.

A more widely used but closely related technique is cyclic voltammetry,[11,18–20] where a saw-tooth potential–time profile is applied to the electrode; in other

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[16] I. M. Kolthoff and J. F. Coetzee, *J. Amer. Chem. Soc.*, 1957, **79**, 1852.
[17] D. Pletcher, unpublished work.
[18] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.
[19] R. N. Adams, 'Electrochemistry at Solid Electrodes', Marcel Dekker, New York, 1969.
[20] G. Cauquis and V. D. Parker, in 'Organic Electrochemistry', ed. M. Baizer, Marcel Dekker, New York, 1973.

words, the potential is scanned linearly from E_i to E_f but the direction of the potential scan is then immediately reversed and the potential scanned in the reverse direction from E_f to E_i.

Cyclic voltammetry is an excellent technique for the qualitative study of the stability and homogeneous reactions of species which may be produced in an electrode reaction. For any particular chemical system, the principal experimental variables are the potential range, E_i—E_f, and the potential scan rate, v. This latter variable is effectively used to vary the timescale on which the chemistry of the reactive species is observed. In addition it will be seen that it is important to note differences between the first potential sweep and later scans when the potential–time profile is applied repetitively. Both cyclic voltammetry and linear sweep voltammetry may be used to obtain the quantitative kinetic data once the mechanism of the reaction is understood.

The simplest electrode reaction is one where a single electron is transferred in a fast process to give a product which is stable, *i.e.*

$$\mathrm{O} + \mathrm{e} \rightleftharpoons \mathrm{R} \qquad (27)$$

Such electrode processes give cyclic voltammograms such as that shown in Figure 4,[18] provided the initial solution contains O but not R, and its form may be understood in the following way. The portion UV of the curve corresponds

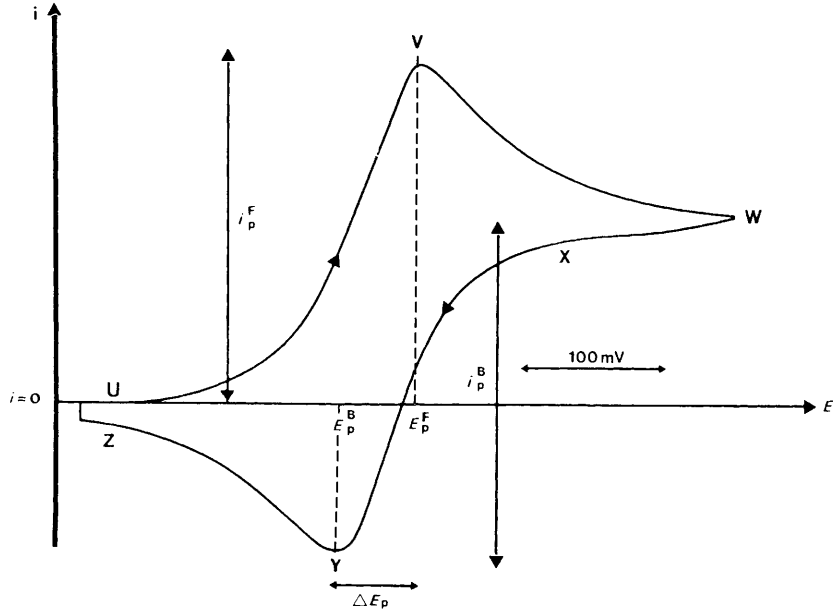

Figure 4 *Cyclic voltammogram for a reversible one-electron transfer reaction* $\mathrm{O} + \mathrm{e} \rightleftharpoons \mathrm{R}$. *Symbols used in the text are defined on this curve.*

to the potential region where the ratio of the surface concentration of R to the surface concentration of O is increasing rapidly [see equation (7)] and hence the current is increasing. At V, the surface concentration of O is tending to zero and the electrode is purely diffusion controlled; the decay in current over the part of the cyclic voltammogram VWX reflects the decrease in the rate of diffusion of O to the surface as its flux falls off with time towards a steady-state value. The portion XY is the potential region where the ratio of R to O at the surface again changes, this time O becoming more favourable. Finally Y is the potential where the flux of R to the surface, and hence the current for the reverse process, are at a maximum and beyond this peak both decrease towards zero, when there is again no electron-transfer reaction taking place.

It has been shown[18] that the cyclic voltammogram will have the following properties at room temperature (see Figure 4 for the definition of the symbols): (i) the separation of the peaks for the forward and reverse processes is given by $\Delta E_{\text{p}} = 60$ mV; (ii) the peak potentials, E_{p}, are independent of the potential scan rate, ν, as are the functions $i_{\text{p}}^{\text{F}}/\nu^{\frac{1}{2}}$ and $i_{\text{p}}^{\text{B}}/\nu^{\frac{1}{2}}$; (iii) the half peak widths for the forward and reverse processes are defined by $[E_p - E_{p/2}] = 57$ mV; (iv) the ratio of the peak currents, $i_{\text{p}}^{\text{B}}/i_{\text{p}}^{\text{F}}$, is unity; (v) the current beyond the peaks decays according to $i \propto t^{-\frac{1}{2}}$; (vi) the peak potentials are related to the polarographic half-wave potential by $E_{\text{p}}^{\text{C}} = E_{\frac{1}{2}} - 28.5$ mV.

Conversely, the observation of a pair of peaks which obey these criteria shows conclusively that the electrode reaction involves the transfer of a single electron and that the product of the electrode reaction is stable. Indeed such cyclic voltammograms form the basis of many electrochemical investigations of the chemistry of anion radicals and cation radicals since they show that under the experimental conditions these species may be prepared and are stable. In addition cyclic voltammetry offers a convenient experimental method for seeking conditions where normally reactive species might be stable, at least on the timescale of the experiment. Cyclic voltammetry may readily be carried out over a wide range of solution conditions and of temperature and such studies have been used to show, for example, the stability of a series of square-planar cobalt complexes,[21] the chromium hexacarbonyl cation,[22] the cation radicals of anthracene,[23] triphenylamine,[24] and hexafluorobenzene,[25] the dications of rubrene[26] and thianthrene,[27] and the dianion of diphenylketone.[28]

$$\text{Co}^{\text{II}}(\text{salen}) + \text{e} \overset{\text{DMF}}{\rightleftharpoons} \text{Co}^{\text{I}}(\text{salen})^{-} \qquad (28)$$

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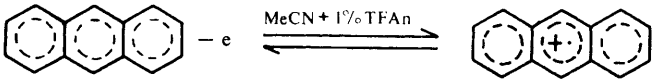
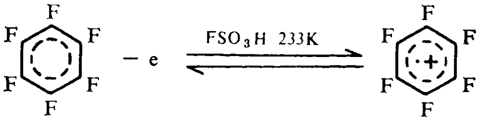
[21] G. Costa, G. Mestroni, A. Puxeddu, and E. Reisenhofer, *J. Chem. Soc.*, 1970, 2870.
[22] C. J. Pickett and D. Pletcher, *J.C.S. Chem. Comm.*, 1974, 660.
[23] O. Hammerich and V. D. Parker, *J.C.S. Chem. Comm.*, 1974, 245.
[24] H. Lloyd Jones, L. G. Boxall, and R. A. Osteryoung, *J. Electroanalyt. Chem.*, 1972, **38**, 476.
[25] J. P. Coleman, M. Fleischmann, and D. Pletcher, *Electrochim. Acta*, 1973, **18**, 331.
[26] L. Byrd, L. L. Miller, and D. Pletcher, *Tetrahedron Letters*, 1972, 2419.
[27] O. Hammerich and V. D. Parker, *Electrochim. Acta*, 1973, **18**, 537.
[28] A. Demortier and A. J. Bard, *J. Amer. Chem. Soc.*, 1973, **95**, 3495.

$$Cr(CO)_6 - e \underset{}{\overset{\text{THF 253K}}{\rightleftharpoons}} [Cr(CO)_6]^+ \qquad (29)$$

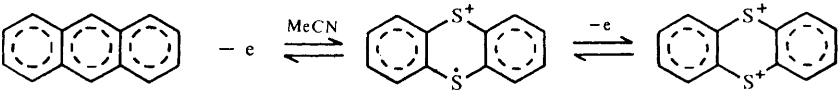


(30)

$$(C_6H_5)_3N - e \overset{\text{NaAlCl}_4\ 423K}{\rightleftharpoons} (C_6H_5)_3N^{\cdot +} \qquad (31)$$



(32)



(33)

$$(C_6H_5)_2C{=}O + e \underset{223K}{\overset{\text{liq NH}_3}{\rightleftharpoons}} (C_6H_5)_2\dot{C}{-}O^- \overset{+e}{\rightleftharpoons} (C_6H_5)_2C^{-}{-}O^- \qquad (34)$$

Typical results for such experiments are those for the oxidation of rubrene in methylene chloride at 203 K shown in Figure 5; the cyclic voltammogram shows two reversible one-electron transfers and hence both the cation radical and the dication are stable under these conditions.

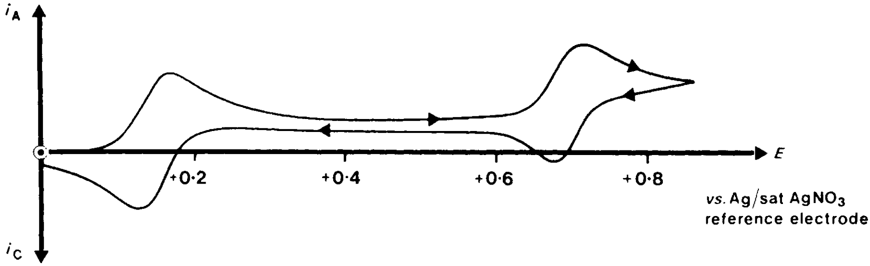


Figure 5 *Cyclic voltammogram for rubrene at a* Pt *wire electrode in methylene chloride–* 0.2M *tetrabutylammonium tetrafluoroborate at* 203 K. *The potential scan rate is* 0.01 V s^{-1}

If the product of the one-electron transfer reaction is not stable on the timescale of the cyclic voltammetric experiment there will be less of the product of the electron-transfer reaction remaining in the vicinity of the electrode surface (*i.e.* its concentration profile is affected) and hence the reverse peak on the cyclic voltammogram will be smaller; i_p^B/i_p^F will be less than unity. As has already been stated above, however, the timescale of the experiment may be changed by varying the potential scan rate. If the potential scan rate is increased, the timescale of the experiment is reduced and the chemical reaction will not occur to the same extent, *i.e.* the ratio i_p^B/i_p^F will then be higher. In the limit at very fast scan rates the system will appear reversible and obey all the properties (i) to (vi) listed above. Conversely by slowing down the potential scan rate, the timescale for observation of the chemical reaction is lengthened and the ratio i_p^B/i_p^F will be less. At this limit all the intermediates will undergo the chemical reaction and no reverse peak will be observed. In practice, if the intermediate produced in the electrode reaction is either highly reactive or very stable only one of the limiting situations may be observable.

Thus in the simplest terms, a cyclic voltammetric experiment may be thought of as two parts. During the part of the sweep UVWX of Figure 4 a reactant for the chemical reaction is generated at the electrode surface. The later part of the sweep analyses the amount of this reactant unchanged during the potential scan.

The ratio i_p^B/i_p^F varies with change in the potential scan rate when the product of the electron-transfer process is unstable; this variation is accompanied by other changes in the cyclic voltammogram. Thus the peak potentials become dependent on the potential scan rate and because in many cases the product of the chemical reaction is itself electroactive, new peaks may appear. The peak for the oxidation or reduction of this product may appear before or beyond the peak for the primary electron-transfer process depending on whether or not it is easier to oxidize or reduce than the initial electroactive species. In the former case, the product of the chemical reaction will be electroactive at the potential of the primary electron transfer process and the function $i_p^F/\nu^{\frac{1}{2}}$ is then dependent on the potential scan rate.[29,30]

The qualitative observation of these changes only tell us that the product of the primary electron-transfer process is unstable, and in order to build up a picture of the detailed mechanism and kinetics of the chemical reaction it is necessary to make quantitative studies of the variation of i_p^F, i_p^B/i_p^F, and E_p^F as a function of potential scan rate. For example it has been shown that the quantity $dE_p^F/d \log \nu$ is 29.1 mV if the chemical reaction is first order with respect to the species produced in the electrode reaction and 19 mV if this reaction is second order;[31] the variation in the concentration of the reactants will also help to establish reaction orders. Furthermore, where the product of the chemical reaction is electroactive the investigation of the mechanisms may be helped by the process of 'peak matching' *i.e.* the cyclic voltammogram of likely intermediates may be run and the peak potentials compared.

Once the qualitative mechanism is known the rate constants can also be found from the variation in either E_p^F or i_p^B/i_p^F with log ν[18,32] and from the use of analytical expressions or working curves derived theoretically. Fortunately, for most mechanisms these are available in the literature.[11,18]

The use of cyclic voltammetry to study homogeneous chemical reactions is best illustrated by some examples.

[29] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1965, **37**, 178, 190.

[30] M. Mastragostini and J. M. Saveant, *Electrochim. Acta*, 1968, **13**, 751.

[31] J. M. Saveant and E. Vianello, *Compt. rend.*, 1963, **256**, 2597.

[32] M. Mastragostini, L. Nadjo, and J. M. Saveant, *Electrochim. Acta*, 1968, **13**, 721.

The Co^{I}(salen)$^-$ + EtBr Reaction.—Figure 6 shows cyclic voltammograms for the Co^{II}(salen) complex [salen is the quadridentate ligand *NN*-ethylenebis(salicylideneimine)] in DMF in the presence and absence of ethyl bromide.[17,33] Curve (a), run between −0.5 and −2.0 V in the absence of the halide, shows a single electron-transfer reaction at $E_p^F = -1.16$ V which has all the characteristics of a reversible 1e process

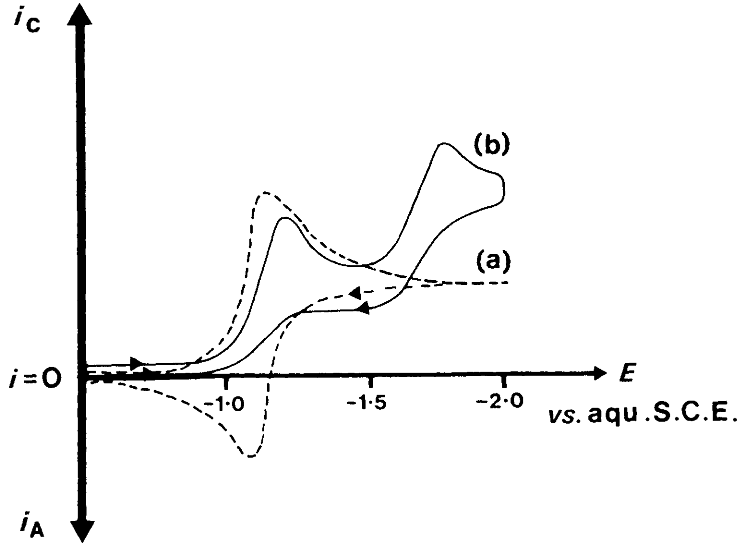


Figure 6 *Cyclic voltammograms run at a vitreous carbon electrode in* DMF–0.1M *sodium tetrafluoroborate. Potential scan rate* 0.1 V s^{-1} (a) - - - - 5 × 10^{-3}M Co^{II}(salen); (b) ——— 5 × 10^{-3}M Co^{II}(salen) + 0.1M EtBr

$$\mathrm{Co^{II}(salen) + e \rightleftharpoons Co^{I}(salen)^-} \qquad (35)$$

In the presence of ethyl bromide the ratio i_p^B/i_p^F becomes dependent on ν, showing that the anion reacts with the alkyl halide. Under the conditions where $i_p^B/i_p^F < 1$, a new reduction peak appears at $E_p^F = -1.76$ V. In the limiting situation at slow scan rates shown in curve (b), the peak for the reoxidation of Co^{I}(salen)$^-$ is not observed and the two reduction peaks are the same height showing that the process at −1.76 V is also a 1e process. It is, however, irreversible even at very fast scan rates. It was postulated that the chemistry of the cobalt anion is

$$\mathrm{Co^{I}(salen)^- + EtBr \rightarrow Et\text{–}Co^{III}(salen) + Br^-} \qquad (36)$$

and that the peak at −1.76 V was due to

$$\mathrm{Et\text{–}Co^{III}(salen) + e \rightarrow Et\text{–}Co^{II}(salen)^-} \qquad (37)$$

where the Co^{II} organometallic is highly unstable. A cyclic voltammogram on

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[33] G. Costa, A. Puxeddu, and E. Reisenhofer, *J.C.S. Dalton*, 1973, 2034.

Et–Co^{III}(salen) under the same conditions confirmed this proposal since it gave an irreversible 1e reduction at $E_p^F = -1.76$ V. Costa *et al.*[33] have found a rate constant for reaction (36) from the dependence of i_p^B/i_p^F on v: it is 7.6 × 10^2 l mol^{-1} s^{-1}.

The Isomerization of the Anion Radical of Diethyl Maleate.—Curve (a) of Figure 7 shows a cyclic voltammogram for the *trans*-isomer, diethyl fumarate (DEF) in DMF. At fairly rapid potential scan rates the *i*–*E* response has the properties of a reversible 1e system

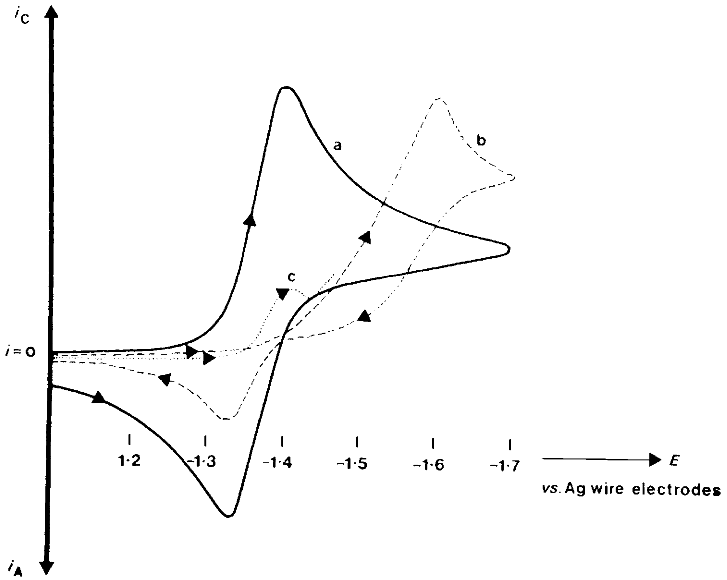

Figure 7 *Cyclic voltammograms run at a hanging mercury drop electrode in* DMF–0.1M *tetrabutylammonium tetrafluoroborate. Potential scan rate* 1.0 V s^{-1}. (a) ——— 4 × 10^{-3}M *diethyl fumarate*; (b) – – – – 4 × 10^{-3}M *diethyl maleate, first sweep*; (c) *as* (b) *but second cycle.*

$$\mathrm{DEF} + \mathrm{e} \rightleftharpoons \mathrm{DEF}^{\cdot -} \qquad (38)$$

although at slow potential scan rates the ratio i_p^B/i_p^F becomes less than unity due to a reaction which has been shown[34,35] to be dimerization with a rate constant 34 mol l^{-1} s^{-1}.

The cyclic voltammetry of the *cis*-isomer, diethyl maleate (DEM), is more complex. The reduction is generally irreversible and only at very fast scan rates is there any sign of reversibility. However, at intermediate sweep rates curve (b),

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[34] A. J. Bard, V. J. Puglisi, J. V. Kenkal, and A. Lomax, *Discuss. Faraday Soc.*, 1973, **56**, 353.
[35] V. J. Puglisi and A. J. Bard, *J. Electrochem. Soc.*, 1972, **119**, 829, 833; 1973, **120**, 748

the reverse sweep, shows a reoxidation peak which corresponds in potential to the oxidation of $DEF^{\cdot -}$. The second sweep also shows a new reduction peak which corresponds to the potential for reaction (38). Thus the cyclic voltammetry indicates the scheme

$$DEM + e \rightleftharpoons DEM^{\cdot -} \qquad (39)$$

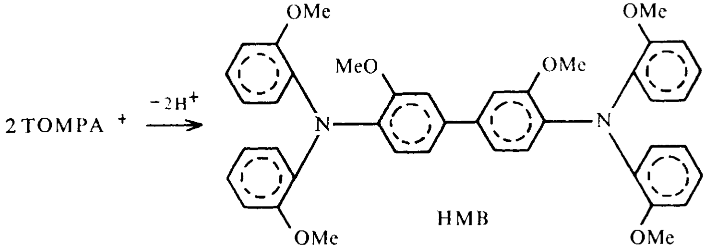
$$DEM^{\cdot -} \rightarrow DEF^{\cdot -} \qquad (40)$$

The rate constant for reaction (40) was found to be *ca.* 10 s^{-1} from a study of the magnitude of the peaks for system (38) as a function of ν. Other experiments (see below) show that $DEM^{\cdot -}$ can also dimerize and that it does so more rapidly than $DEF^{\cdot -}$.

The Oxidation of Tertiary Aromatic Amines.—Adams and co-workers[36,37] have used cyclic voltammetry to study the oxidation of a wide range of tertiary aromatic amines, paying particular attention to the stability and reactions of the cation radicals. A typical example is tri-*o*-methoxyphenylamine (TOMPA) in acetonitrile. At fast potential scan rates the cyclic voltammogram is simple, showing a single couple with the properties of a reversible 1e process.

$$\text{TOMPA} \overset{-e}{\rightleftharpoons} \text{TOMPA}^{\cdot +} \qquad (41)$$

At slower potential scan rates the curves are more complex (see Figure 8). Firstly the reverse peak for reaction (41) diminishes and simultaneously it may be noted that $i_p^F/\nu^{\frac{1}{2}}$ is no longer independent of ν and, indeed, increases as the scan rate is slowed down. At the same time two new reduction peaks appear at less positive potentials and the second cycle becomes different from the first. These observations indicate that the cation radical undergoes a chemical reaction and that the



(42)

$$\text{HMB} \overset{-e}{\rightleftharpoons} \text{HMB}^{+} \overset{-e}{\rightleftharpoons} \text{HMB}^{2+} \qquad (43)$$

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[36] E. T. Seo, R. J. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *J. Amer. Chem. Soc.*, 1966, **88**, 3498.

[37] R. F. Nelson and R. N. Adams, *J. Amer. Chem. Soc.*, 1968, **90**, 3925.

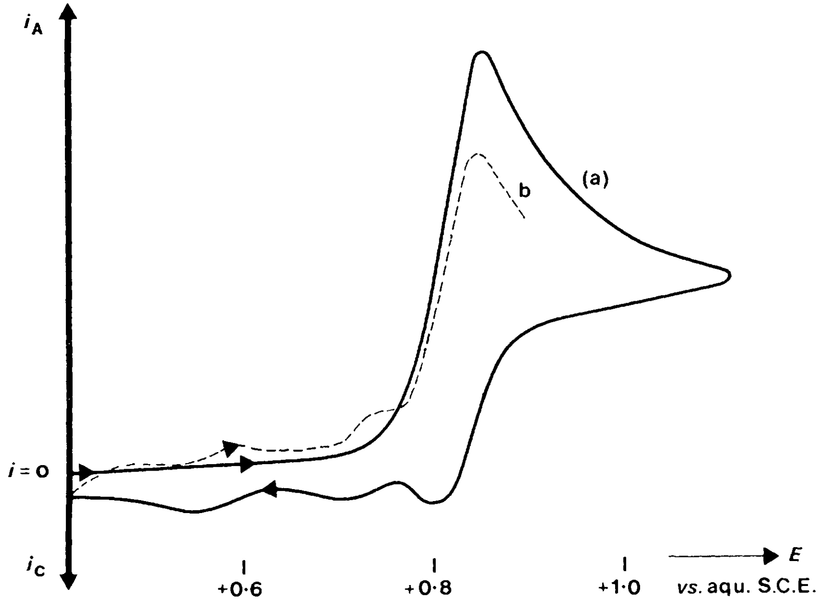

Figure 8 *Cyclic voltammogram at a* Pt *electrode in acetonitrile*–0.1 M *tetraethylammonium perchlorate. Potential scan rate* 0.05 V s^{-1} (a) 10^{-3}M *tri-*o*-methoxyphenylamine, first cycle*; (b) *as* (a) *but second cycle*

product is oxidized at a lower potential than the parent amine. The reaction scheme (43) was postulated, and it was found that the cyclic voltammogram for HMB had two reversible systems whose potentials coincided with the peaks of curve (a). The dependence of $i_p^F/v^{\frac{1}{2}}$ on v arises because when the potential scan through the peak is fast compared with the half life of $TOMPA^{\cdot+}$, the overall process involves the transfer of only one electron. At the other limit when the scan is slow compared with this half life, three electrons are transferred. Under these latter conditions such processes are widely known as ecee processes (e denotes electron transfer, c chemical reaction). For an ece process, i_p^B/i_p^F changes very rapidly with v in the situation between the limiting 1e and 3e cases. The rate constant for the dimerization of $TOMPA^{\cdot+}$ may be obtained from such a study and suitable working curves: it is 6 l mol^{-1} s^{-1}.

In all the three examples discussed above, interpretation is assisted by the observation of a reversible 1e process under certain conditions. Systems involving only slow electron transfers (for such couple $\Delta E_p > 60/n$ mV and both ΔE_p and E_p^F are dependent on v), multiple electron transfers (for a reversible ne process $\Delta E_p = 59/n$ mV), and totally irreversible electrode reactions can also be investigated, but the interpretation must be viewed more cautiously and supplementary evidence will be essential. Cyclic voltammetry has also been widely used for the study of more complex systems, *e.g.* the chemistry of vitamin B_{12},[38] catecholamines,[39] and dopaquinone.[40]

Thus cyclic voltammetry is probably the best electrochemical technique for the qualitative investigation of the chemical reactions of species which may be formed by electron transfer and whose half-life lies in the range 1 ms to 100 s.

6 Potential Step Techniques

In such experiments the potential of a stationary micro-electrode is changed instantaneously and the resulting *i–t* transient as the system relaxes to the steady state is monitored. In chronoamperometry[10,11] the *i–t* transient is recorded directly and analysed in that form; it is, however, sometimes advantageous to integrate the current with respect to time (electronically) and to present the transient as a plot of charge (q) *vs.* time. The technique is then known as chronocoulometry.[11]

Potential step techniques are very poor for investigating the mechanism of homogeneous chemical reactions coupled to the electrode reaction; all mechanisms give transients which look qualitatively similar and such an approach would require theoretical analysis to obtain the expected *i–t* response for all possible mechanisms, followed by curve fitting. On the other hand, if the mechanism is known, they offer a simple method for obtaining quantitative rate data. The method has the advantages over cyclic voltammetry in such studies that it is conceptually and commonly experimentally simpler. Certainly the mathematical analysis is easier since the differential equations describing the experiment have time-independent boundary conditions and the electrode potentials may be selected so that the electrode surface conditions are simple.

The *i–t* transients may be monitored over a period of a few seconds or on a much shorter timescale of a few μs. Since the portion of the *i–t* transient analysed corresponds to the timescale on which the chemical reaction is observed, it is generally the case that the study of fast reactions requires measurements at short times and some sophisticated innovations have been introduced to overcome the non-Faradaic current observed at times < 0.5 ms.[41] Furthermore it should be noted that at $t = 0$, the rate of diffusion of a species to the electrode is infinite (see Figure 2) and the technique for obtaining the rate constant for very fast reactions usually involves extrapolation of the *i–t* data to $t = 0$.

Single potential step experiments may be used to obtain kinetic constants for systems where the chemical reaction precedes the electron-transfer process [*e.g.* equation (16)] and systems where the product of the primary electron-transfer process is unstable and leads to a species which is further oxidized or reduced at the same potential [*e.g.* equations (17) and (18)]. Generally the potential will be stepped from a value where the electrode reaction does not occur at a measurable rate to a value where all the electroactive species reaching the surface under-

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[38] R. L. Birke, G. A. Bryden, and M. F. Boyle, *J. Electroanalyt. Chem.*, 1974, **52**, 233.

[39] M. D. Hawley, S. V. Tatawawadi, S. Piekarski, and R. N. Adams, *J. Amer. Chem. Soc.*, 1967, **89**, 447.

[40] T. E. Young, J. R. Griswold, and M. H. Hulbert, *J. Org. Chem.*, 1974, **39**, 1981.

[41] H. W. Nürnberg, in 'Polarography, 1964', ed. G. J. Hills, MacMillan, London, 1966.

goes electron transfer. Thus, for example, chronoamperometry was the method used to obtain the numerical values for the rate constants for the dimerization of the tertiary amine cation radicals [equation (42)];[37] other systems which have been studied include the protonation of carboxylate anions,[42] complex formation by metal ions,[43] catalytic systems,[44] and the dehydration of *p*-hydroxyphenylhydroxylamine.[45]

When the species to be studied is formed by the electrode reaction and the product of the chemical reaction is not electroactive, the kinetics of the chemical

$$\mathrm{O} + n\mathrm{e} \rightleftharpoons \mathrm{R} \qquad (44)$$

$$\mathrm{R} \xrightarrow{k} \mathrm{P} \qquad (45)$$

reaction must be obtained by a double potential step experiment. The electrode potential is first stepped from where no electrode reaction occurs to a value where O → R occurs at a diffusion-controlled rate. After a time interval, τ s, the electrode potential is again stepped, this time to a value where the reverse process R → O is diffusion controlled (note that the electrode reaction need not be electrochemically reversible). The first pulse may be thought of as a period of generation of the reactant, during which a defined concentration profile for R (sensitive to k) will be set up, and the second pulse as an analysis of this profile. Figure 9 shows a typical i–t response for a double potential step experiment. Clearly the current at any particular time t during the second pulse is a reflection of the amount of R remaining in solution and hence the rate constant, k and its value, should be obtainable from a dimensionless plot of say, $i_{t+\tau}/i_t$ *vs.* log $t/\tau_{\frac{1}{2}}$.

The double potential step method has been used to study, for example, the benzidine rearrangement,[46] the hydrolysis of 1,4-benzoquinone 4-imine,[47] the disproportionation of the technetate ion,[48] and the hydration of ascorbic acid.[49]

7 The Rotating-disc Electrode

A rotating-disc electrode[10,11,50,51] consists of a smooth disc of the electrode material surrounded by a cylindrical sheath of an insulator; the face of the sheath should be flush with the surface of the disc and the radius of the sheath should be large compared with that of the disc. The complete structure is rotated about an axis perpendicular to the surface of the disc.

In experiments with such rotating electrodes, the principal mode of mass transport of species to and from the electrode surface is convection rather than diffusion as is the case with experiments at stationary electrodes in unstirred

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[42] P. Delahay and S. Oka, *J. Amer. Chem. Soc.*, 1960, **82**, 329.
[43] H. Gerischer, *Z. Elektrochem.*, 1960, **64**, 29.
[44] P. Delahay and G. L. Stiehl, *J. Amer. Chem. Soc.*, 1952, **74**, 3500.
[45] G. S. Alberts and I. Shain, *Analyt. Chem.*, 1963, **35**, 1859.
[46] W. M. Schwarz and I. Shain, *J. Phys. Chem.*, 1965, **69**, 30.
[47] A. J. Bard and S. V. Tatawawadi, *J. Phys. Chem.*, 1964, **68**, 2676.
[48] G. Kissel and S. Feldberg, *J. Phys. Chem.*, 1969, **73**, 3082.
[49] S. P. Perone and W. J. Kretlow, *Analyt. Chem.*, 1966, **38**, 1760.
[50] A. C. Riddiford, *Adv. Electrochem. and Electrochem. Eng.*, 1966, **4**, 47.
[51] V. G. Levich, 'Physiochemical Hydrodynamics', Prentice Hall, New Jersey, 1962.

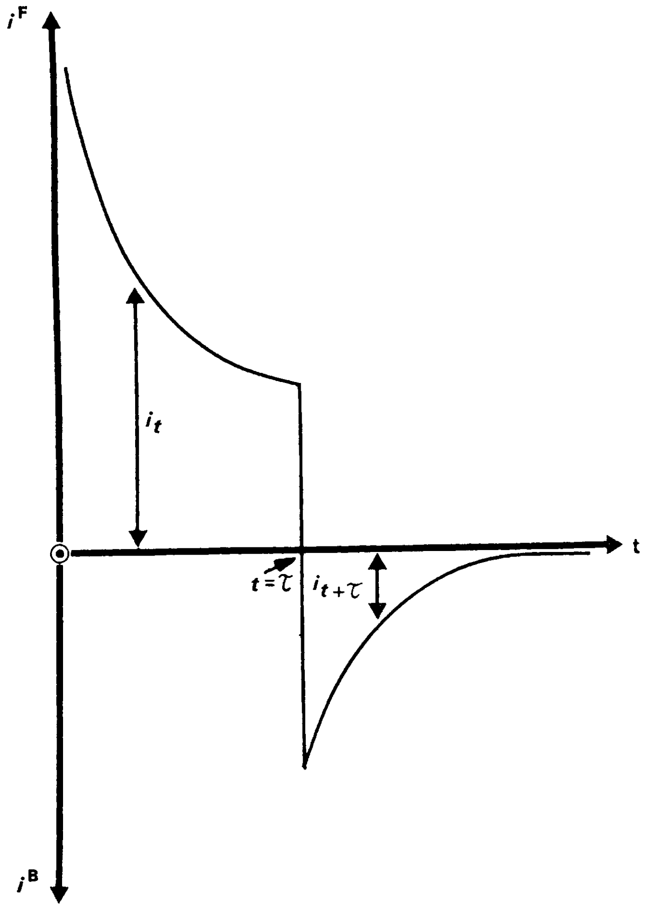

Figure 9 *Generalized i–t response to a double potential step experiment. The detailed form of the i–t response will depend on both the mechanism and kinetics of the homogeneous chemical reactions for the species produced during the* A *pulse.*

solution. The rate of convection is dependent on the rotation rate of the disc, ω, and hence the rate of rotation can be employed to control the supply of the electroactive species to the surface and the removal of the product and, in consequence, the residence time of species at the electrode surface. In general the complete steady-state i–E curve is obtained as a function of ω, although in some experiments it is only necessary to investigate the steady-state current as a function of ω at one particular potential.

The i–E curve at one rotation rate is very much the equivalent of a polarogram at one droptime and the $E_{\frac{1}{2}}$, $E_{\frac{3}{4}} - E_{\frac{1}{4}}$, and i_L values may be used in the study of homogeneous chemical reactions in an analogous way. In most instances, however, use is also made of ω as a variable.

In the case of chemical reactions which precede the electron-transfer process [*e.g.* equation (16)], the i–ω dependence is investigated at a potential on the limiting current plateau for the electrode process. If the chemical reaction is very slow, the current will be independent of ω while, conversely, if it is fast the current will be determined only by the rate of convection and it will be found that $i \propto \omega^{\frac{1}{2}}$. In the intermediate case, the current is determined partly by convection and partly by the kinetics of the chemical step (i *vs.* $\omega^{\frac{1}{2}}$ will be non-linear) and the pure kinetic information is obtained by extrapolating the i–ω data to conditions where the rate of convection is infinite, *i.e.* $\omega \rightarrow \infty$. This extrapolation may be carried out employing a plot of $1/i$ *vs.* $1/\omega^{\frac{1}{2}}$ when theory shows that the intercept on the $1/i$ axis is simply related to the rate constant for the chemical process. Systems studied in this way include the dehydration of $PhCH(OH)_2$[52] and the dissociation of weak acids[53,54] using rotating lead electrodes.

The rotating-disc electrode has also been used in the study of ece systems [*e.g.* equations (16) and (17)]. In such studies the i–ω data are usually presented as a plot of $i/\omega^{\frac{1}{2}}$ *vs.* ω. At slow rotation rates the residence time of any intermediate produced at the electrode is relatively long and it has the maximum opportunity to react chemically to form the species which can be oxidized or reduced further. Conversely, at fast rotation rates the intermediate has a greater opportunity to escape the electrode system before the chemical reaction can occur. Thus, $i/\omega^{\frac{1}{2}}$, which is a direct reflection of the number of electrons transferred, will decrease with increasing rotation rate. Ideally the $i/\omega^{\frac{1}{2}}$ *vs.* ω plot will be S-shaped with limiting situations at low and high ω, and the rate constant for the chemical reaction may be obtained from the transition region at intermediate ω. Examples of reactions studied in this way include the reaction of the diphenylanthracene cation radical with a set of pyridines[55] and the dehydration of *p*-hydroxyphenylhydroxylamine.[56]

8 The Rotating Ring–Disc Electrode

In order to investigate the chemistry of species which are produced in an electrode process, we have already seen that it is generally necessary to make effectively two separate measurements, *e.g.* double potential step, cyclic voltammetry. In experiments with the rotating ring–disc electrode[57] the measurements are made at different electrodes. The electrode structure consists of a central disc electrode surrounded by a concentric insulating annulus, a concentric ring electrode and finally an insulating sheath. The ring and disc electrodes may be controlled

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[52] R. G. Barradas, O. Kutowy, and D. W. Shoesmith, *Canad. J. Chem.*, 1974, **52**, 1635.
[53] D. Jahn and W. Vielstich, *Z. Elektrochem.*, 1960, **64**, 43.
[54] W. J. Albery and R. P. Bell, *Proc. Chem. Soc.*, 1963, 169.
[55] G. Manning, V. D. Parker, and R. N. Adams, *J. Amer. Chem. Soc.*, 1969, **91**, 4584.
[56] P. A. Malachesky, L. S. Marcoux, and R. N. Adams, *J. Phys. Chem.*, 1966, **70**, 4068.
[57] W. J. Albery and M. L. Hitchmann, 'Ring Disc Electrodes', Clarendon Press, London, 1971.

separately and, generally, a reactant is generated at the disc and the amount of it arriving at the ring is monitored. It may be noted that the time interval for transport of the species from the disc to the ring is a function of ω and the width of the insulating annulus.

Commonly there are three simple controlled potential experiments which are carried out with a rotating ring–disc electrode as a function of rotation rate.

(i) The potential of the disc is held constant at a potential where a reactive species is formed and a voltammogram is run at the ring, *i.e.* an i–E curve is obtained for the reactive species as a function of the rotation rate.

(ii) The potential of the disc is varied linearly and the i_{disc}–E curve is recorded, while the potential of the ring is held constant at a value where a particular species is electroactive. By this experiment it is possible to delineate the potential regions where the species is produced at the disc.

(iii) The potentials of both the disc and ring are held constant and the current at both is recorded as a function of the rotation rate.

The first two types of experiment are useful in the qualitative investigation of reaction mechanisms and jointly allow a similar range of information to cyclic voltammetry. Indeed additional information is sometimes available.

The latter experiment is that normally used to obtain the quantitative kinetic data. Even if the species formed at the disc is completely stable, not all of it will arrive at the ring and hence it is necessary to define the collection efficiency, the fraction of the species formed at the disc which reaches the ring; the collection efficiency, N_0, is given by the ratio $i_{\text{ring}}/i_{\text{disc}}$. Clearly, if the species formed at the disc undergoes a chemical reaction the collection efficiency will be less. In both cases it depends both on the gap between the disc and ring electrodes and the rotation rate of the electrode assembly. It is possible to construct ring–disc electrodes suitable for the study of species with a half life in the range 1 ms to 10 s.

The rotating ring–disc electrode has been used in the study of the anion radicals of dimethyl fumarate (DEF) and dimethyl maleate (DEM).[34] Experiments of types (i) and (ii) above were used to confirm the conclusions drawn from the cyclic voltammetry of the two compounds (see earlier section). Further, an experiment of type (iii) could be used to obtain the information that $\text{DEM}^{\cdot-}$ had a second fast reaction in addition to isomerization to $\text{DEF}^{\cdot-}$. In solutions of DEM or DEF, the potential of the disc was held at a value where the anion radicals were produced at a diffusion controlled rate and the potential of the ring was such that both $\text{DEF}^{\cdot-}$ and $\text{DEM}^{\cdot-}$ would be reoxidized. For the solution of DEF the collection efficiency was 0.55, essentially the value for a completely stable intermediate, while for the solution of DEM it was only 0.25—0.35. Hence in the latter solution, the $\text{DEM}^{\cdot-}$ disappeared by a reaction whose product was other than $\text{DEF}^{\cdot-}$. This reaction is probably a coupling and it appears that the equivalent reaction of $\text{DEF}^{\cdot-}$ is much slower.

Other reactions which have been studied by this technique include those of bromine with arsenic(III),[58] allyl alcohol,[59] and anisole,[60] the reactions of the anion radicals of activated olefins,[35,61] and the chemistry of intermediates produced during reduction of *p*-nitroaniline[62] and nitrobenzene[63] and oxidation of aniline.[64]

9 Controlled Potential Coulometry

For controlled potential coulometry[11,65] a macro working electrode, or rather a cell with a large electrode area to solution volume ratio is employed and the working electrode is placed in a separate compartment to prevent interference from the reactions occurring at the other electrodes. A controlled potential is applied to the working electrode and the i–t response recorded until the current drops to zero, *i.e.* all the electroactive species are removed from the bulk solution.

Controlled potential coulometry is principally used to confirm the overall number of electrons transferred in the electrode reaction; the i–t data may be integrated to give the total charge, q, associated with the electrode process and this is related to the n value by Faraday's Law. Such electrolysis is also used to confirm that the final products of the electrode process, as determined by the normal analytical procedures of organic and inorganic chemistry, are consistent with the mechanistic information found with the other techniques. It should, however, be remembered that the timescale of a controlled potential electrolysis, generally 10—300 min, is much longer than all the experiments discussed above and it is therefore possible for systems with slow homogeneous chemical reactions to give apparently conflicting results. In addition, account must be taken of the increased concentrations of reactants typically used in experiments designed to study products.

Controlled potential electrolysis offers a technique for the study of slow chemical reactions.[65] The i–t data are replotted in the form of log i–t or i–q graphs; such plots are linear for uncomplicated electrode reactions whereas for systems where the product of the electron-transfer step can undergo a slow chemical reaction the plots are more complex. It is common for the concentration of such intermediates to be followed spectroscopically by carrying out the electrolysis in a u.v. or i.r. spectrometer or by sampling the solution and determining the concentration by analysis.

10 Concluding Remarks

The aim in this review has been to outline the principles of the most important electrochemical techniques employed for the study of homogeneous chemical reactions. Because of the restriction on space the theoretical equations for each

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of the methods, necessary for quantitative work, have not been presented and the interested reader is referred to the original papers; it must be remembered that the equations will also depend on the detailed mechanism of the homogeneous chemical reaction. Likewise, details of the instrumentation and glassware and the experimental difficulties and pitfalls are best sought in these references.

The reader will note that the review concentrates on controlled potential techniques. The controlled current techniques, chronopotentiometry,[11,66,67] reverse current chronopotentiometry,[68] and controlled current coulometry,[69] will often yield the same results as the methods discussed but they never have a marked advantage. Of the other techniques which might have been discussed, thin layer cells,[70-72] a.c. polarography,[73,74] and spectroelectrochemical techniques,[75-77] including *in situ* e.s.r.,[78,79] are perhaps the most important. In the spectroelectrochemical methods the intermediate to be studied is formed electrochemically and monitored simultaneously by an electrochemical and a spectroscopic technique. They are particularly useful since the optical readout is sensitive to the whole of the concentration profile and its variation with time, whereas the current is a reflection only of the gradient of the profile at the surface.

Finally I would plead with prospective workers in the field that they attempt to use a number of electrochemical methods and where possible, other techniques, on each system. The techniques are complementary and the mechanistic and kinetic conclusions should be uniform!

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