CHAPTER 5

Chemical Kinetics, Charge Transfer and Diffusion

5.1 INTRODUCTION

Electrochemistry would have been a monotonous dry subject if it was concerned only with interfacial electron transfer and nothing else. The attractive aspects of electrochemistry are the variety of processes that take place before, during and after the interfacial charge transfer. In this chapter, the chemical reactions that are associated with charge transfer are analysed. The electroactive species itself may be produced by a chemical reaction before charge transfer. Very reactive chemical species such as the radicals, radical ions and very active reducing and oxidizing agents are formed during electron transfer. These entities then react chemically in a variety of ways. Understanding such chemical changes is certainly one of the challenging and rewarding tasks in electrochemistry.

We have already considered the simple charge transfer processes in the last two chapters. Whether the charge transfer rate constant is fast (Chapter 3) or slow (Chapter 4), one can increase the charge transfer rate by increasing the overpotential in the necessary direction; but at the peak current region in LSV or CV, the charge transfer rate is primarily controlled by the mass transport or more specifically diffusion. If any chemical reaction associated with charge transfer is fast it will only influence the peak potential and not the peak current. The peak current values are again controlled by the same mass transfer equations of reversible or irreversible charge transfer. It is for this reason that such equilibrium chemical reactions are considered along with charge transfer in the last two chapters.

In direct contrast to the above case, there may be a process the rate of which is not at all controlled by mass transfer but a slow chemical reaction associated with the charge transfer reaction. Such 'kinetic currents' in polarography were first noticed at least four decades ago [1, 2]. A number of such reactions was studied subsequently. Extensive polarographic literature on such reactions is also available [3, 4]. In these early days, relaxation techniques for the measurement of the kinetics of fast chemical reactions were not available. Hence polarography was in fact considered as a unique technique in this regard which could measure the rate constants of fairly fast reactions that were not measurable by the then existing steady state techniques.

During the sixties and the seventies, a number of relaxation techniques was developed for the study of chemical kinetics [5, 6]. These techniques can now practically measure the rate constants of the fastest known chemical reactions. Some of these techniques such as fluorescence spectroscopy and ESR spectroscopy are also used to evaluate the chemical kinetic parameters of electrochemically generated reactive species [7, 8]. However, a number of electro analytical transient techniques have been evolved, which can be used to generate and simultaneously characterize such reactive intermediates—LSV and CV techniques are certainly quite prominent among them.

At the modelling level, any chemical reaction may be described by just two parameters—the rate constant k and equilibrium constant K. However, any overall electrochemical process may consist of a number of chemical (C) and electrochemical (E) steps. The number of such possible combinations, competition among different reaction schemes and acid-based equilibria associated with them [9] really make numerous reaction schemes possible. Digital simulation techniques [10–12] enable the solution of a number of such reaction schemes, rather an easy task at least to specialists. It is literally impossible in the present context to elaborately discuss all such simulation works or possible reaction schemes. Hence discussions in this chapter will necessarily be brief and selective, and primarily concentrate on the model parameters and their methods of evaluating them for a few important chemical reactions. A number of experimental studies are also cited. Quite detailed discussions may be found in some recent publications [13–15]. An interesting brief review of theoretical as well as experimental studies of chemical reactions by electrochemical techniques [16] is also available.

5.2 THE MODEL

5.2.1 CHARGE TRANSFER

It is worthwhile repeating here that by using electrochemical methods one cannot study any chemical reaction that is not associated with a charge transfer process. Hence all chemical reactions should be linked with the central act in electrochemistry, the charge transfer step.

Consider the following general expression for the charge transfer reaction:

$$Ox + ne \rightleftharpoons R \qquad 5.1$$

There is a great deal of electrochemical processes in organic chemistry and even in inorganic coordination complex chemistry where the charge transfer step is reversible. For such cases as in Chapter 3, the Nernst equation for the boundary condition is used.

$$E = E^f + \frac{\mathbf{R}T}{nF} \ln \frac{C_{Ox}(o, t)}{C_R(o, t)} \qquad 5.2$$

A great number of reaction schemes involving chemical kinetics have been worked out for a reversible charge transfer. The experimental data of a number of processes also substantiate this viewpoint as seen later in section 5.4.

However, it is also possible to consider chemical kinetics associated with quasi-reversible and irreversible charge transfer. As discussed in Chapter 4.1 the boundary condition for a quasi-reversible process then becomes

$$\frac{i}{nFA} = k_h^o [C_{Ox}(o, t) \exp\{-\alpha n_a f(E - E^f)\} - C_R(o, t) \exp\{(1-\alpha) n_a f(E - E^f)\}] \qquad 5.3$$

In fact, the charge transfer process can be considered with a wide range of k_h^o values. If k_h^o values are very high one can obtain Nernstian boundary condition from equation 5.3. If k_h^o is very small the boundary condition is reached for irreversible charge transfer. In LSV and CV experiments, it is convenient to employ a dimensionless parameter Λ related to k_h^o [17].

$$\Lambda = \frac{k_h^o}{(nf\nu D_{ox})^{1/2}} \qquad 5.4$$

Although k_h^o value for any electrochemical reaction is a fixed quantity, it can be varied by varying the sweep rate. This Λ and αn_a are the two parameters that completely define the charge transfer properties of the electrochemical reaction.

The objective of this brief discussion of charge transfer here is only to present the relevant expressions that will be used in this chapter in a continuous fashion. These aspects have been discussed in greater detail in Sections 3.2 and 4.2.

5.2.2 THE MASS TRANSPORT

The mass transport associated with charge transfer has also been discussed. The mass transport at stationary conditions and in the presence of excess supporting electrolyte is given by Fick's second law of diffusion. For O_X it may be written as

$$\frac{\partial C_{ox}(x,\,t)}{\partial t} = D_{ox}\,\frac{\partial^2 C_{ox}(x,\,t)}{\partial x^2} \qquad 5.5$$

Similar diffusion expressions for R and for any other chemical species in solution can also be written (which will be denoted Z, A, B, C etc.). However, it must be remembered that the diffusion coefficient D (which is the paramenter that completely describes the mass transfer behaviour) may be different for different chemical species. Since Ox and R in equation 5.1 differ only by one electron, it may be assumed that they possess similar diffusion coefficients. This type of assumption is also usually made in processes involving chemical kinetics. Usually it is assumed that $D_{ox}=D_R=D_Z = D_A$...More often than not, this assumption may not be correct. Recently, this aspect has been treated theoretically as well as experimentally [18, 19], and it shall be referred to while considering redox catalysis (Sections 5.3.5 and 5.4.4).

5.2.3 THERMODYNAMICS AND KINETICS OF A CHEMICAL REACTION

Consider a simple chemical reaction 5.6 which consumes R to produce an electroinactive compound Z.

$$R \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Z. \qquad 5.6$$

One can describe the rate of this chemical reaction by equation 5.7

$$\text{Rate} = k_f C_R - k_b \cdot C_Z \qquad 5.7$$

The rate constants k_f and k_b depend on two parameters, the frequency factor (ν_k) and the free energy of activation $\Delta_f^{\pm}$ and $\Delta_b^{\pm}$ for the forward and reverse reactions respectively.

$$k_f = \nu_k \exp\left(\frac{-\Delta G_f^{\pm}}{RT}\right)$$

$$k_b = \nu_k \exp\left(\frac{-\Delta G_b^{\pm}}{RT}\right) \qquad 5.8$$

The frequency factor of a chemical reaction is the rate at which the reacting molecules comes into contact. This property generally depends only on temperature. At least for any specific reaction one may assume that ν_k is constant.

Hence equation 5.7 suggests that $\Delta G_f^{\pm}$ and $\Delta\ G_b^{\pm}$ are the important parameters that determine the rate constants of a chemical reaction. If the activation energy required for a chemical reaction is very small, its rate constant will be very large and *vice versa*.

Depending upon the relative values of $\Delta G_f^{\pm}$ and $\Delta G_b^{\pm}$ one can encounter three limiting conditions in a chemical reaction (Fig. 5.1).

a) If the activation free energies of both the forward and reverse reactions are small, both k_f and k_b would be very large. The Z and R species would then attain their equilibrium concentration values very quicky and the net reaction rate would be zero. From equation 5.6 the equation obtained is

$$k_f \cdot C_R = k_b \cdot C_Z \qquad 5.9$$

$$\therefore \qquad \frac{k_b}{k_f} = \frac{C_R}{C_Z} = K \qquad 5.10$$

This ratio of k_b/k_f or C_R/C_Z then defines the equilibrium constant K. This type of reversible equilibrium is represented by Fig. 5.1a.

b) If $\Delta G_f^{\pm} \ll \Delta G_b^{\pm}$ then the forward reaction rate will be very much faster when compared with the reverse reaction (Fig. 5.1b). In such cases, we may neglect the second term in equation 5.6 and write the rate expression as

$$\text{Rate} = k_f\, C_R \qquad 5.11$$

This type of irreversible chemical reactions are completely described by the single rate constant k_f if the number of chemical reactions coupled to charge transfer are treated in this fashion.

c) If $\Delta G_f^{\ddagger}$ as well as $\Delta G_b^{\ddagger}$ are fairly high and are of approximately equal values, both forward and reverse reactions should be considered (Fig. 5.1c). k_f as well as k_b have a control over the kinetics. The reactions may also be described by k_f and K since k_b after all is equal to $k_f \cdot K$ from equation 5.10.

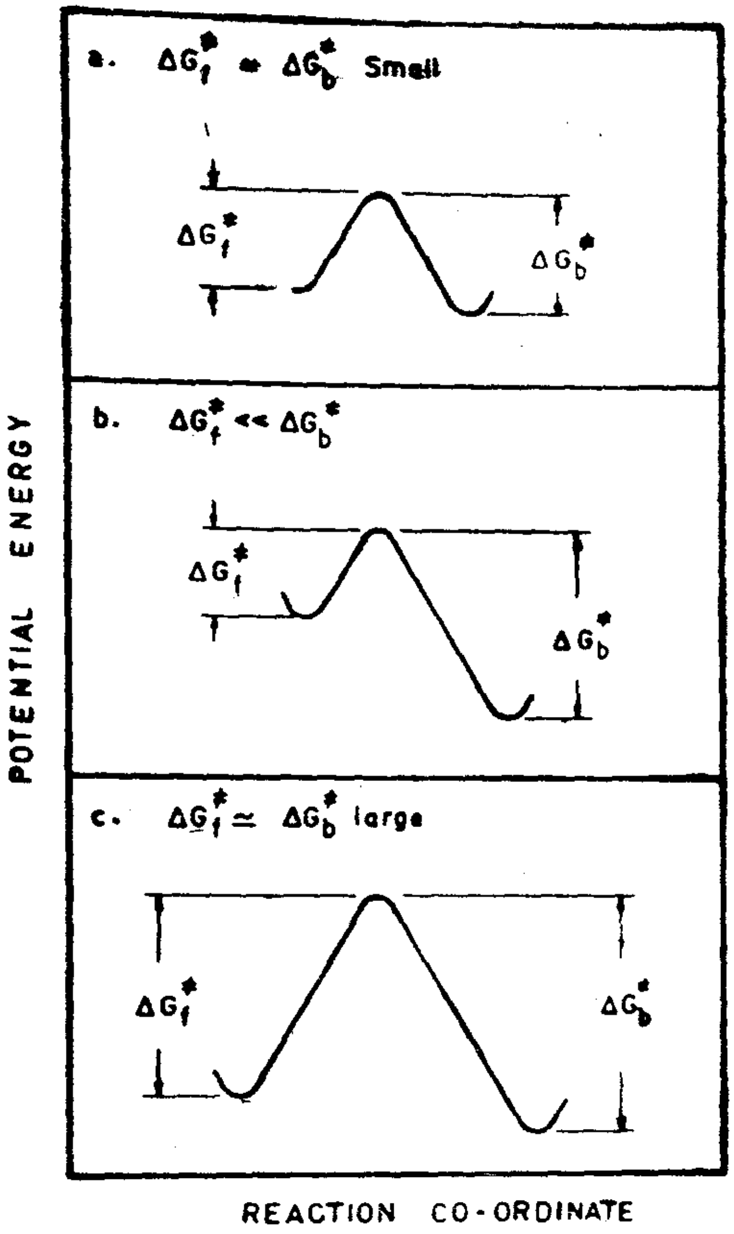

Fig. 5.1. Potential energy diagrams for three types of chemical processes (a) Reversible chemical equilibrium, (b) Irreversible chemical kinetics, (c) Reversible chemical kinetics.

It may be noticed that there is again classification of the chemical reactions into reversible, irreversible and quasi-reversible cases based on k_f and k_b values. This is exactly similar to the situations encountered in the charge transfer processes (Chapters 3 and 4). These three cases are examined separately in some more detail.

a) *Chemical equilibrium*

As discussed above, this type of situation corresponds to very high values of k_f and k_b. The concentration of R at the surface for the electro-oxidation 5.1, for example, is determined by the equilibrium constant K and C_R (5.10)

$$C_R = C_Z \, . \, K \qquad 5.12$$

This relation always holds during LSV or CV sweep experiments. When the surface concentration $C_R\,(o,t)$ increases because of electron transfer, C_Z at the surface also simultaneously increases according to equation 5.10 very quickly so that equation 5.12 always holds at the surface.

$$C_R\,(o,t) = C_Z\,(o,t) \, . \, K \qquad 5.13$$

This equilibrium process is essentially time-independent. Hence in such processes the chemical reactions would not have any influence as far as the peak current is concerned. The peak current expressions derived under purely diffusion controlled conditions are applicable here.

However, as described earlier (Section 3.2.2) the equilibrium constant strongly influences the peak potential of the LSV or CV curves. The shifts in peak potential due to other electro-inactive reactant concentrations such as H^+ and OH^- ions, complexing agents and ion-pair forming cations and anions may be used to evaluate the equilibrium properties of these reactions (Section 3.4).

b) *Irreversible chemical kinetics*

Basically one refers to any reaction as a fast or slow one depending on the relative values of time taken by the reaction to proceed and the time necessary to measure the reaction rate. If the time taken for measurement is shorter than the reaction time, one can measure the thermodynamic behaviour before the setting in of the chemical reaction as well as its kinetics and so, it is called a *slow reaction* with respect to that measuring technique. If the time taken for measurement is much larger than the reaction time, one can only measure the properties of the overall process and hence call it a *fast reaction*. It is very important to keep this basic consideration in mind especially when dealing with relaxation or transient techniques. Hence this idea with some examples are attempted to be grouped here.

Consider the first order reaction (equation 5.5). If k_f of this reaction is 10^3 sec^{-1}, one can define the reaction time of this reaction as $1/k_f$ or 10^{-3} sec. This is the time taken for the conversion of 0.33 of initial concentration of R into Z. Now, if one wants to measure the kinetics of this reaction, one must monitor the concentration changes in R at times much shorter than this time.

Now the measurement technique is LSV or CV. The time taken for measurement is determined by sweep rate. The present day instrumental and cell capabilities (Chapter 2) allow one to employ sweep rates ranging from 0.020 V sec^{-1} to 10,000 V sec^{-1}. The measurement time can be easily obtained from sweep rates by computing RT/nfv sec or $1/nfv$ where v is the sweep rate and other parameters have been defined earlier.

In order to find out if this technique is capable of measuring the kinetics of the reaction mentioned above, if the lowest sweep rate is chosen, then the time of measurement is ($1/nf \times 0.020$) about one sec. Thus much longer time is taken to measure the reaction when compared with its reaction time (10^{-3} sec). Only then can the overall process after the chemical change has taken place be noticed.

However, if a sweep rate of 100 V sec^{-1} is employed, the time taken for the measurement would be 10^{-4} sec. One can then measure the properties of the chemical system before substantial chemical changes take place. By slightly varying the measurement time, one can evaluate the influence of kinetics.

The above discussions suggest that for the analysis of totally irreversible chemical reactions by LSV or CV, two time parameters $1/k_f$ and $1/nfv$ are important. As a dimensionless parameter Λ was defined expressing the relative importance of charge transfer kinetics and diffusion (Sections 4.2 and 5.2.1) one can also define another dimensionless parameter λ relating the above two functions [20].

$$\lambda = \frac{k_f}{nfv} \qquad 5.14$$

Consider now the influence of λ on the reaction scheme involving a chemical reaction and electron transfer:

$$O_x + ne \rightleftharpoons R \qquad 5.1$$

$$R \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Z; \; K = \frac{k_b}{k_f} \qquad 5.6$$

Scheme 1

One also assumes that the chemical reaction is totally irreversible ($k_f \gg k_b$) and the electron transfer is very fast. Now if λ value is very small (or for a specific reaction if the sweep rate v is very large) one can measure the current-potential response very quickly when compared with the time taken for the chemical reaction to proceed. Therefore reaction 5.6 will not influence the measurement in this time scale. At such short time scales one measures the equilibrium concentration of R and hence equilibrium properties of this reaction. This region of λ value where the chemical reaction has no significant effect at all is called pure diffusion (DP) region (Fig. 5.2).

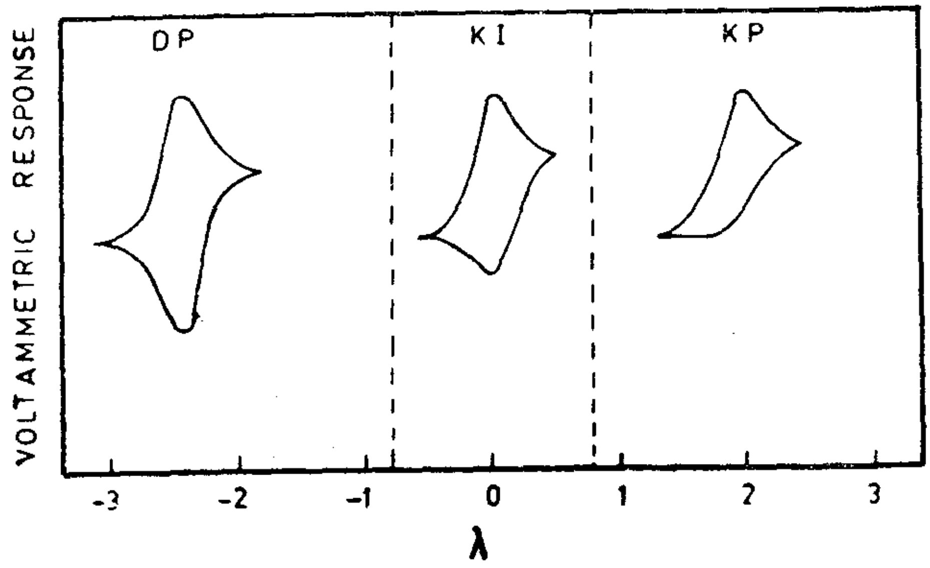

Fig. 5.2 Reaction zone diagram for EC_i reaction scheme. Typical CV curves corresponding to different λ values are also shown as insets.

Now, at the other extreme situation, when λ is very large, the chemical reaction reaches a steady state value with the time scale of the experiment. The overall current response in the experiment will now measure the rate at which the chemical reaction proceeds. This type of current is usually termed as pure kinetic current (*KP*). Much of the earlier polarographic reports on kinetic currents [3, 4] belong to this group.

In between these two extreme situations, there may be λ values where both k_f and v show their effects. The response would then depend on the mass transfer of R (diffusion component) as well as on the chemical consumption of R (kinetic component). The type of response region is termed as intermediate kinetic (KI) region (Fig. 5.2).

Digital simulation of voltammetric curves for the entire range of values is of course possible. But such works show that the current or potential expressions take much simpler forms in the DP and KP regions. In fact, it is only from such simulation works that one obtains the zone diagrams [20] discussed here.

From the experimental viewpoint, one can easily vary the λ value by about 10^6 times by changing the sweep rate in LSV and CV. Hence one notices that one can reach both KP and DP zones by changing the sweep rate in the proper direction. Evaluation of kinetic and thermodynamic parameters can then be achieved using much simpler expressions as shall be discussed later (Section 5.3).

Throughout the discussion, only a first order chemical reaction was considered (equation 5.5). However, most of the chemical reactions are second order in nature. For example, an anion radical generated in an electrochemical reaction may undergo an electrophilic substituent Y in a second order chemical reaction. One can write the general chemical reaction in the form

$$Y + R \xrightarrow{k_f} Z \qquad 5.15$$

The second order rate constant has the dimension of litres mole^{-1} sec^{-1}. How is the dimensionless parameter for this reaction defined and how does one handle the problem in general?

One general approach is to use excess concentration of Y when compared with R (in the present case O_x) as in chemical kinetics. Then the parameter k_f'. C has the dimension of sec^{-1}. In the theoretical expressions desired using first order chemical reactions, one can substitute k_f by $k_f' \, . \, C$ and get the equations of interest. The dimensionless parameter λ for example becomes

$$\lambda = \frac{k_f' C_Y}{n f v} \tag{5.16}$$

If necessary one can also treat the problem for any concentration of C_Y as well as C_{OX}. To handle this situation, one must introduce one more dimensionless parameter, say C_Y/C_{OX}. This type of parameter is termed as the excess factor [21].

c) *Reversible chemical kinetics*

Transient techniques are of course useful in measuring the thermodynamics of totally reversible processes (K) and thermodynamic as well as kinetic parameters of irreversible processes discussed above. These treatments are also easier to handle since only one property (K or k_f) is considered as the controlling parameter. However, there are occasions when the reactions are indeed reversible and both k_f as well as K influence the properties of the system. Treatment of the chemical reaction as a function of k_f, k_b and K thus must be desirable. Such a treatment would give the totally reversible equilibrium and totally irreversible chemical reactions as limiting cases of the general solution.

Such kinetic treatments of reversible chemical kinetics are available [22, 23]. Again the kinetic zone diagram approach to chemical equilibrium constant and rate constants under such conditions are employed [22].

Consider the CE mechanism presented in scheme 2.

$$Z \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ox; \; K = \frac{k_f}{k_b} \tag{5.17}$$

$$O_x + ne \rightleftharpoons R \tag{5.1}$$

Scheme 2.

(Note that for an *EC* mechanism of scheme 1, K as k_b/k_f was defined and for the CE mechanism considered here K as k_f/k_b is defined. This is done to have the same general form of zone diagrams as suggested for example in ref. 22). The entire behaviour of the system now depends on two dimensionless parameters K and λ_r which is now defined as

$$\lambda_r = \frac{k_f + k_b}{n f . v} \tag{5.17}$$

The resulting zone diagram is represented in Fig. 5.3.

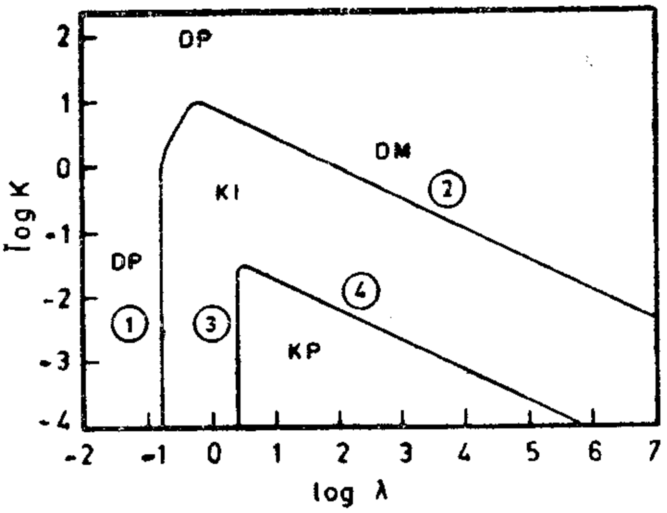

Fig. 5.3 Reaction zone diagram for C_rE_r reaction scheme as a function of K and . *DP*—Pure diffusion; *DM*—diffusion modified by chemical equilibrium. *KP*—Pure kinetics, and *KI*—Intermediate kinetics. [From JM Saveant and E Vianello, Electrochem Acta 8 (1963) 905].

When the equilibrium is in the forward direction ($K > 1$), one can conceive two situations. If k_f and k_b are small when compared with v, the reversible charge transfer reaction can be measured without the influence from the chemical step (*DP* region). If k_f and k_b are very large, then one can measure the reversible charge transfer with the influence of chemical equilibrium. The chemical step influences charge transfer only in the thermodynamic sense. The kinetic control of the process would not be noticed. This region is denoted by *DM* which implies modified diffusion. It is this type of processes that was considered in detail in Chapter 3.

If K is very small (the bottom region in Fig. 5.3) there is a situation similar to irreversible chemical reaction. At very small λ values there is a pure diffusion region. As λ increases one notices *KI* and *KP* regions. At very high λ values we can again notice a *KI* region because of a combined influence of forward and reverse reactions.

When *K* values lie in the intermediate region, one notices the *DP* region again at low λ values. At high λ values one notices the *DM* region. In between these ranges there may be the *KI* region alone or *KI, KP* and *KI* regions in sequence.

As in the case of irreversible chemical reaction (Section 5.2.3b) the overall current-potential expressions simplify very much in *DP, KP* and *DM* regions. Hence if one finds that a reaction is in the *KI* region (according to the diagnostic criteria of peak current or peak potential variation with λ) one may preferably try to reach *KP* and *DP* regions to evaluate the parameters of interest to him.

5.2.4. MULTISTEP PROCESSES

As long as the reversible electrochemical step is associated with the kinetics of a single chemical step, the analysis of the data is a fairly easy task (Sections 5.2.3 and 5.3). However, a number of electrochemical processes involve a number of electrochemical (*E*) and chemical steps. Consider for example the most common scheme of reduction of an organic compound *A* in a 2*e*, $2H^+$ step to form AH_2. The whole process may be represented as a square scheme [24, 25].

$$\begin{tikzcd}
A \arrow[r, shift left, "E_1^0"] \arrow[d, shift left, "K_1"] & A^- \arrow[l, shift left] \arrow[r, shift left, "E_2^0"] \arrow[d, shift left, "K_2"] & A^{2-} \arrow[l, shift left] \arrow[d, shift left, "K_3"] \\
AH^+ \arrow[u, shift left] \arrow[r, shift left, "E_3^0"] \arrow[d, shift left, "K_4"] & AH \arrow[u, shift left] \arrow[l, shift left] \arrow[r, shift left, "E_4^0"] \arrow[d, shift left, "K_5"] & AH^- \arrow[u, shift left] \arrow[l, shift left] \arrow[d, shift left, "K_6"] \\
AH_2^{2+} \arrow[u, shift left] \arrow[r, shift left, "E_5^0"] & AH_2^+ \arrow[u, shift left] \arrow[l, shift left] \arrow[r, shift left, "E_6^0"] & AH_2 \arrow[u, shift left] \arrow[l, shift left]
\end{tikzcd}$$

Scheme 3

In this scheme, six possible chemical steps (vertical equilibrium) and six possible charge transfer steps (horizontal equilibrium) are involved. If one wishes to evaluate all the possible thermodynamic (6 E^o values and 6 K values) as well as kinetic (6 k_h^o values, 6 k_b values and 6 k_f values) even for a single electroactive compound, the attempt would be rather challenging, if not impossible. The situations become even more involved if reactions other than the protonations considered above are also taken into account. For example, dimerizations [26], acid-base and complex formation equilibria (Sections 3.2 and 4.2).

Already the methods for handling the situation have been described if all the chemical and electrochemical steps are faster ones (Chapter 3). The approach required to deal with the multi-step processes where the electron transfer step is slow was also dealt with earlier (Chapter 4). The approach adopted in dealing with a single slow chemical step in a multistep process is also very similar as shown here (Section 5.2.4a). Models have evolved where more than one slow step can be handled for an overall process making use of the wide time scale available in LSV and CV techniques (Section 5.2.4b). Another possibility in a multistep process is the existence of multistep pathways. Note, for example, that six possible routes exist for the reduction of A to AH_2 in scheme 3. (*EECC, ECEC, ECCE, CEEC, CECE, CCEE*). At present, the models and methods have been developed at least to handle a few such competitive pathways (Section 5.2.4c).

a) *Single slow chemical step*

Consider an electrochemical process in which A is converted to B by n electron single step reduction process similar to equation 5.1. A may be formed by some preceding chemical steps. The product B may undergo some further chemical reactions. It is practically impossible to evaluate the parameters of all the steps independently from one set of measurements. But one can effectively calculate the overall kinetics of the slowest chemical reaction in the sequence. This is very similar to the method adopted in the multistep electron transfer process (Section 4.2). There it was noted that one could measure the overall charge transfer rate (exchange current density i_o) even though one could not evaluate the k_h^o values of individual steps. In a similar fashion one can evaluate an overall chemical rate constant k_{ob} instead of k_f of a specific reaction (for a few exceptions see Sections 5.2.4, b and c).

Just as in chemical kinetics, one can define the electrochemical reaction orders of the reactants involved in the slow chemical step. There may be a slow chemical reaction in which reactant A, its reduced product B, any other added reactant species X (such as H^+ or any nucleophile) and the product formed in a previous chemical equilibrium before the *rds* I are the participants. One can then express the observed rate as [27]

$$\text{Rate} = k_{ob} \cdot C_A^a \cdot C_B^b \cdot C_X^x \cdot C_I^i \qquad 5.18$$

The peak potential (E_p) shift with sweep rate, reactant concentration and the concentration of addition agent X can then be expressed as

$$\left(\frac{dE_p}{d\log_v}\right)_{C_A, C_X} = -59.2\left(\frac{I}{b+1}\right) = -59.2, S_1 \qquad 5.19$$

$$\left(\frac{dE_p}{d\log C_A}\right)_{v, x} = 59.2\left(\frac{+b+i-I}{b+1}\right) = 59.2, S_2 \qquad 5.20$$

$$\left(\frac{dE_p}{d\log C_X}\right)_{v, C_A} = 59.2\left(\frac{X}{b+1}\right) = 59.2, S_3. \qquad 5.21$$

where S_1, S_2, S_3 are constants containing reaction order parameters. These values may be very helpful in evaluating the reaction pathway in an overall electrochemical pathway. The reaction order estimations would then be used to calculate the observed chemical rate constants using the appropriate dimensionless parameters and rate constants.

However, it is very important to note that these expressions are valid only if the kinetic behaviour corresponds to the pure kinetic region (Figs. 5.2 and 5.3). This method must not be applied if the limiting current is in the intermediate kinetic region (where the mass transfer effects will also be present) or if the slow step is reversible (then K will influence the process). If proper care is not taken, such simplified generalizations may lead to inaccurate conclusions [28, 29].

b) *More than one slow step*

In the discussions on chemical kinetics so far, we have assumed that the charge transfer is reversible. This assumption is found to hold in a number of cases where organic reactions have been considered. However, it is also desirable to consider processes involving charge transfer kinetics. A number of organic processes on solid electrodes in recent years [30, 31] do suggest that the charge transfer is the rate determining step on these electrodes.

Again consider the EC reaction (Scheme 1). The dimensionless parameters defining the kinetics of E and C steps respectively are Λ and λ. Both these parameters are dependent on sweep rate. For convenience, one may define $\alpha = 0.5$. Kinetic zone diagrams may again be used to describe the behaviour of these processes [32]. Figure 5.4 represents the zone diagram of such a process.

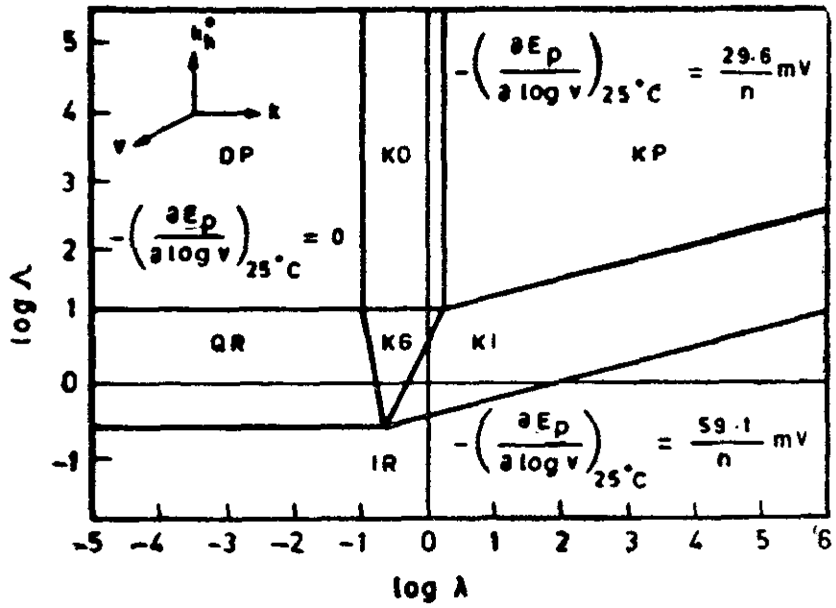

Fig. 5.4 Reaction zone diagram for E_qC_I reaction scheme as a function of two kinetic parameters λ & Λ. *QR* —Quasi-reversible charge transfer kinetics; *IR* — Irreversible charge transfer kinetics; *KG* — General kinetics; Other symbols as in Fig. 5.3. [From L Nadjo and JM Saveant, J Electroanal Chem 48 (1973) 113].

One important difference must be noted between Fig. 5.3 and Fig. 5.4. In a reversible chemical process the system properties are defined by K and λ where λ alone is dependent on sweep rate. Hence when the sweep rate is varied, one moves the λ value alone and moves the system response horizontally. In two-rate process, both the parameters depend on sweep rate and hence the system response moves in a slanting fashion (as indicated by the dotted line) when v is varied. As in the earlier case, however, the response to the convenient zones can be shifted to measure the required properties.

The top portion of Fig. 5.4 corresponds to the zone diagram of a process with reversible charge transfer considered earlier (Fig. 5.2). The *KP* and *DP* regions are separated by an intermediate region where mass transfer as well as kinetics has the influence. The measurable parameter $dE_p/d\log v$ in different regions are given for quickly locating the various regions from the measurable properties.

The bottom portion of Fig. 5.4 corresponds to irreversible charge transfer. Here we cannot get any idea of the following chemical reaction since the first charge transfer step is very slow when compared with the chemical reaction. Between the region of reversible charge transfer (*DP*) and irreversible charge transfer (*IR*) there is a region of quasi-reversible charge transfer.

The zone defined as *KG* is the most involved region of the two rate processes. In this region the voltammetric behaviour depends on both charge transfer kinetics as well as chemical kinetics.

Although construction of such zone diagrams is certainly a tough task, their use in experimental studies is not so difficult especially if one reaches the proper limiting regions by varying the sweep rate. For example, in studying an *EC* process at slow sweep rates, the chemical kinetics would be rate limiting (*KP* region). One can increase the sweep rate to reach *DP* region from which E° of electron transfer may be determined. On further increase in sweep rate, one would reach *QR* or *IR* region where the kinetics of charge transfer k_h^0 can be measured.

In a multistep process, one may also have chemical steps. Similar zone diagram analysis is also possible for these cases. The dimensionless parameters would of course be two values or their ratios. Some specific examples are discussed later.

c) *Competitive pathways*

In a multistep process, one must also consider the possibility of the same product from two entirely different routes. Consider the $2E$, $2C$ process presented in Scheme 3. One pathway which is often considered in experimental studies is the *ECEC* pathway represented in Scheme 4 (since the last chemical step is very fast when compared with the other steps and hence does not require detailed consideration, this scheme is also called *ECEC* mechanism).

$$A + e \rightleftharpoons B \qquad E_I^o \tag{5.22}$$

$$B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C \qquad K = \frac{k_b}{k_f} \tag{5.23}$$

$$C + e \rightleftharpoons D \quad E_2^o \gg E_1^o \tag{5.24}$$

$$D \rightleftharpoons E \tag{5.25}$$

Scheme 4: ECEC Mechanism

Formation of E from A may also be accomplished by another reaction schemes

$$A + e \rightleftharpoons B \, E_1^o \tag{5.22}$$

$$B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C \quad K = \frac{k_b}{k_f} \tag{5.23}$$

$$B + C \overset{k_d}{\rightleftharpoons} A + D \tag{5.26}$$

$$D \rightleftharpoons E \tag{5.25}$$

Scheme 5: Disproportionation Mechanism

Schemes 4 and 5 are different only in one step. The second electron transfer to C takes place at the electrode in Scheme 4 and hence it is called *ECE* mechanism. The reduction of C in Scheme 5 takes place by a redox reaction between B and C. Since both B and C have the same reduction state reaction, equation 5.26 may be considered as a disproportionation reaction. Hence Scheme 5 is called disproportionation mechanism.

In Scheme 5, there are two possible slow chemical steps. If the first chemical step (equation 5.23) is slow, it is denoted as Disp-1 mechanism. If the second chemical step is a slow step, it is called Disp-2 mechanism.

If all heterogeneous electron transfer steps and the last chemical step (equation 5.25) are assumed to be fast, there can be a possibility of distinguishing between these three reaction schemes (*ECC*, Disp-1 and Disp-2) [33]. One can again adopt a zone diagram approach where *K*, λ_r and λ_d define the overall behaviour of the competitive pathways (Fig. 5.5). The λ values are again defined by the following expressions:

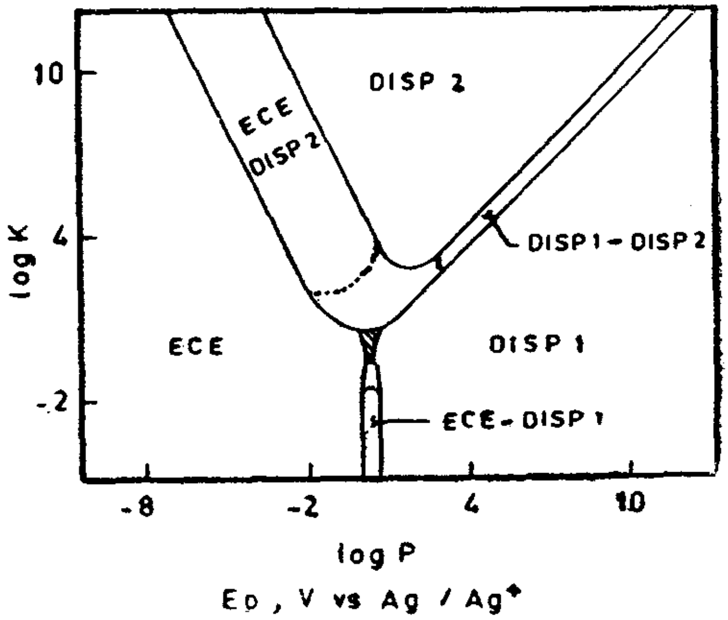

Fig. 5.5 Kinetic zone diagram featuring the transition between the limiting mechanisms as a function of parameters *K* and *p*. [From C Amatore and JM Saveant, J Electroanal Chem 85 (1977) 27].

$$\lambda_r = \frac{k_f + k_b}{nfv} \tag{5.17}$$

$$\lambda_d = \frac{k_d}{nfv} \tag{5.27}$$

in Fig. 5.5, the variables are further reduced to 2 by introducing a new parameter P, containing λ_r, λ_d and K.

$$P = \lambda_d \left(\frac{1+K}{\lambda_r}\right)^{3/2} \qquad 5.28$$

The parameter P of a chemical system can be varied by varying the sweep rate.

Qualitatively, there may be an attempt to understand the kinetic zone diagram as follows. When P is very small, it means λ_r, and hence k_b and k_f of the first chemical step (equation 5.23) are very large. Hence the species C will be formed very near the electrode surface before electrochemically produced B can move away into the solution. Therefore the second electron transfer involving C would predominantly take place at the electrode surface. That is, *ECE* mechanism would prevail under these conditions. As P value increases substantially, conversion of B to C occurs at a much slower rate. Therefore C is formed at distances far off from the electrode surface. Hence C preferentially reacts with a B molecule rather than diffuse back to the electrode surface to react there. Thus disproportion scheme predominates. Now if reaction 5.23 is fast and reversible (large K and large P) reaction 5.26 becomes the slow step (Disp-2). If K is small, Disp-1 mechanism predominates [33].

As discussed in the earlier zone diagrams, in this case also one can vary the P value by changing the sweep rate to reach various kinetic zones. The variations of peak current-peak potential characteristics can then be used for discriminating between such parallel pathways.

In this major subsection (5.2), the basic principles and approaches adopted to handle electrochemical processes involving chemical kinetics have been presented. The basic rate expressions for any overall processes are built employing the relevant expressions for charge transfer (Section 5.2.1), mass transfer (Section 5.2.2) and chemical processes (Sections 5.2.3 and 5.2.4). Many new reaction schemes are being proposed and solved, but the models considered are the same. Hence a little effort to understand these concepts clearly would help in understanding and utilizing such new reaction schemes even if they are not considered in detail here.

5.3 THE METHOD

There is indeed a great variety of chemical reactions which are closely associated with interfacial charge transfer. Hydration-dehydration reactions, acid-base reactions, monomerization-dimerization reactions, disproportionation-redox catalysis reactions, isomerization reactions, hydrogen abstraction reactions and electrochemically induced catalytic reactions are only a few examples of possible chemical reactions that may be dealt with here. Developing electrochemical methods for the analysis of such a wide variety of chemical reactions in the electrochemical context where charge transfer as well as mass transfer effects must also be considered is indeed an unending task in itself. And this is exactly why one finds extensive work on methods to handle chemical kinetics.

Although the chemical reactions vary widely at the process level, one notices a general uniformity in the model level (Section 5.2). Any charge transfer reaction is defined by E^o and n value if it is reversible (E_r); two additional parameters Λ and αn_a are required to characterize the kinetics of charge transfer (E_i or E_q). Any irreversible chemical reaction (C_i) is defined by λ. If the chemical reaction is reversible λ_r and K define its behaviour completely. When more than one chemical reaction is an electrochemical process, the number of K values as well as λ values would increase correspondingly. With the help of the few parameter mentioned above, one can describe the voltammetric behaviour of any electrochemical process at the solution side of the interface. It is the presence of this general structure that enables one to develop the methods for the study of all the chemical reactions based on a few simple reaction schemes.

In this section the LSV and CV methods of analysing some of the frequently encountered chemical reaction schemes shall be considered. The discussion of each reaction, however, will necessarily be brief. The relevant equations will be presented in the form of tables for each reaction scheme and the method of evaluating the thermodynamic and kinetic parameters will be described. For more detailed discussions, one may refer to the original literature cited.

As seen later, most of the simulation work on chemical reactions is carried out for LSV and CV under semi-infinite linear diffusion conditions. Some efforts for correcting non-linear diffusion [23] have been made. Different sweep rates for the forward and reverse scan have been recommended [34]. New methods of data analysis such as derivative cyclic voltammetry [35] and linear current-potential analysis [36] have been proposed. Convolution sweep voltammetry or semi-integral voltammetry has received even greater attention in the analysis of chemical reaction kinetics [37–40]. Recently a kinetic convolution integral was proposed [41] which enables analysis of data even more convenient. In all the methods described above, the experimental data are analysed to obtain the reaction parameters of interest. In recent years, increasing attention is being paid towards digitally simulating voltammetric curves to match the experimental voltammograms by proper and judicious guessing of rate parameters [42, 43].

All these developments are of course pointing towards the developments that can take place in this technique. But by and large, these developments must be considered as the extension of the basic techniques of LSV and CV. These developments invariably require increasingly greater mathematical as well as instrumental sophistication. For this reason, these advances have found little use by workers other than the proponents of the methods themselves. Some glimpses of such developments were also presented earlier in this work while dealing with the less involved charge transfer processes (Chapters 3 and 4). Hence, selectively the basic methods of analysing the peak currents and peak potentials and their variations with experimental variables such as sweep rate and reactant concentration shall be considered. With this background knowledge, the advances mentioned above may be followed with much more ease.

5.3.1 THE PRECEDING CHEMICAL REACTION

If the electro-inactive species Z is more stable than the electroactive species OX, then, formation of OX from Z is termed as a preceding chemical step. For example, in the reduction of formaldehyde (OX), its hydrated form is electroinactive (Z).

$$\mathrm{HCH\,(OH)_2} \rightleftharpoons \mathrm{HCHO} + \mathrm{H_2O} \qquad 5.29$$

A few more experimental systems are discussed later (Section 5.4.1). But in this general case it is important to note that since Z

is more stable than OX, k_b is always greater than k_f (Fig. 5.6 a). Hence in the treatment of CE mechanism, C must always be considered as C_r [22, 23, 44]. However, the electrochemical step E may

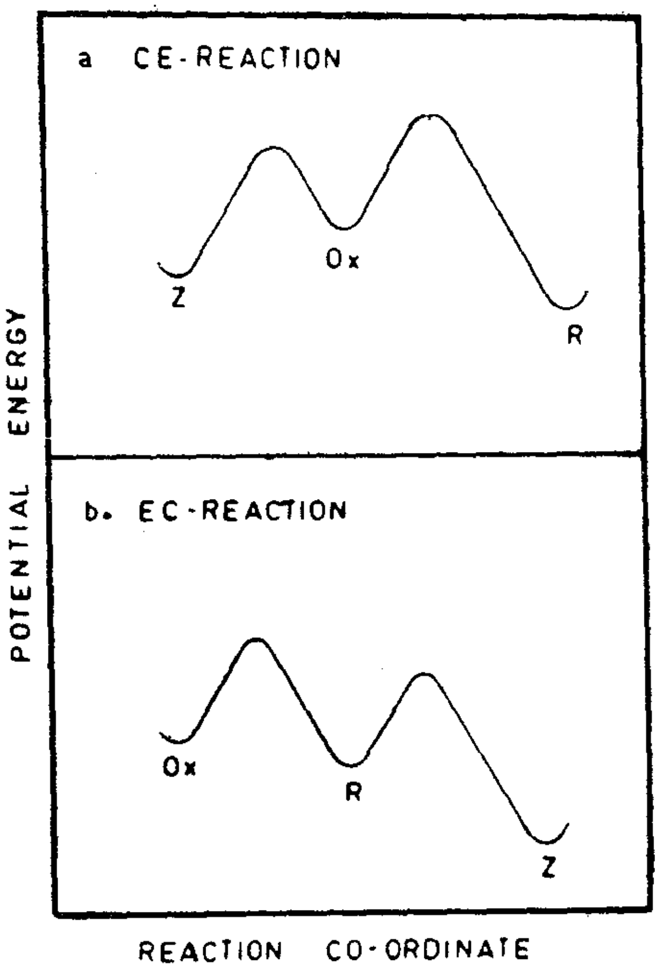

Fig. 5.6 Activation energy diagrams for CE and EC reaction schemes (A) $\Delta G_f^{\pm}$ always $> G_b^{\pm}$ (B) $\Delta G_f^{\pm} \leqslant \Delta G_b^{\pm}$ for the chemical step.

be E_r or E_i. We shall consider the C_rE_r and C_rE_i combinations separately.

a) C_rE_r *mechanism*

For this mechanism, the voltammetric behaviour depends on two parameters K and λ_r [22, 23]. The reaction scheme and all the relevant rate expressions to characterize this mechanism are presented in Table 5.1. Typical linear sweep voltammograms at two different K values and a number of λ values are presented in Fig. 5.7.

Table 5.1

Voltammetric characterstics of C_rE_r reaction scheme

Scheme : $Z \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ox$ $\qquad k = \frac{k_f}{k_b}$

$Ox + ne \rightleftharpoons R.$ $\qquad \lambda_r = \frac{k_f + k_b}{nfv}$

DP Zone:

$$i_p = 2.69\times10^5 . n^{3/2} . AC_{Ox}\ v^{1/2}\ D_{Ox}^{\frac{1}{2}}\left(\frac{K}{1+K}\right) \qquad 5.1a$$

KP Zone:

$$i_k = nFA\ C_{Ox}\ D_{Ox}^{\frac{1}{2}}\ K\cdot k_b^{\frac{1}{2}} \qquad 5.1b$$

$$\frac{dE_p}{d\log v} = \frac{29.6}{n}\ \text{mV}. \qquad 5.1c$$

$$\frac{i_k}{i_{p,d}} = \frac{1}{1.02+0.471/K\cdot\lambda_r^{\frac{1}{2}}} \qquad 5.1d$$

$$\frac{i_{p,a}}{i_{p,c}} > 1. \qquad 5.1e$$

At very high sweep rates ($\lambda \rightarrow 0$) when the preceding chemical reaction has no effect on voltammetric behaviour, the LSV and CV curves correspond to diffusion controlled behaviour, but the peak current in this DP region (Fig. 5.3) is smaller by the factor $\{K/(1 + K)\}$ as represented in equation 5.1a. Note that if $K \gg 1$, OX would be more stable than Z and hence the peak current would become equal to the diffusion limited current without any chemical kinetic effect. $\{K/(1 + K)\} \approx K/K \approx 1$. Compare i_p expression in Table 3.2.

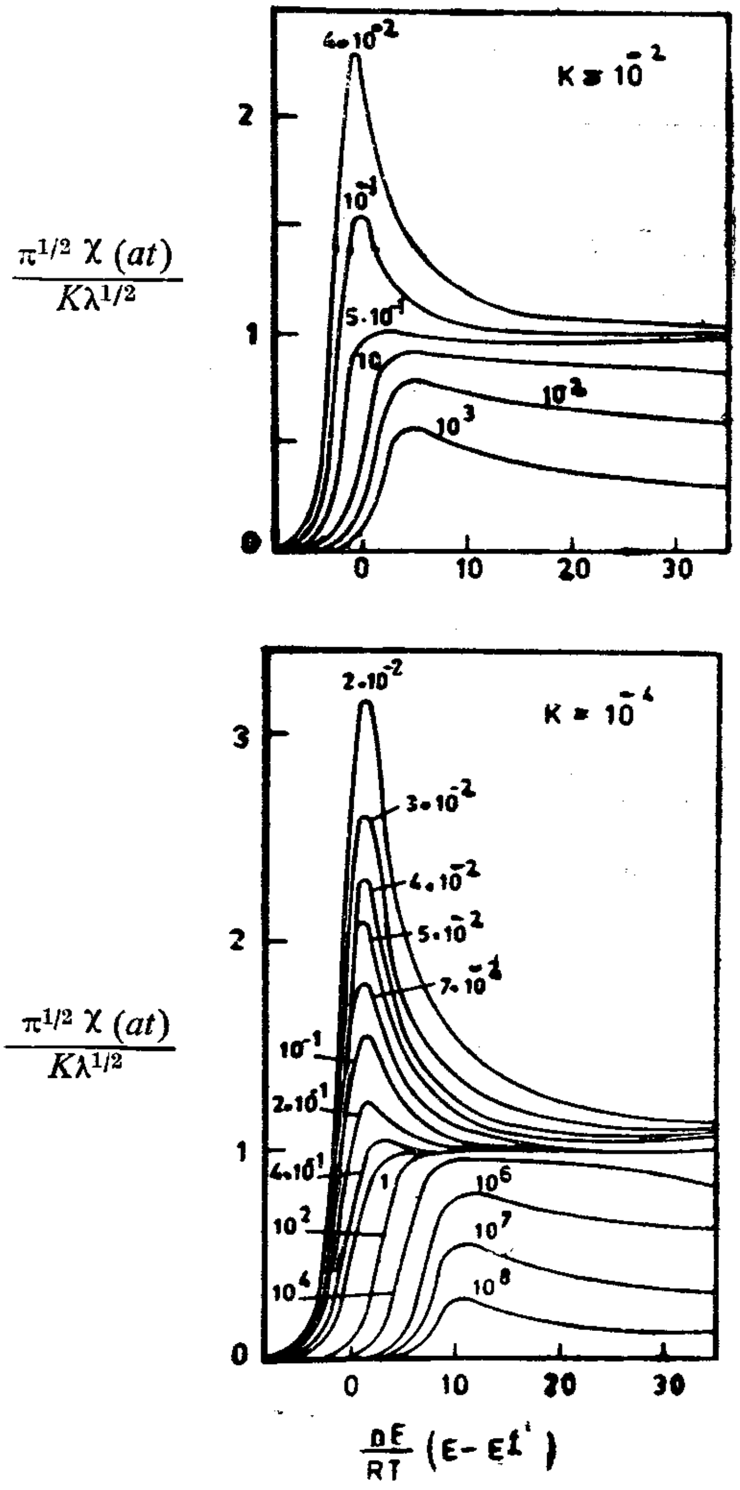

Fig. 5.7 Linear sweep voltammograms (simulated) as a fnnction of K and λ values (shown in the figure) for C_rE_r reaction scheme.

As the sweep rate is decreased (λ incrcases), the peak current transforms into a sigmoid shaped wave (Table 5.7) (without any peak). In this *KP* region, the peak current is given by equation 5.1b and the $dEp/d \log v$ value reaches $(29.6/n)$ mV (equation 5.1c). At still lower sweep rates (very high λ) the LSV curve would again take a peak shape. This corresponds to the *DM* region (Fig. 5.3).

Chemical reaction influences the formation of *OX* alone and the species *R* is left intact. Hence the reverse anodic peak current in *CV* is always diffusion controlled, and the peak current ratio $i_{p,a}/i_{p,c}$ is always greater than unity in the *KP* region (equation 5.1e).

If these qualitative and quantitative features are noticed, one can conclude that the process belongs to C_rE_r mechanism. The reaction parameters can then be evaluated as follows. In the linear region the $dEp/d \log v$ value would give n value (equation 5.1c). The reversible wave at very slow sweep rate would then give the D value since all the other terms in the peak current expressions are known. Now the reversible wave at very high sweep rate ($\lambda \rightarrow 0$) in the *DP* region would give the equilibrium constant K (equation 5.1a) and also the $E°$ value of the uncomplicated Ox/R redox reaction. Using this K, n, D values, we may then use the λ shaped sweep rate independent wave in the middle sweep rate range to calculate k_b using (equation 5.1b) and hence k_f which is given by $K.k_b$. Hence all the parameters related to C_r (K, k_f and k_b) and E_r ($E°$, n) can be evaluated.

The ratio between i_k (equation 5.1b) and the diffusion controlled peak current $i_{p,d}$ (which may be obtained experimentally in the absence of kinetic influence of the same compound or by calculation knowing the D value of *OX* or closely related compound) in the entire kinetic region is given by equation 5.1d. This can be used to obtain $K\ k_b^{1/2}$ value of the kinetic reaction by LSV measurements even if *KP* region alone is accessible by experiment [23]. The ratio $i_{p,a}/i_{p,c}$ is also tabulated for various $K\ \lambda^{1/2}$ values [23]. Hence this experimental ratio from *CV* [45] may also be used to evaluate $K\ k_b^{1/2}$ [23].

However, such a complete analysis may be possible only in a few cases where the sweep rate can be varied widely to reach all the *DP*, *KP* and *DM* regions (Fig. 5.3). If this is not true, one may have to content with some partial information.

position *A* and *B*, we can use the symbol ≀ it available. Otherwise, use the word "sigmoid".

b) C_rE_i mechanism

The reaction scheme and all the relevant expressions for the analysis of this reaction scheme [23] are presented in Table 5.2.

Table 5.2

Voltammetric characteristics of C_rE_i reaction scheme

Scheme

$$Z \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ox \qquad K = \frac{k_f}{k_b}$$

$$Ox + ne \xrightarrow{k_h^o} R \qquad \lambda_r = \frac{k_f + k_b}{n f v}$$

DP region :

$$i_p = 2.98 \times 10^5 \times n.\ (\alpha n_a)^{1/2} A\ C_{Ox}\ v^{1/2}\ D_{Ox}^{1/2} \left(\frac{K}{1+K}\right) \tag{5.2a}$$

$$\frac{dEp}{d \log v} = \frac{29.6}{\alpha\, n_a}\ \mathrm{mV} \tag{5.2b}$$

$$\frac{i_{p,a}}{i_{p,c}} = 0 \tag{5.2c}$$

KP region

$$i_p = nFA\ C_{Ox}\, D_{Ox}^{1/2}\ K\,.\,k_b^{1/2} \tag{5.2d}$$

$$\frac{dEp}{d \log v} = 0 \tag{5.2e}$$

$$\frac{i_k}{i_{p\cdot d}} = \frac{1}{1.02 + 0.531\ (\alpha n_a)^{1/2}/K\,\lambda_r^{1/2}} \tag{5.2f}$$

$$\frac{i_{p,a}}{i_{p,c}} = 0 \tag{5.2g}$$

At very high sweep rates (λ → 0) the peak current exhibits irreversible charge transfer behaviour (Table 4.1)). The peak current value, however, is smaller by $\{K/(1+K)\}$ (equation 5.2a). The transfer coefficient (αn_a) value may be obtained using equation 5.2b in this region. In *CV* experiments, no anodic value would be noticed (equation 5.2c) and hence the E^o of this reaction cannot be evaluated under these conditions. If E^o values are evaluated under conditions where the chemical reactions have no effect, then the methods described for simple irreversible charge transfer (Table 4.1) may be used for the estimation of k_h^o.

In the peak kinetic region the peak current again takes a wave shape as in C_rE_r case. The kinetic current expression for both the cases are the same (equation 5.2d). In this case, however, the E_p value (or more easily measurable $E_p/2$) values are independent of sweep rate (equation 5.2e). The current ratio $i_k/i_{p,d}$ is given by a slightly different expression (equation 5.2 f). From the experimentally measured current ratio and (αn_a) values obtained using equation 5.2b one may easily obtain $K.k_b^{1/2}$ as before. The cyclic voltammetric response in this case, however, will only serve to show that the charge transfer is irreversible.

At still slower sweep rates ($\lambda \rightarrow \alpha$) one may reach the *DM* region but pure irreversible charge transfer (with peak shaped waves) would again be noticed. This would be noticed when $K \gg 1$.

5.3.2 THE FOLLOWING CHEMICAL REACTION

The driving force for the *CE* reaction scheme is the instability of the electroactive reactant. There are of course a few cases where this situation prevails. However, in a number of electrochemical processes, the reactants are very stable. But the product of electron transfer such as the radical anions in reduction and radical cations in oxidation are comparatively unstable (Fig. 5.6b). The electron transfer thus initiates a number of subsequent chemical processes. In a number of cases $k_f \gg k_b$ and hence EC_i situations generally (Fig. 5.2). However, reversible chemical reactions may also be encountered following charge transfer (EC_r). Both these cases will be considered subsequently.

a) *EC_i mechanism*

The EC_i reaction scheme and the relevant rate expressions are presented in Table 5.3. The peak current in LSV is primarily due to the diffusion behaviour of *OX*. This is not affected to any great extent by the following chemical reaction. The peak current at very low sweep rate ($\lambda \rightarrow \alpha$) is about 10 per cent higher (equation 5.3a) than the peak current at the highest sweep rate ($\lambda \rightarrow 0$) where no subsequent chemical reaction takes place [23, 44]. However, the cathodic peak potential is a much better diagnostic criteria. At very high sweep rates, the peak potential corresponds to the unperturbed charge transfer reaction. At higher λ values the chemical reaction stabilizes the product and hence the peak potential shifts positively with increasing λ value (equation 5.3.b). The $dEp/d \log v$ value shifts cathodically by $(29.6/n)$ mV (equation 5.3.c). The peak width $(E_p - E_{p/2})$ value ($48/n$ mV; equation 5.3.d) is sharper than the simple charge transfer processes ($56.5/n$ mV); the cyclic voltammetry offers a bright chance for characterizing this process. At very slow sweep rates, the peak current ratio is close to zero if Z, the product of chemical reaction, is electro-inactive. As the sweep rate is increased if one obtains the anodic wave in the anodic scan, it may be taken as a positive indication of EC mechanism. At sufficiently higher sweep rates, the peak current ratio would reach unity.

If the process shows the above characteristics, the Table 5.3 may then be used to evaluate the rate parameters. n may be evaluated from equations 5.3c and 5.3d. The $E_{1/2}$ (or E^o since it is assumed that $D_{ox} = DR$) may be evaluated by obtaining the reversible cyclic voltammogram at the higher sweep rates ($E_{1/2} = E_{p,a} + E_{p,c/2}$). One may then use equation 5.3b and slower sweep rates to obtain λ and hence k. Numerically simulated $i_{p,a}/i_{p,c}$ values for a wide range of λ values are available [23]. This may also be used to obtain λ from an experimentally measured current ratio. However, it must be noted that the time taken between $E_{1/2}$ and the inversion potential must also be taken into consideration in this method.

The E_rC_r case has been discussed. The charge transfer may also be quasi-reversible or irreversible (Fig. 5.4) [33]. If charge transfer becomes irreversible at higher sweep rates, the behaviour corresponding to equations 5.3f and 5.3g would be noticed. In between the region showing pure kinetic (KP) and irreversible charge transfer (IR) behaviour, a region of quasi-reversible behaviour may also be encountered where $E_{1/2}$ and k_h^o may be calculated by the methods discussed earlier (Table 4.2).

Since the EC_i wave with large λ is very similar to the simple irreversible charge transfer, both these processes must be carefully

Table 5.3

Voltammetric characteristics of EC_i reaction scheme

Scheme :

$$Ox + ne \rightleftharpoons R$$

$$R \xrightarrow{k_f} Z \qquad \lambda = \frac{k_f}{n f v}$$

DM region :

$$i_p = 2.98 \times 10^5 \times n^{3/2} A\, C_{Oa}\, \nu^{1/2}\, D_{Ox}^{1/2} \qquad \text{...5.3,a}$$

KP region:

$$E_p = E_{1/2} - \frac{0.0592}{n}(0.780) + \frac{0.0296}{n} \log \lambda \qquad \text{...5.3b}$$

$$\frac{dEp}{d \log v} = -\frac{29.6}{n} \text{ mV.} \qquad \text{...5.3.c}$$

$$E_p - E_{p/2} = \frac{48.0}{n} \text{ mV} \qquad \text{...5.3.d}$$

$$\frac{i_{p\cdot a}}{i_{p,c}} = 0 \text{ (at slow sweep rates)}$$

$$= 1 \text{ (at high sweep rates)} \qquad \text{...5.3.e}$$

IR region :

$$\frac{dEp}{d \log v} = -\frac{29.6}{\alpha\, n_a} \text{ mV} \qquad \text{...5.3.f}$$

$$E_p - E_{p/2} = \frac{48.0}{\alpha\, n_a} \text{ mV} \qquad \text{...5.3,g}$$

---

distinguished. The peak shape will be sharper in the former (equations 5.3.c and 5.3.d where n is $\geqslant 1$) when compared with the latter (equations 5.3.f and 5.3.g where $\alpha\, n_a$ is usually less than 1). If $n = \alpha\, n_a$, this distinction is impossible. One must then draw his conclusion from the nature of the system. Appearance of anodic peak with increasing sweep rate is however very useful in confirming EC_i mechanism.

b) *E_rC_r mechanism*

If the chemical reaction is reversible, the voltammetric behaviour would depend on K and λ_r. The kinetic zone diagram is again very similar to Fig. 5.3 presented for C_rE_r case. The reaction scheme with relevant rate expressions are presented in Table 5.4.

Table 5.4

Voltammetric characteristics of EC_r reaction scheme

Scheme.

$$Ox + ne \rightleftharpoons R \qquad K = \frac{k_b}{k_f}$$

$$R \xrightleftharpoons[k_b]{k_f} Z \qquad \lambda = \frac{k_f + k_b}{n f v}$$

DM region :

$$i_p = 2.98 \times 10^5 \times n^{3/2} \; A \; C_{ox} \; v^{1/2} \; D_o^{1/2} \qquad \ldots 5.4.a$$

KP region:

$$E_p = E_{1/2} - \frac{0.0592}{n}(0.780) + \frac{0.0296}{n} \log \lambda_r - \frac{0.0592}{n} \log \frac{K}{1+K} \qquad \ldots 5.4.b$$

$$\frac{dE_p}{d \log v} = -\frac{29.6}{n} \text{ mV} \qquad \ldots 5.4.c.$$

$$\frac{i_{p,a}}{i_{p,c}} = 0 \text{ (at intermediate v)}$$

$$= 1 \text{ (at very low and high v)} \qquad \ldots 5.4.d.$$

General:

$$(E_p)_{\lambda \to \alpha} - (E_p)_{\lambda \to 0} = \frac{0.0592}{n} \log \left(\frac{1 + K}{K} \right) \qquad \ldots 5.4.e$$

The cathodic peak current expression in this case is also very similar to that of uncomplicated reversible charge transfer (equation 5.4.a) and hence will not be of great help in the study of this reaction scheme. The peak potential shifts cathodically with sweep rate (equation 5.4.b) but its slope may vary between 0 and $(-59.2/n)$ mV depending on the kinetic parameter and K (equation 5.4.c) and hence this relation again will be of little use. Tne most important feature of this reaction scheme is represented in Fig. 5.8. At very high sweep rate, the reversible cyclic voltammogram with reversible charge transfer is noticed. At very low sweep rate again $(\lambda \rightarrow \alpha)$ one notes a reversible cyclic voltammogram which is shifted in the positive direction. In between these two limiting sweep rates, one notices irreversible charge transfer. Such behaviour will give enough confidence that the E_rC_r mechanism operates (equation 5.4.d). The difference in half peak potentials between these two extreme reversible waves is given by equation 5.4.e. This expression straightaway gives K value.

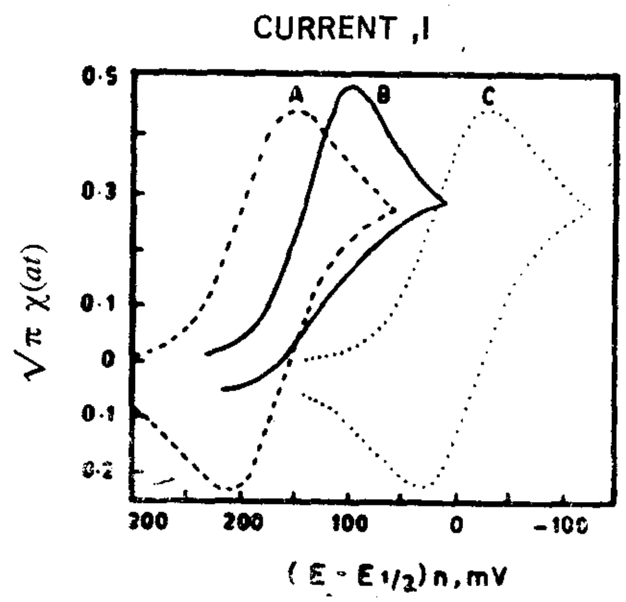

Fig. 5.8 Typical cyclic voltammetric curves for E_rC_r reaction scheme. $K = 10^{-3}$. (A) $\lambda_r \rightarrow \alpha$ (B) $\lambda_r = 10^4$ (C) $\lambda_r = 0$.

Once K value is available, one may choose the KP region where equation 5.4.b is obeyed. The $dEp/d \log v$ in this region must be $(-29.6/n)$ mV. Under these conditions, equation 5.4.b gives λ, from which k_f can be calculated.

5.3.3 DIMERIZATION REACTIONS

Although a number of subsequent chemical reactions may follow charge transfer, the dimerization is commercially very important especially in electro-organic synthesis of adiponitrile [46]. This has prompted a number of theoretical as well as experimental reports of this type of reactions. In this EC scheme, one notices that the forward chemical reaction follows a second order kinetics (Table 5.5) Hence this reaction scheme is denoted as EC_2 scheme. Again EC_{2i} and EC_{2r} reaction mechanisms may be dealt with separately.

Table 5.5

Voltammetric characteristics of dimerization reactions

Scheme :

$$Ox + e \rightleftharpoons R \qquad K = \frac{k_b}{k_f}$$

$$2R \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R - R \qquad \lambda = \frac{k_f \cdot C_{ox}}{nfv}$$

KP region :

$$i_p = 3.17 \times 10^5 \times A \cdot C_{ox}\, v^{1/2}\, D_{ox}^{1/2} \qquad \ldots 5.5.a.$$

$$E_p = E_{1/2} - 0.058 + 0.0197 \log \frac{k_f\, C_{ox}}{v} \qquad \ldots 5.5.b.$$

$$E_p - E_{p/2} = -38.8 \text{ mV} \qquad \ldots 5.5.c$$

$$\frac{dE_p}{d \log v} = -19.7 \text{ mV} \qquad \ldots 5.5.d$$

$$\frac{dE_p}{d \log C_{ox}} = -19.7 \text{ mV} \qquad \ldots 5.5.e$$

$$\lambda_l = \frac{k_f\, C_{ox}}{nfv_l} = 0.80 \qquad \ldots 5.5.f$$

DM region :

$$E_p = E_{1/2} - 0.018 + 0.0297 \log \frac{C_{ox}\, v}{K} \qquad \ldots 5.5.g$$

---

a) EC_{2i} *mechanism*

This reaction scheme and the equations that characterize them completely are presented in Table 5.5 [46-49]. The peak current characteristics are very similar to reversible charge transfer (equation 5.5.a). When the sweep rate is very slow ($\lambda \rightarrow \alpha$) the peak current will be 20 per cent higher when compared with the reversible charge transfer, that is $\lambda = 0$ (equation 5.5.a). However the peak potential variations are very useful in characterizing this scheme (equation 5.5.b). The peak width will be 39 mV. (Note that we have written the reaction scheme with $n = 1$ since this is the only experimental situation known.) The E_p shift with sweep rate and concentration reflects the second order nature of the chemical step. $dE_p/d \log v$ value is around $- 20$ mV when compared with all the first order chemical kinetics discussed earlier (equation 5.5.d). In the first order reactions the E_p is independent of C_{Ox}. However, in the second order dimerizations they shift by 20 mV in the positive direction for 10 times increase in sweep rate (equation 5.5.e). These relations may be used to characterize the reaction scheme very easily.

Once the process is characterized, estimation of the physical quantities follows. At sufficiently fast sweep rate ($\lambda = 0$) one may observe a reversible cyclic voltammogram [47, 48]. This would enable the determination of $E_{1/2}$. Now at lower sweep rates in the pure kinetic region, equation 5.5.b can be used to evaluate k_f using various values of C_{Ox} and v. In the cyclic voltammetric method $i_{p,a}/i_{p,c}$ values have been tabulated for various λ values [47, 49]. Hence this method may also be used to evaluate λ.

A third and simpler method has also been proposed and used widely [50]. The E_p log v plot is first constructed over a wide range of potential. At slow sweep rates the slope would be 20 mV and at very high sweep rates the slope is zero (Fig. 5.9). The intersection point of these two linear portions then occurs at a particular sweep rate, v_i. The λ value at this sweep rate for this dimerization mechanism is 0.80. Hence the rate constant can be directly determined by evaluating this sweep rate v_i (5.5. f).

The second order dimerization is the most widely encountered reaction. However, extensions to higher order reactions can be made in a simple and straightforward fashion [51]. The problem of monomerization before charge transfer may also be treated in a similar fashion [48].

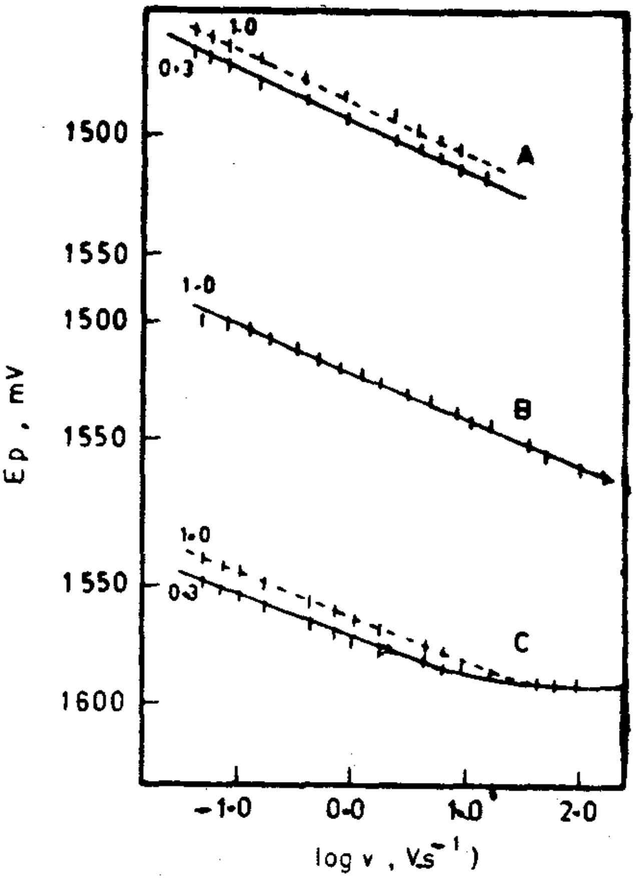

Fig. 5.9 E_p — log v diagram for benzaldehyde. (A) 0.1 *M* veronal buffer/Ethanol; (B) 0.1 *M* phenol buffer/ethanol (C) 0.1*M* Bu_4 N^+ OH^-/ethanol. Number in each curve indicates benzaldehyde concentration in mM [From L Nadjo and JM Saveant, J Electroanal Chem 33 (1971) 419].

In the EC_{2i} mechanism discussed above, one has considered the charge transfer to be reversible. The influence of charge transfer kinetics [32, 52] on this dimerization reaction has also been considered. At very high sweep rate the dEp/d log v would be 60 mV ($\alpha n_a = 0.5$ for single electron transfer) if the irreversible charge transfer controls the overall kinetics.

b) *EC_{2r} mechanism*

In the EC_{2i} mechanism k_b is assumed to be very small compared with $k_f.C_{ox}$. Situations where both the processes are fast may also exist. This situation was dealt with very briefly in a previous work [48]. A more general and comprehensive treatment of EC_2 process covering E_iC_{2i}, E_iC_{2r}, E_rC_{2i} and E_rC_{2r} regions has appeared very recently [53]. The complete LSV behaviour is controlled by three parameters Λ, λ and K in the general case.

From very high sweep rates, one can slowly vary the sweep rate and measure dEp/d log v values and reach various kinetic regions. At a very high sweep rate, the charge transfer itself is comparatively slow and the slope is 60 mV. At slightly slower sweep rates, the charge transfer is fast but the chemical reaction does not exert its influence. The slope in this region is zero. At still slower sweep rates, the *KP* region where dimerization is fast and irreversible would be reached. The slope now will be 20 mV (Table 5.5). At still slower sweep rates, the dimerization reaction would reach equilibrium. The slope again will be zero. However, the peak potential will shift with C_{ox} concentration in this region (equation 5.5.g). If such wide λ regions can be reached for any specific reaction then the system parameters E^o, k_h^o, αn_a, k_f, k_b and K can be completely evaluated [53].

c) *Other dimerization reaction schemes*

Formation of dimer $R-R$ from OX needs do not always proceed in the manner discussed above. A few other reaction schemes are included in Table 5.6 [50, 54, 55]. R for example can couple with OX in a chemical step. The R-OX thus formed being a larger molecular species would also get reduced at the same electrode potential to form $R-R$. Another possibility is the direct $2e$ reduction of OX to give R^- which can react with OX species chemically to form $R-R$.

Since the dimerization reactions are widely observed in organic chemistry, the three mechanisms are termed radical-radical, radical-substrate and ion-substrate mechanisms [54, 55] taking note of the fact that R is a radical, R^- is an ion and OX is the substrate. The name of each mechanism actually derives from the reactant molecules in the slow chemical step. As in the case of radical-raidcal mechanism discussed above dEp/d log v values can be

Table 5.6

Comparative features of dimerization reaction schemes under pure kinetic conditions

Scheme	$\frac{dEp}{d \log v}$ mV	$\frac{dEp}{d \log C_{Ox}}$ (mV)	$\lambda_l = \frac{k_f C_{Ox}}{n f v_l}$
Radical-Radical $Ox + e \rightleftharpoons R$ $2R \xrightarrow{k_f} R - R$	-19.7	19.7	0.8
Radical-Substrate $Ox + e \rightleftharpoons R$ $Ox + R \xrightarrow{k_f} Ox{-}R$ $Ox - R + e \rightleftharpoons R - R$	-29.6	29.6	0.27
Ion-Substrate $Ox + 2e \rightleftharpoons R^-$ $Ox + R^- \xrightarrow{k_f} R - R$	-14.8	14.8	0.060

used to distinguish between these three possibilities. Once the action reaction mechanism is established by this method, one can increase the sweep rate and prepare the E_p – log v plot (similar to Fig. 5.9). λ_i values presented in Table 5.6 may then be used to evaluate the rate constant k_f. More detailed discussions including a few other variations are also available in the literature [50, 54, 55].

5.3.4 ECE MECHANISMS

In all the discussions of following chemical reactions above, one has assumed that the chemical reaction product Z formed from R is not electro-active. In a number of cases, however, further electron transfer after chemical steps is possible. Consider the case where a chemical reaction step is preceded and followed by two electrochemical steps (ECE mechanism Scheme 4). All the three steps can be reversible or irreversible, and hence theoretically one can consider six possible reactions $E_iC_rE_r$, $E_rC_rE_r$, $E_rC_iE_r$ etc. [56–59]. However, the simplest (and probably the only experimentally significant) case where both the charge transfers are reversible shall be considered.

Even in this simplest case, two further possibilities must be considered. If the reduction potential of the product of the chemical reaction C (see reaction scheme 4) is more negative when compared with A ($E_2^o \ll E_1^o$), C would be reduced at more negative potential and A as well as C reduction waves would be distinct and different. In the reverse case ($E_2^o \gg E_1^o$) C would also be reduced at the same potential and only one wave would be noticed. These two cases are considered subsequently. Some other closely related reaction schemes also will be considered subsequently.

a) *More difficultly reducible chemical reaction product* $E_2^o \ll E_1^o$

The voltammetric behaviour under these conditions is presented in Fig. 5.10. At very high sweep rates, no chemical reaction can take place before the measurement time and hence the first wave due to A/B couple would show reversible behaviour. The second will not appear. As the sweep rate is decreased, more and more B would be converted to C and the first wave would show irreversible character. Since C is now available at the electrode surface, the reversible C/D wave is noticed in the more negative potential (Fig. 5.10 b).

If the above qualitative behaviour is noticed over a wide range of sweep rates, one may conclude in general that this mechanism is operative. An analysis of the chemical kinetics can however be done using the first wave alone. This wave will correspond to simple EC_i mechanism discussed earlier (Table 5.3; Section 5.3.2).

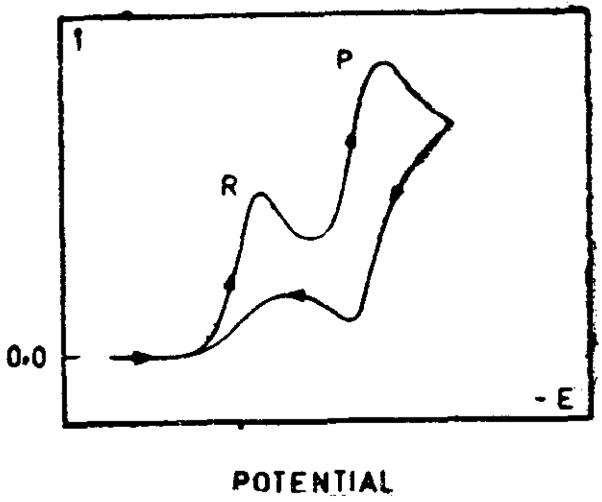

Fig. 5.10 Typical cyclic voltammetric curve for *ECE* reaction scheme when $E_2^o \ll E_1^o$ and k_1 is very large.

b) *More easily reducible chemical reaction product* $E_2^o \gg E_1^o$

In a number of experimental cases, however, the species C formed during the chemical reaction would be much more easily reducible. The reaction scheme and the corresponding equations of interest [59–62] are presented in Fig. 5.11. At sufficiently slow sweep rates the peak current will correspond to $(n_1 + n_2)$ electrons. Otherwise its variation with respect to v and C_A will be quite similar to that of a simple diffusion controlled process. As the sweep rate is increased, the contribution of reduction current due to C will decrease and the wave height would slow approaching that of n_1 electron wave. At sufficiently high sweep rate, the reversible redox wave due to A/B couple alone would be noticed. In the pure kinetic region the $dEp/d \log v$ would correspond to $-$ 29.6 mV (5.7.b). The E_p would be independent of the concentration C_A at constant sweep rate.

If this mechanism is qualitatively established by the above method, kinetic parameters may easily be evaluated as follows. The peak current at very high sweep rate i_p and the kinetic current i_k at slow sweep rates can be measured. The ratio i_k/i_p may be termed as n_{ap} which would be equal to $(n_1 + n_2)$ at slow sweep rates and n_1 at high sweep rates. n_{ap} value versus λ plot has been computed [59–62] and is presented in Fig. 5.11a. Knowing experimental value of n_{ap} the corresponding λ value may be obtained from this figure and hence k_f may be calculated. The numerical equation 5.7.c may also be used for computing λ. In the E_p vs. $\log v$ plot the v_i corresponding to the intersection of the high sweep rate and low sweep rate straight line segments may be obtained (similar to Fig. 5.9). λ_i corresponding to this sweep rate is 0.52 (5.7.d). This function may also be used to compute λ_i.

The presence of *ECE* mechanism of this type can also be qualitatively inferred from multiple sweeping of cyclic voltammograms. At low sweep rates, if B is converted to C during the cathodic sweep, the anodic oxidation wave due to B may not appear in the reverse sweep. However, the C/D couple is now present in the solution and hence oxidation of D and the subsequent reduction of C should now be observed in the multiple sweep experiments (Fig.

Table 5.7

Voltammetric characteristics of EC_iE reaction scheme

Scheme

$$A + n_1 e \rightleftharpoons B \qquad E_1^f \qquad E^f \gg E_1^f$$

$$B \xrightarrow{k_f} C$$

$$C + n_2 e \rightleftharpoons D \qquad E_2^f \qquad \lambda = \frac{k_f}{n f v}$$

DM region:

$$i_p = 2.69\,(n_1 + n_2)\, n_1^{1/2}\, A C_A\, v^{1/2}\, D_A^{1/2} \qquad \ldots 5.7.\text{a}$$

KP region:

$$\frac{dEp}{d \log v} = -\,29.6 \text{ mV} \qquad 5.7.\text{b}$$

$$\frac{i_k}{i_{p,d}} = \frac{0.4 + \lambda}{0.396 + 0\ 469\ \lambda} \qquad \ldots 5.7.\text{c}$$

$$\lambda_i = 0.52 \qquad 5.7.\text{d}$$

5.12). More than one redox couple may also be formed and hence characterized. This, in fact, is one of the very attractive aspects of cyclic voltammetric technique.

c) *ECE and disproportionation reaction schemes*

When an *ECE* process takes place, two redox couples A/B and C/D with the standard electrode potential of E_1^o and E_2^o are present near the interface. A redox reduction between these two couples (equation 5.26) is naturally possible.

$$B + C \rightleftharpoons A + D \tag{5.26}$$

Since B and C are in the same oxidation state, this reaction is often termed as the disproportionation reaction. The equilibrium constant for this reaction is given by the following expression (Section 3.3).

$$K_D = \exp \left\{ \frac{nF(E_2^o - E_1^o)}{RT} \right\} \tag{5.29}$$

Now if E_2^o is more negative than E_1^o (Section 5.3.4a above) K_D will be less than unity and hence the chemical reaction (equation. 5.26) will be shifted to the right. For a few years, some controversy existed as to whether some processes with $E_2^o \ll E_1^o$ could undergo disproportionation [63, 64]. But now it is generally agreed that this type of disproportionation will not be significant unless E_2^o and E_1^o are at least very close to one another [65, 66].

However, reaction 5.26 can indeed become very important when $E_2^o \gg E_1^o$ (Section 5.3.4 b above). Then K_D is greater than 1. The rate constant k_d can reach very high values even if the E^o values vary by 100–200 mV. This fact has prompted the thinking that *ECE* reactions must in effect proceed only through this disproportionation reaction mechanism [67–69].

The overall reaction $A - E$ can proceed by *ECE* (Scheme 4) or disproportionation route. In the disproportionation route one can have any one of the three chemical reactions following charge transfer as the slow step. These reactions are termed as Disp. 1 [67–69], Disp. 2 [24, 70, 71] and Disp. 3 [72]. These reaction schemes and the diagnostic criteria for distinguishing these reaction schemes are presented in Table 5.8. From these studies, one may easily distinguish between EC_iE and Disp. 1 mechanism on the one hand and Disp. 2 and Disp. 3 mechanism on the other hand. Once a particular mechanism is established, one may establish the sweep rate v_i corresponding to λ_i. From the value of λ_i given in Table 5.8, the rate constant can be calculated.

Table 5.8

Comparative features of ECE and disproportionation reaction schemes under pure kinetic conditions

Scheme	$\frac{dEp}{d \log v}$ (mV)	$\frac{dEp}{d \log C_A}$	λ_i
EC_iE mechanism: $A + e \rightleftharpoons B$ $B \xrightarrow{k_f} C$ $C + e \rightleftharpoons D$	−29.6	0	$0.52 = \frac{k_f}{nf v_i}$
Disp−1 mechanism: $A + e \rightleftharpoons B$ $B \xrightarrow{k_f} C$ $B + C \rightleftharpoons A + D$	−29 6	0	$0.52 = \frac{k_f}{n f v_i}$
Disp−2 mechanism: $A + e \rightleftharpoons B$ $B \rightleftharpoons C$ $B + C \xrightarrow{k_f} A + D$	−19.7	19.7	$3.21 = \frac{k_f \cdot C_A}{n f v_i}$
Disp−3 mechanism: $A + e \rightleftharpoons B$ $B \rightleftharpoons C$ $B + C \rightleftharpoons A + D$ $D \rightarrow E$	−19.7	0	—

However, it is obvious from the Table that the diagnostic criteria are very similar for *ECE* and Disp. 1 mechanism. The $n_{ap} - \lambda$ curve for these two mechanisms are also qualitatively very similar. The quantitative features are not different except in a narrow region. (Fig. 5.11). This is so in essence because both these mechanisms involve the same $B - C$ reaction as the slow step. However, all these mechanistic schemes have received a thorough consideration in recent times [28, 33, 73]. Both zone diagram analysis using purely theoretical modelling [28] and analysis of actual experimental results using LSV, CV and a few other techniques [33, 73] suggest that Disp. 1 is a more likely reaction mechanism. However, one may employ EC_iE scheme for mechanism analysis if the diagnostic criteria for this mechanism are fulfilled as has been done for such a long period so extensively. However, problems will crop up when another competitive reaction (say nucleophilic substitution) is to be considered along with the *ECE* mechanism (say hydrogenation). Then the rate parameters will be different depending on whether EC_iE-substitution or Disp-Substitution pathways are followed [74].

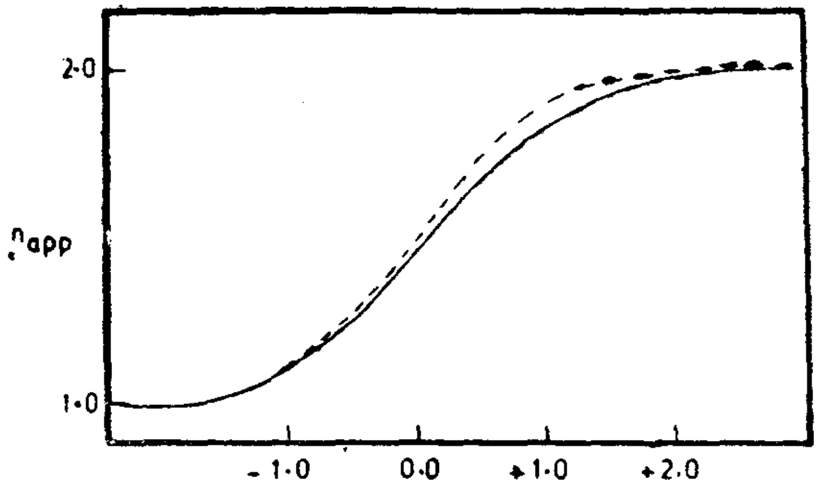

Fig. 5.11 n_{app} value for Disp. 1 (———) and *ECE* (– – – –) reaction schemes as a function of λ [From L Nadjo and JM Saveant, J Electroanal Chem 33 (1971) 419].

5.3.5 HOMOGENEOUS REDOX CATALYSIS

In most of the solution phase redox reactions, the electron transfer would be fast but there are occasions when this can indeed be very slow. Redox couples that are small and highly solvated in the medium and large biological redox species whose redox centres are spatially hindered from approaching the electrodes are examples of such difficultly reducible species. If E_2^o is the redox potential of these species (A/B say) one may have to apply an excess cathodic overpotential (which at times may approach as much as 1.0 V) to carry out the reduction of A to proceed at appreciable rate (Chapter 4).

Now suppose another species OX is added to a solution containing A. If the E_1^o of OX/R couple is more negative than E_2^o an interesting situation would develop. Around E_1^o, the OX would be reduced to form R (see reaction scheme in Table 5.9). In the solution, however,

Table 5.9

Voltammetric characteristics of EC_{redox} reaction schemes

Scheme

$$Ox + ne \rightleftharpoons R \quad E_1^f$$

$$R + A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ox + B \qquad \lambda = \frac{\sigma\, k_f\, C_A}{n\, f\, v}$$

$$A + \sigma\, e \rightleftharpoons P$$

KP region:

$$i_k = nFA\; C_{Ox}\; D_{Ox}^{1/2}\; (\sigma\, k_f\, C_A)^{1/2} \qquad \ldots 5.9.a$$

$E_r C_i$, redox:

$$\frac{i_k}{i_{p,d}} = \frac{\lambda^{1/2}}{0.446} \qquad \ldots 5.9.b$$

$E_i C_i$, redox:

$$\frac{i_k}{i_{p,d}} = \frac{\lambda^{1/2}}{0.496\; (\alpha\; n_a)^{1/2}} \qquad \ldots 5.9.c$$

R is less stable when compared with *A*. Hence the reaction between *R* and *A* would proceed spontaneously in solution. Note that this reaction regenerates *OX*. In this way, the surface concentration of *OX* increases to very high values. In effect, during the electrochemical process more and more of *A* is converted into the product. But the redox couple *OX*/*R* remains unaffected. Hence this type of overall reaction schemes is called homogeneous redox catalysis.

LSV and CV techniques may be very conveniently used for studying this type of reactions. In the absence of *A*, the redox system alone would show behaviour corresponding to reversible charge transfer. The peak current $i_{p,d}$ under these conditions can be measured. Now if *A* is added, the current would increase substantially depending on the value of λ (Table 5.9). At sufficiently small sweep rates the kinetic current i_k would become independent of sweep rate (equation 5.9 a). This expression straightaway gives k_f value. The λ value and hence k_f value may also be obtained from $i_k/i_{p,d}$ expression (equation 5.9. b) [20, 23, 75].

Redox catalysis would also be noticed for irreversible charge transfer behaviour of *OX*/*R* couple as long as *OX*/*R* reduction at the electrode surface is kinetically easier when compared with *A*/*B*

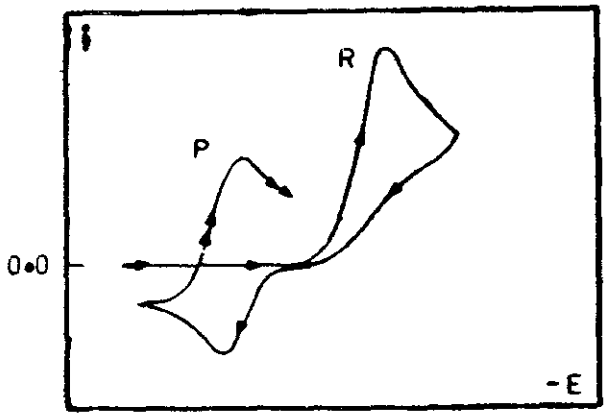

Fig. 5.12 Typical multisweep cyclic voltammogram for an *ECM* reaction scheme when $E_2^o \gg E_1^o$ and k_1 is very large. The reversible wave corresponding to the second process is noted in the second sweep.

reduction [23, 76]. The current ratio expression, of course, is slightly different since the $i_{p,d}$ expression for *OX*/*R* is different (equation 5.9 c). In the above equations σ is the stoichiometric number or the number of electrons for converting one molecule of A into the final product P. These equations were derived under the assumption that $C_A \gg C_{OX}$ which can also be satisfied experimentally by taking large excess of A when compared with OX ($C_A/C_{OX} \gg 10$).

Redox catalysis where the $A + R$ reaction is reversible has been analyzed for LSV studies [77]. The kinetics is now controlled by equilibrium constant K as well as k_f. In situations where k_f and k_b are very fast and C_A is not very much greater than C_{OX}, two reduction waves are noticed [21]. By measuring the catalytic current of the same substrate couple (A/B) with different redox catalysts, one can in fact obtain parameters such as E_2^o of AB couple which cannot be obtained by any other method [21, 78]. This approach may serve as a potential tool for the estimation of redox behaviour of biological molecules which are directly reducible at the electrode surface.

In the redox catalytic simulations $C_A \gg C_{OX}$ and $D_{OX} = D_R = D_A = D_B$ are the general assumptions. However, both these assumptions can be eliminated [18, 21, 79]. Peak current ratios can still be employed to evaluate the rate constants. However the dimensionless parameter λ must be suitably defined for these cases.

5.3.6 ELECTROCHEMICAL INDUCTION

In all the reaction schemes considered so far (including redox catalysis), n electrons are actually consumed for the conversion of any reactant to product. Recently it has also been established that electricity can be used to stimulate or induce chemical processes.

Consider the reactant R reduced at the electrode to R^-. In this electronically excited state, it can be converted to a product P^-. Now if E_2^o of P/P^- couple is more negative when compared with E_1^o of R/R^- couple, around E_1^o, R^- would tend to react with P. The whole sequence can be represented as follows:

$$R + e \rightleftharpoons R^- \qquad 5.30$$

$$R^- \rightarrow P^- \qquad 5.31$$

$$P^- + R = R^- + P \qquad 5.32$$

Scheme 6

Reaction 5.31 produces P^- from R^- and in reaction 5.32 this P^- in turn produces R^- from R. In this cycle, the reactant R gets converted to the product P without the consumption of electricity. In the most efficient reaction of this type, the electricity consumption should approach zero. However, in practical situations R^- as well as P^- may undergo some other chemical reactions.

LSV and CV experiments may be used not only to quickly establish the presence of this type of electrochemical induction but also to evaluate the efficiency of this process [80]. During the time scale of LSV experiment for example, if reactions 5.31 and 5.32 are very slow, the peak current due to R would correspond to a 1 electron wave. If on the other hand these reactions are very fast, they would lower the surface concentration of R to a level close to zero. This would lead to a complete disappearance of R/R^- wave and the appearance of a new wave due to P/P^- at more negative potentials. If there are other side reactions which reduce the efficiency of induction, the n_{ap} value of R/R^- peak current would be between 0 and 1. This n_{ap} ratio thus is a measure of the efficiency of the electrochemical induction process.

Digital simulation works on electrochemical induction have been carried out primarily for nucleophilic substitution of haloaromatic compounds [80, 81].

$$ArX + e \rightleftharpoons ArX^{-\cdot} \qquad 5.33$$

$$ArX^{-\cdot} + \overset{k_1}{\underset{k_2}{\rightleftharpoons}} Ar^{\cdot} + X^- \qquad 5.34$$

$$Ar^{\cdot} + Nu^{-\cdot} \overset{k_2}{\rightleftharpoons} Ar\,Nu^{-\cdot} \qquad 5.35$$

$$Ar\,Nu^{-\cdot} + ArX \rightleftharpoons Ar\,Nu + ArX^{-\cdot} \qquad 5.36$$

Scheme 7

In aprotic media, the most important competing pathway for the above process is the further reduction of $Ar^{\cdot}$. This is the typical *ECE* process.

$$ArX + e \rightleftharpoons ArX^{-\cdot} \qquad 5.33$$

$$ArX^{-\cdot} \overset{k_1}{\rightleftharpoons} Ar^{\cdot} + X^- \qquad 5.34$$

$$Ar^{\cdot} + e \rightleftharpoons Ar^- \qquad 5.37$$

$$Ar^- + H^- \rightleftharpoons ArH \qquad 5.38$$

Scheme 8

The main factor that decides whether the substitution (Scheme 7) or hydrogenation (Scheme 8) is the predominant process is the competition between reactions 5.34 and 5.35. If k_1 is very large, the anion radical $ArX^{\overline{\cdot}}$ will decompose very near the electrode and hence further electron transfer will predominate. If $k_2 C_{Nu} \gg k_1$ then the $Ar^{\cdot}$ radical would undergo substitution and hence electrochemical induction. The n_{app} value as a function of the dimensionless parameter $k_1/k_2 C_{Nu}$ is presented in Fig. 5.13. Thus by a few LSV curves in the presence and in the absence of *Nu* in the medium one can estimate the efficiency of electrochemical induction by this method.

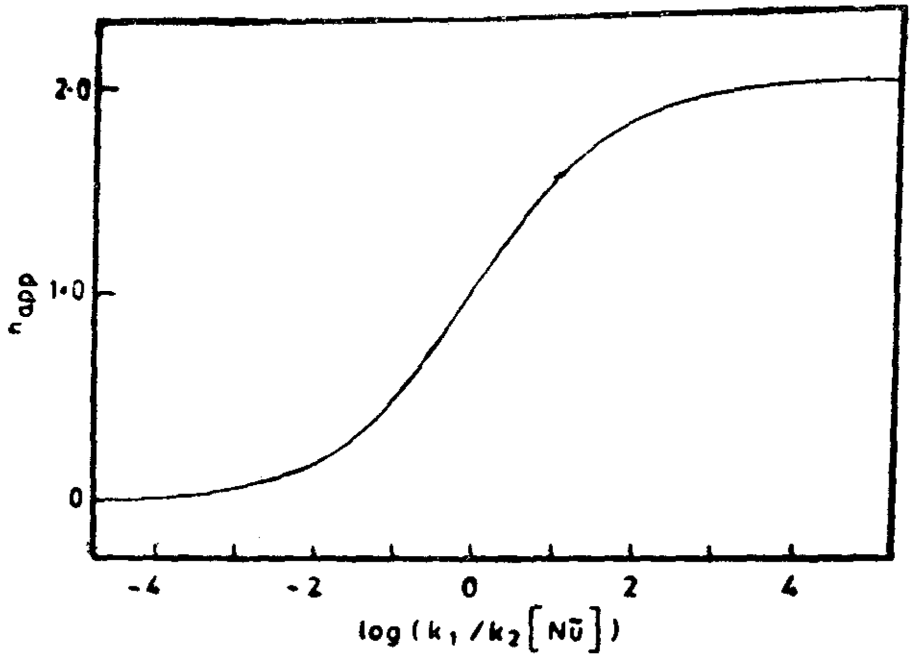

Fig. 5.13 n_{app} value in an electrochemical induction process. Competition between electrochemical induction ($n_{app} \rightarrow 0$) and simple ECE reaction ($n_{app} \rightarrow 2$), as a function of nucleophile concentration. [From C Amatore, JM Saveant and H Thiebault, J Electroanal Chem 103 (1979) 303].

5.3.7 EFFECT OF MEDIUM

In the discussion so far in this section (Section 5.3) a number of possible reaction schemes have been considered. However, all the possible reaction schemes have not been exhausted. A few possible chemical reactions following charge transfer ($A + e \rightleftharpoons B$) are presented in Table 5.10. In addition, we may also consider substitution reactions [82], intra-molecular cyclization [83, 84], isomerization reactions and a number of other chemical reactions associated with charge transfer. However, these multifarious reactions may also be treated using the same principles and methods discussed above. For example, the same methods for the study of *EC* reaction scheme (Table 5.3) may be employed for the study of decomposition of anion/cation radicals, substitution and elimination reactions.

However, when attempts are made to apply the general reaction schemes discussed above to new reaction schemes, the reaction sequence and reaction orders of each reactant must be carefully considered. The reaction schemes mentioned above contain only the reactant molecules, intermediates and products. In actual experiments, the chemical reactions may be affected by acid-base reactions, complex formation, solvation and ion-pair formation as well. In some cases the chemical reactions like protonation, formation or dissociation of a complex or even solvation may be the slow chemical step. For example, if one considers the protonation steps in a dimerization sequence considered in Section 5.3.3, one may get a number of reaction sequences with a large variety of reaction order sequences [85-87]. The variation of E_p (or $E_{p/2}$ if a wave is noticed) with sweep rate concentration of reactant A and the concentration of other medium component X may be utilized to establish the reaction orders experimentally and compared with the ones predicted experimentally [85–87].

The general method for the evaluation of these reaction order parameters were introduced earlier (Section 5.2.4a). Model calculations of the values S_1, S_2, S_3 values corresponding to equations 519 to 5.21 are presented in Table 5.10 for a few reaction schemes following charge transfer. These constants multiplied by 59.2 mV. give the $(dEp/d \log v)$, $(dEp/d \log C_A)$ and $(dEp/d \log C_X)$ values straightaway. By matching the predicted values with those of experiments, one can easily ascertain the actual reaction mechanism.

However some caution must be exercised in using these expressions.

a) These expressions are valid only when the whole process is under pure kinetic control. Some variations in the values may be noticed if the sweep rate or rate constants possess such values where mixed

Table 5.10

Comparative features of different reaction schemes under pure kinetic conditions.

No.	Mechanism	Rate law	b^B	a^B	i^B	x^B	S_1^C	S_2^C	S_3^C
1.	$B + X \rightarrow C$	$k\,C_B C_X$	1	0	0	1	$\frac{1}{2}$	0	$\frac{1}{2}$
2.	$B + X \rightarrow C$ $B + C \rightleftharpoons A + D$	$k\,C_B C_X$	1	0	0	1	$\frac{1}{2}$	0	$\frac{1}{2}$
3.	$2B \rightarrow C + A$ $C \rightleftharpoons D$	$k\,C_B^2$	2	0	0	1	$\frac{1}{3}$	$\frac{1}{3}$	0
4.	$2B \rightleftharpoons C + A$ $C + X \rightarrow D$	$\frac{k\,K\,C_B^2\,C_X}{C_A}$	2	-1	0	1	$\frac{1}{3}$	0	$\frac{1}{3}$
5.	$B + A \rightarrow C$	$k\,C_B . C_A$	1	1	0	0	$\frac{1}{2}$	$\frac{1}{2}$	0
6.	$B + A \rightleftharpoons C$ $C + B \rightarrow D + A$	$k\,C_B^2\,C_A$	2	1	0	0	$\frac{1}{3}$	$\frac{1}{3}$	0
7.	$2B + X \rightarrow C + I$	$\frac{k\,C_B^2\,C_X}{C_I}$	2	0	-1	1	$\frac{1}{3}$	0	$\frac{1}{3}$
8.	$B + A \rightarrow C$	$k\,C_B C_A$	1	1	0	0	$\frac{1}{4}$	$\frac{1}{4}$	0
9	$B + X \rightleftharpoons C + I$ $C \rightarrow D$	$\frac{k\,C_B C_X}{C_I}$	1	0	-1	1	$\frac{1}{4}$	$-\frac{1}{4}$	$\frac{1}{4}$
10.	$A + 2e \rightleftharpoons B$ $B + X \rightarrow C$	$k\,C_B C_X$	1	0	0	1	$\frac{1}{4}$	0	$\frac{1}{4}$

First step for Mechanism 1 – 9. $A + 1e \rightleftharpoons B$.

B – refer eq. 5.18

C – refer eq. 5.19 to 5.21.

kinetic and diffusion control exists. These small variations must not be taken to mean that the reaction mechanisms have changed.

b) The above generalization would hold only if the rate determining chemical step is completely irreversible (similar to EC_i in Table 5.3). If the reverse reaction also becomes important (similar to EC_r in Table 5.4) these expressions would not be applicable.

c) In the same reaction sequence, the *rds* can change with concentration. Consider for example the dimerization reaction following the radical-substrate coupling mechanism.

$$O_X + ne \rightleftharpoons R \tag{5.1}$$

$$R + O_X \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O_X{-}R \tag{5.37}$$

$$O_X - R + R \xrightarrow{k_2} R - R + O_X \tag{5.38}$$

Scheme 8

Note that reaction 5.38 is second order in R whereas reaction 5.37 is only first order in R. Hence as concentration C_{OX} is increased, reaction rate of 5.38 would increase much faster than 5.37. Hence the *rds* can be reaction 5.38 at low C_{OX} values whereas reaction 5.37 may become *rds* in the opposite case [28]. This type of change in *rds* has in fact been established in the case of oxidative dimerization of 4-methoxy biphenyl [28].

d) With change in concentration, the reaction mechanism may also change from one pathway to another competitive pathway (*ECE* to disproportionation etc.). Hence any mechanistic analysis of a new system must take into consideration all these possibilities and a correct mechanistic prediction also requires good physicochemical reasoning in addition to the methodology discussed above.

5.4 THE PROCESS

From the early sixties, extensive qualitative and quantitative information on chemical reactions associated with charge transfer have been obtained from LSV and CV studies. Some important aspects have also been reviewed from time to time [16, 88–92]. Most of these studies however are confined to organic processes associated with electron-transfer. In spite of the fact that these methods are equally applicable to the analysis of inorganic, organometallic and biologically important molecules [93], developments in these directions are indeed rather slow. There is ample scope for the study of inorganic systems using these techniques.

In the literature, one often finds that LSV and CV are first used to obtain the qualitative information on the nature of the process and subsequently a number of other techniques are employed to obtain quantitative data. Use of additional technique to obtain more solid evidence for a specific mechanism is always a welcome feature. Coulometry may, for example, be employed to obtain *n*, the number of electrons involved in the process. Chronoamperometry may be more straightforwardly employed to determine diffusion coefficient. Double potential step chronoamperometry would be useful to get a few kinetic parameters by simulation and curve fitting where competitive pathways are involved. With a sound knowledge of the methods developed for LSV and CV here, it is not difficult to follow these methods wherever required [13–16].

However, it would be worthwhile to stress that both LSV and CV may be used to obtain practically all the quantitative information of chemical and electrochemical steps involved in the overall process. As discussed above, quantitative relations for a number of reaction schemes have been worked out. The same methodology is applicable for newer schemes that may be evolved in future. Although literally hundreds of experimental works may be quoted to substantiate this viewpoint, this chapter shall restrict itself to very few works which have primarily employed LSV and CV for data analysis.

5.4.1 PRECEDING CHEMICAL REACTIONS

Formaldehyde dehydration (equation 5.29) was in fact one of the early examples of preceding chemical reaction associated with charge transfer kinetics. However LSV and CV were not employed extensively for the study of this process. Polarographic techniques have been extensively employed to obtain the kinetic information [94; 95]. Recently some qualitative information on dehydration kinetics [96] has been obtained from cyclic voltammetry on glassy carbon electrodes.

Dissociation kinetics of weak acids can be obtained by this method. The acid dissociation kinetics of phenazine [97] was quantitatively investigated using LSV. The presence of acidic and basic forms of phenyl glyoxalic acid over a narrow pH range was established by this method [98].

Formation of reversibly reducible complexes can be a slow step in a number of electron transfer processes. Typical CV curve showing the formation of thiocyanate complex of Ti^{4+} is shown in Fig. 5.14b.

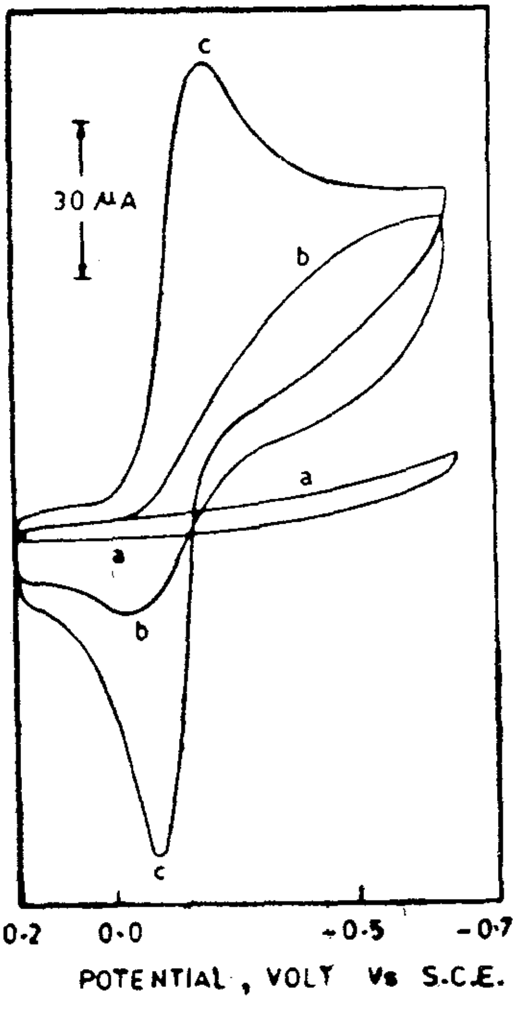

Fig. 5.14 Cyclic voltammograms of Ti^{4+}/Ti^{3+} couple in presence of CNS^- anions on glassy carbon electrodes. (a) 2.0 *M* H_2SO_4 + 8.5 mM Ti^{4+} (b) a + 0.2*M KCNS* (c) *a* + 0.8 *M KCNS*.

Note the wave form in the cathodic sweep and the peak form in the anodic sweep. The kinetic influence disappears at higher sweep rates as well as on adding higher concentration of thiocyanate (Fig. 5. 14 c) [99]. Similar studies can provide information on complex formation kinetics of a number of inorganic systems.

5.4.2 FOLLOWING CHEMICAL REACTIONS

In aprotic media, organic molecules gave two successive one electron waves during reduction as well as oxidation. However, the dianions formed during the second reduction steps were shown to react very strongly with the medium in a following chemical step [100, 101]. On increasing the sweep rate or on increasing the solvent purity [102, 103], the influence of this chemical reaction could be eliminated. Similar dication activity was also observed during anodic oxidation. Instability of dianion was also noticed for a number of other substituted aromatic compounds. Typical CV curve for the reduction of m-bromobenzophenone is presented in Fig. 5.15a [104]. The first wave due to the formation of anion radical is stable. The second wave is unstable and undergoes a fast protonation even at a fast sweep rate of 10 V/sec.

However, in a number of inorganic [105, 106] as well as organic compounds, the chemical species formed by the first electron transfer itself was found to be unstable. Some interesting electro-generated organic species of this type are substituted cyclobutene cation radicals [107], oxidized azide radicals [108], fluoromethyl radicals [109], and oxidized carboxylates [110, 111]. The LSV and CV techniques described earlier (Section 5.3.2) for the study of *EC* reaction schemes have been employed to evaluate the rate parameters. If the chemical reactions are very fast, we may resort to low temperature experiments to evaluate the chemical reaction kinetics [112].

The electro-generated anion radicals are very reactive towards weak acids. The rate constant of the following chemical reaction of the electrogenerated base with various weak acids can be evaluated using LSV and CV technique [113]. This method seems to have a great potential for evaluating the acidities of very weak acids. Anodically generated cation radical reactivity may similarly be utilized to evaluate the basicity of very weak bases.

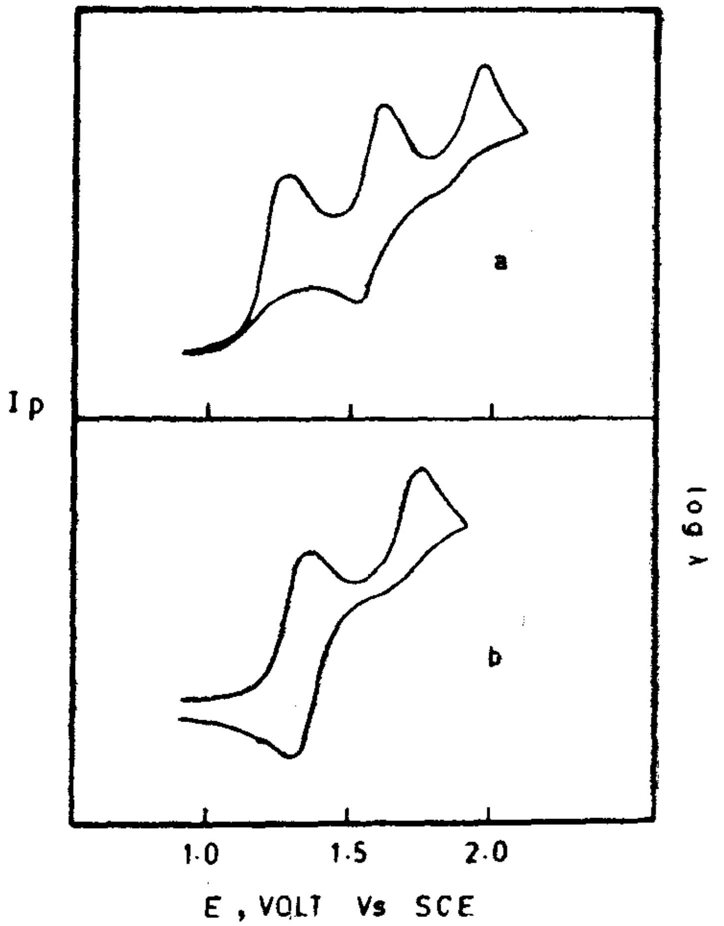

Fig. 5.15 Cyclic voltammograms of m bromo benzophenone in DMF containing 0.1*M* $Et_4N^+ClO_4^-$ at 20°C. (A) 0.1 V sec^{-1} (B) 200 V sec^{-1}.

[From L Nadjo and JM Saveant, J Electroanal Chem 30 (1971) 41]

5.4.3 DIMERIZATION REACTIONS

Being the basic mechanism of the commercially successful adiponitrile process (equation 5.39), this type of reaction has been studied very extensively [91, 114]. Very early LSV studies on dimerization reactions were however reported on the reduction of carbonyl compounds [71] and imminium cations [115]. Quantitative dimerization works on activated olefins were reported very soon. The dimerization kinetics of diethyl fumarate, diethyl maleate [116, 117] and a few other related compounds [118–120] were studied in quick succession. Radical-radical dimerization was found to be the most widely observed mechanistic pathway in these studies. Some detailed studies on a large number of activated olefinic compounds including the influence of added water and proton donors were also reported [121].

Recently it was noticed that a few organic compounds also undergo reversible dimerization. The CV curves show totally reversible behaviour both at high as well as slow sweep rates [122]. Another extreme case of slow charge transfer kinetics followed by reversible dimerization was also established experimentally [123].

In recent years, the electrodimerization of 9-cyano anthracene in aprotic media has been considered for detailed studies by a number of research groups [53, 114, 124, 125]. The influence of water addition as well as the question of whether radical-radical or radical-substrate mechanism predominate in this reaction mechanism have been analyzed in some detail. Figure 5.16 illustrates the $dE_p/d \log v$ behaviour of this reversible dimerization process over a very wide sweep rate (and hence λ) range [53]. In this detailed work, complete details of electron transfer and dimerization steps have been evaluated.

It must be noted, however, that all these dimerization studies were mostly confined to aprotic medium. Studies of these reactions in aqueous medium containing tetra-alkyl ammonium salts would be of great commercial interest. Some polarographic work on these lines have already been reported [126, 127]. Studies on other solid electrodes are also of interest [128]. Some attempts are being made to predict the dimerization reactions on quantum mechanical basis.

5.4.4 ECE REACTIONS

The *ECE* reactions are the general class of reactions which incorporates a variety of chemical steps such as dissociation, protonation, substitution, elimination and isomerization reactions in between two charge transfer steps. Hence this class of reactions have been studied very extensively.

As discussed earlier, when the second electron transfer is more difficult than the first one (Section 5.3.4) both the voltammetric peaks would be separately noticed and their study is very much easier. The voltammetric behaviour of *m*-bromobenzophenone at slow sweep rate is given in Fig. 5.15b. [104]. At slower sweep rates, the anion radical dissociates and undergoes further electron transfer and protonation to form benzophenone according to the following overall reactions:

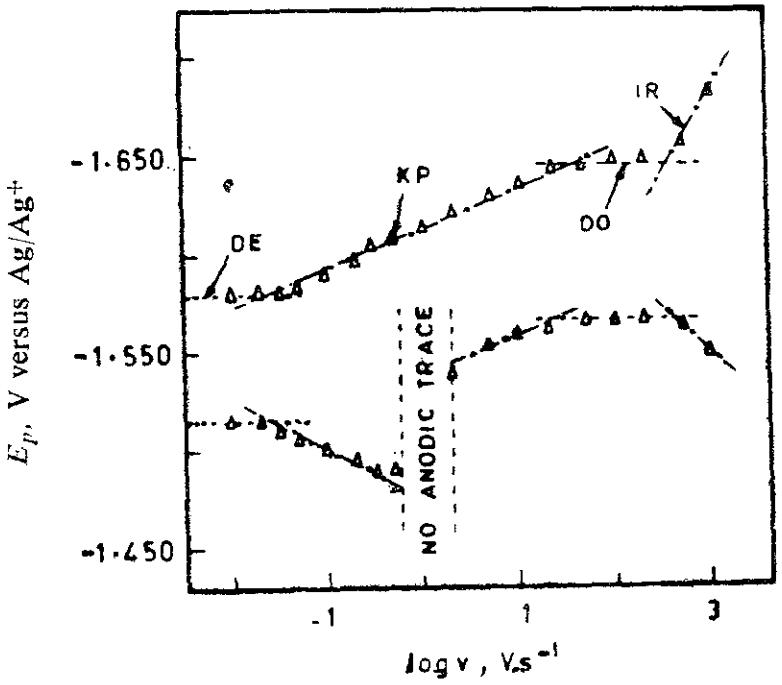

Fig. 5.16 $E_p - \log \nu$ curve for the reduction of 9 cyano anthracene (1 mM) in *DMSO* containing 0.1*M* *Li*ClO$_4$ at 20°C. The straight lines correspond to theoretical predictions at various zones (Top curve Δ) cathodic and (bottom curve Δ) anodic experimental E_p values.

[From C Amatore, D Garreau, M Hammi, J Pinson and JM Saveant, J Electroanal Chem 184 (1985) 1].

$$BrC_6H_4\ CO\ C_6H_5 + 2e + H^+ \longrightarrow C_6H_5\ CO\ C_6H_5 + Br^- \qquad 5.39$$

The benzophenone formed undergoes further two step reduction at more negative potentials to form stable anion radical (reversible second wave) and unstable dianion (irreversible third wave). This type of behaviour is generally noticed with other halogen substituted aromatic hydrocarbons [130, 131] as well.

When a protonating agent such as phenol is added to an aprotic medium containing, for example, substituted anthracenes, the anthracene anion radicals formed during CV experiments are protonated in a slow chemical step. The protonated species undergo further reduction at the same electrode potential [132]. This type of ECE electrohydrogenation processes where $E_2 \ll E_1$ have been studied for a number of aromatic compounds [29, 72, 73, 132]. The general discussions on *ECE* and disproportionation pathways discussed earlier (Section 5.3.4.) have also been mainly considered for this type of reaction [29, 133]. However, it is needless to say that these diccussions are relevant to all the *ECE* processes discussed below.

The ECE reaction scheme is applicable to anodic oxidation followed by deprotonation [134]. These reactions are the exact anodic analogues of the cathodic electrohydrogenation processes considered above. The cation radicals generated by anodic oxidation [135-137] may easily undergo substitution by pyridines and substituted pyridines which are more easily oxidizable. The anion radicals generated by electrochemical reduction may also undergo substitution after decomposition [82]. Such substitution processes may be important from synthetic as well as mechanistic angle.

A classical example of the *ECE* reaction pathways was the oxidation of aniline on carbon paste electrode [138]. The oxidized aniline cation can couple with another aniline molecule in two ways. If N-N bond coupling occurs, hydrozo benzene is formed which further rearranges to benzidine in the same medium. If N-C bonding takes place, *p*-amino diphenylamine is formed. Hence in the second CV sweep, one notes the redox waves due to benzidine and *p*-amino diphenylamine in the same solution containing aniline alone (Fig. 5.17). By taking the CV of the above two authentic samples in the same solution, this conclusion would be clearly easily verified (Fig. 5.17 b c). Recently substituted anilines were shown to exhibit similar CV behaviour.

The electrolyte medium can influence the electrochemical behaviour in a variety of ways. The pH of the medium, for example, can influence cyclization [139] and hydrolysis [140]. It may be stated that the type of chemical reactions studied in this type of situation is only limited by one's imagination and the capability to select appropriate electroactive molecules and reaction medium.

Another type of electrochemical processes that can be handled by ECE reaction scheme is the isomerization reactions. The *cis*-

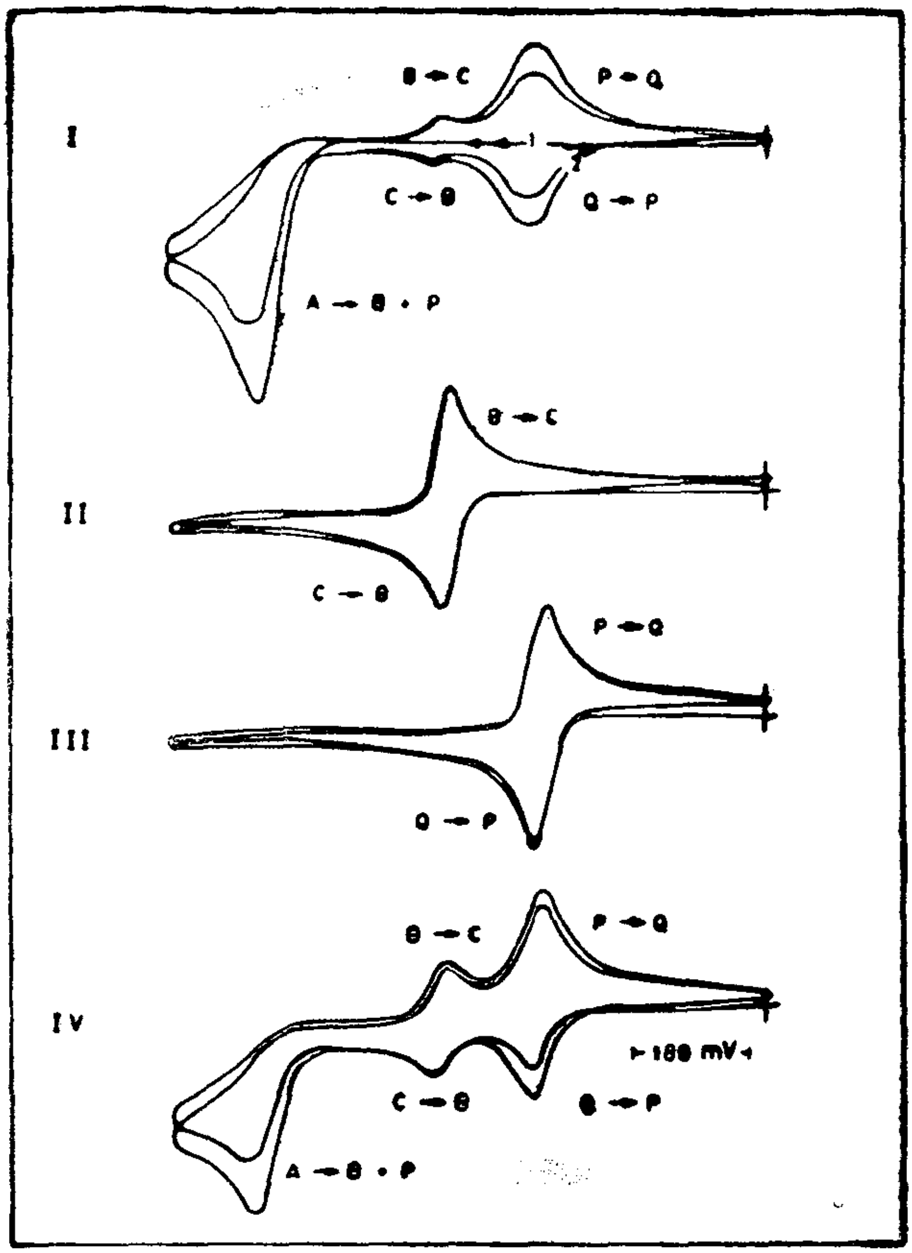

Fig. 5.17 Multisweep cyclic voltammograms for the oxidation of aniline showing the formation of two different electroactive products (I) aniline *A* alone (II) benzidine *B* alone (III) *p*-amino diphenylamine *P* alone (IV) Mixture of *A*, *B* and *P*.
[From RN Adams, Electrochemistry at Solid Electrodes, Marcel Dekker, N York (1969)].

trans isomerism of substituted olefins [141, 142] axial, equitorial isomerism of substituted cyclohexanes and related molecules [42, 43], 9–9′ bond twisting of bianthrene and substituted bianthrene molecules [143–146] and elimination of 1–2 dihalides [147] are some of the classical isomerization reactions studied by this method. The CV behaviour of bianthrene that exists in two isomeric forms, *A* and *B*, is presented in Fig. 5.18 [145]. On reduction in the first sweep, the *A* form is reduced in a two-electron step to B^{2-} species. These show reversible redox waves in the less negative potential region (Fig. 5.18). More comprehensive results on this type of processes have also appeared recently [148, 149].

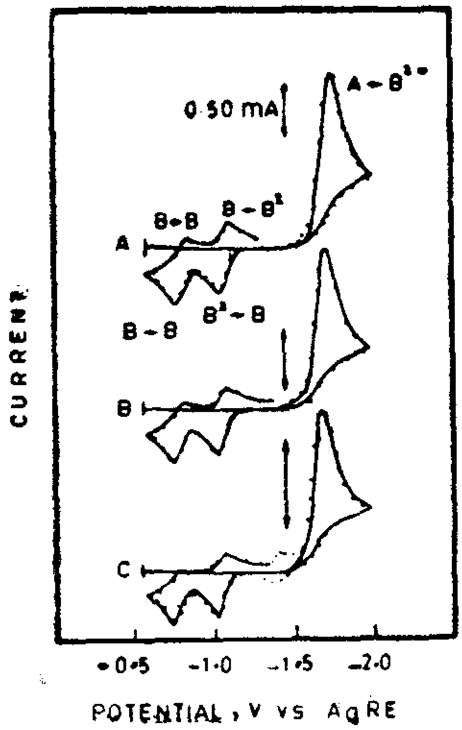

Fig. 5.18 Experimental (——) and digitally simulated (......) cyclic voltammograms for the reduction of 2,3,2′,3′ dibenzo-7, 7′-dimethyl bianthrone (1.04 mM) in *DMF* containing 0.1*M* Et_4 N^+ ClO_4^- at 20°C on Pt electrode. Sweep rate (A) 20.0V sec^{-1} (C) 10.0V sec^{-1} (C) 5.0 V sec^{-1}

[From T Matsue, DH Evans and T Agranat, J Electroanal Chem 163 (1984) 137].

ECE reactions must occur quite frequently in inorganic redox processes. They have not yet been considered in greater detail.

Some excellent quantitative work on a few selected systems are however available [93, 150, 151]. There is large scope for the study of inorganic redox systems of biological interest.

5.4.5 HOMOGENEOUS REDOX CATALYSIS

CV was first employed to measure the redox catalytic reduction of NH_2OH to NH_3 using Ti^{4+}/Ti^{3+} redox system as the catalyst [76] and H_2O_2 reduction to H_2O using Fe^{3+}/Fe^{2+} system as the catalyst [76]. Recently the same processes were also studied on glassy carbon electrode to establish that the solution phase chemical reaction kinetics is indeed independent of the electrode material used [152].

Studies on this type of processes have indeed received greater attention in recent years. Organic redox catalysts like diphenyl anthracene, napthalene anion radicals are being extensively used to catalyze a number of reductive and oxidative catalytic processes [153-155]. Extensive theoretical developments have enabled the elucidation of thermodynamics and kinetics of redox systems that undergo slow electron transfer at the electrode surface [21, 78]. A number of new organic compounds such as nitroimidazoles [156], methylene blue [157] and tosyl esters [158] have been catalytically reduced. Amines have been shown to be catalytically oxidized to nitriles [159]. Redox catalytic oxidation of pyridine derivatives also have been studied [160].

Over the past few years, the redox catalytic reactions have also approached the areas of some challenging electrochemical processes that are being actively studied. The very important O_2 reduction reaction has been shown to be catalyzed by methyl viologen redox couple [18]. The CV of methyl viologen in the absence and in the presence of O_2 is shown in Fig. 5.19. The peak current of the first reduction wave of methyl viologen increases substantially due to the redox catalytic reduction of oxygen at this potential. Similarly, ruthenium bipyridyl complex can catalyze hydrogen evolution reaction. CV has been used to study the catalytic reduction of CO_2 by inorganic redox catalysts [161, 162]. Redox catalysis has been shown to be useful for carrying out some substitution reactions [163].

The term ‘electrocatalysis’ itself is used in a very wide sense. All aspects of heterogeneous electrocatalysis have been reserved,

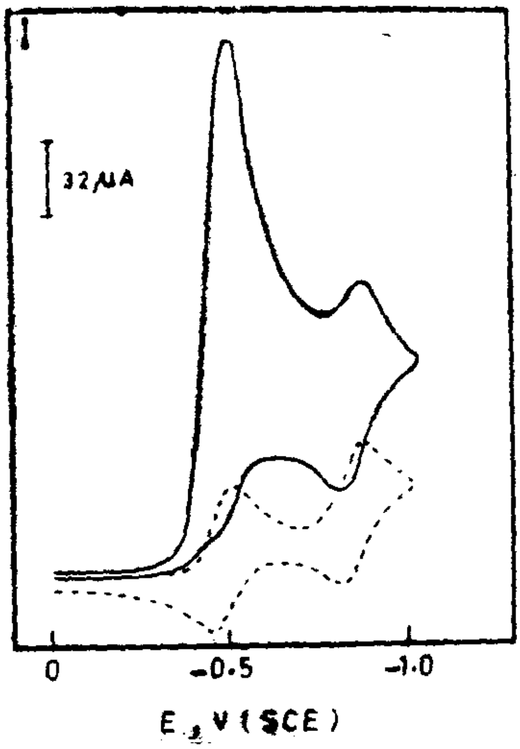

Fig. 5.19 Cyclic voltammograms of methyl viologen dication (2 mM) in DMSO containing 1.0 *M* $ClCH_2COOH$ and 0.1 *M* $Bu_4N^+BFu^-$ at 25°C in the absence (....) and in presence (——) of O_2 (2.1 mM). sweep rate 0.2 V sec^{-1}
[From CP Andrieux, P Hapiot and JM Saveant, J Electroanal Chem 189 (1985) 121]

where an electrode has a specific role to play, for a later section (Chapters 11 to 14). Only those processes are being considered where the redox catalytic effect is due to a chemical reaction in the solution close to the electrode surface. Other chemical reactions that influence the electrochemical processes are also sometimes called 'electrocatalysis'. For example, acid-base reactions [164] and complex formation reactions [165] are termed as 'electrocatalytic' reactions. Some protonation processes that ultimately result in hydrogen evolution are conventionally called catalytic hydrogen evolution reactions [166]. These reactions can usually be treated using other reaction schemes discussed above such as *CE*, *EC*, *ECE* reactions. However, it must be emphasized that these are not redox catalytic reactions discussed above. In all these processes, the electron transfer is facilitated by the formation of a new electroactive **species** (such as protonated or complexed species) and hence are called catalytic processes. However, in homogeneous redox catalysis one is enhancing the charge transfer of the *same electroactive species* by carrying out the reaction in solution using other redox catalyst. A clear understanding of these facts can avoid a lot of confusion when the literature on these processes are scanned through.

5.4.6 ELECTROCHEMICAL INDUCTIONS

The problem of nomenclature was discussed regarding the all-encompassing term 'electrocatalysis' which is also relevant for this type of process. An excellent review dealing with this type of process terms this as 'electrocatalysis' [167]. At least to distinguish this type of process from the other, a distinct term is desirable. Since in these processes one gets yields much larger than the electricity consumed [168–170] 'electrochemical induction' [82] seems to be a suitable term.

Nucleophilic substitutions are the most widely studied reactions of this type [80–82, 167, 170–173]. The electrochemical induction would be very efficient if the E° of the product is more negative than the reactant. However, even if the E° of the product is slightly less negative, the influence of the overall chemical reaction would still effect electrochemical induction. Some interesting CV curves obtained experimentally with such less favourable systems are compared with those simulated with the numerically simulated ones using appropriate kinetic parameters in Fig. 5.20. The excellent agreement between theory and experiment may be noticed very easily [81]. However, if the product has a much positive redox potential when compared with the substrate, no electrochemical induction would be noticed. The whole process would then correspond to a simple *ECM* reaction scheme (Section 5.4.4 and Fig. 5.18).

Electrochemical inductions are also observed in other types of chemical reactions such as cyclo additions [174], isomerizations [175], ligand substitutions [176] and decarboxylation [177]. This exciting branch of chemical synthesis may develop very well in the years to come and CV would remain a simple and convenient tool

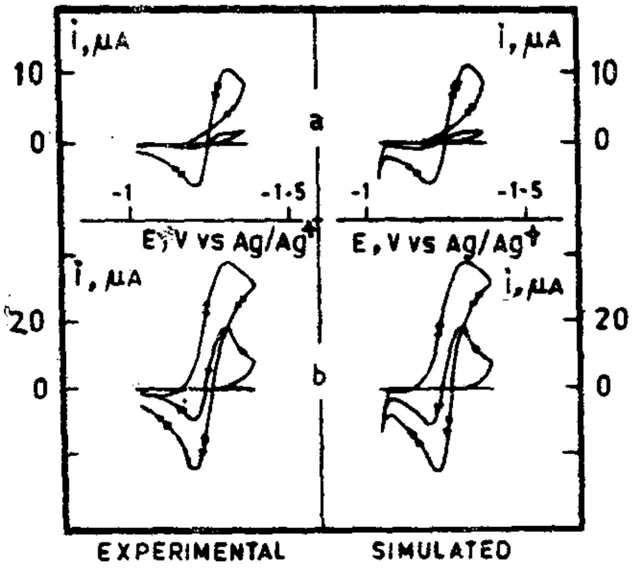

Fig. 5.20 Electrochemical induction of diethyl phosphate (0.663 M) substitution on 4 chlorobenzonitrile by scanning the potential in the substituted product redox region. Sweep rate 0.115 V $\sec^{-1}$. Concentration of the depolarizer (a) 1.08×10^{-3} M (b) 1.55×10^{-3} M.
[From C Amatore, J Pinson, JM Saveant, and A Thiebault, J Electroanal Chem 107 (1980) 59].

for establishing electrochemical induction and evaluating the process kinetics.

5.5 APPLICATIONS AND SCOPE

Study of reactions of molecular entities in condensed media is a fascinating area of research in itself. If any one of the steps in the overall process involves charge transfer, electrochemical methodologies can be employed to monitor the whole process. LSV and CV have certainly reached a mature state where they can be used to monitor a large number of these processes. In fact, much less use of the techniques has been made for quantitative analysis than it is capable of. The tool is well equipped and ready. One only hopes that a much better use of the tool would be forthcoming.

One need not go too far to predict the possible applications of this technique in future. A number of new organic electrode processes would be studied in more and more quantitative terms in future.

Inorganic and organo-metallic reactions have received greater attention recently. Biochemists are also being attracted to electrochemistry in recent times. They can probably expect a great deal of information on biological redox processes from this technique. From the analytical point of view, interestingly the peak current or limiting current is always proportional to concentration of active species, whatever be the reaction mechanism. At sufficiently low level of concentration, linearity of current response to concentration is always noticed. The evaluation of low levels of electroactive species by CV in liquid chromatography, for example [178, 179], must be possible even if the overall process is controlled by the kinetics of some chemical reaction. Novel analytical applications of this type would also continue to grow.

In the last three chapters, the dramatic activities have been considered of electroactive species at one side of the interface—the solution side. The molecular movements towards and away from the interface were also considered. The charge transfer thermodynamics and kinetics was dealt with. The chemical reactions of these electroactive molecules before and after charge transfer were also treated.

Interesting as they may be, only a part of the whole has been seen. In these studies, it was assumed that the electrodes are inert. They are assumed to be only suppliers or acceptors of electrons that again depend on the applied potential. It was also assumed that the voltammetric behaviour of reactive molecular species would be the same whatever the electrode may be. It is indeed heartening to note that simplified models with such gross assumptions work so well for such a wide variety of processes. Later (Chapters 11 to 14) when these questions arise at great detail to seek verifications, a great deal of surface effects are found on electrochemical processes. Before then, this book will concentrate on the structure, reactivities and other properties of the electrode surface (Chapters 6 to 10).

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