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Fundamental Principles of Organic Electrochemistry: Fundamental Aspects of Electrochemistry Dealing with Organic Molecules

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Chemists often encounter situations in which a reaction does not proceed at a convenient rate under the initially selected set of conditions. In chemistry, activation energy is defined as the minimum energy required to start a chemical reaction, and hence the activation energy must be put into a chemical system in order for a chemical reaction to occur. Catalysts are often used to reduce the activation energy but a high temperature is still required for the reaction to proceed at an appreciable rate. Electrochemical reactions, however, can generally be carried out under mild conditions (room temperature and ambient pressure).

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In electrochemical reactions there is an additional experimental parameter, the electrode potential, involved in the manipulation of electrochemical reaction rates. Electron transfer rates can easily be varied over many orders of magnitude at a single temperature by proper control of the electrode potential. Indeed, electrode potential is so powerful a parameter for controlling the rates of electrochemical reactions that most reactions can be carried out at or near room temperature.

An understanding of the nature of the dependence of electron transfer rates on potential is important for understanding electrode processes and constitutes the central theme of this chapter. Because electron transfer at an electrode surface is necessarily a heterogeneous process, it will be necessary to examine briefly the structure of the electrode–solution interface and its effects on the course of an electrochemical reaction. It is not enough, however, to simply derive the relationship between electron transfer rate and electrode potential. This is because as a result of the dramatic changes in these rates with potential, it is generally found that at certain potentials electron transfer is so fast that the overall process is actually limited by the rate of mass transport of the substrate from the bulk solution to the electrode surface. There are different modes of mass transport, and they differ in efficiency, therefore it will be necessary to examine each of these influences.

1.1 FORMATION OF ELECTRICAL DOUBLE LAYER

When electrodes are polarized in an electrolyte solution, the charge held at the electrodes is important. In order to neutralize a charge imbalance across the electrode–solution interface, the rearrangement of charged species like ions in the solution near the electrode surface will occur within a few hundredths of a second, and finally result in strong interactions occurring between the ions in solution and the electrode surface. This gives rise to the electrical double layer, whose thickness is usually between 1 and 10 nm (Figure 1.1) [1]. There exists a potential gradient over the electrical double layer and the gradient is no longer confined to the bulk electrolyte solution. The potential difference between the electrode surface and the bulk solution illustrated in Figure 1.1 may amount to a volt or more, over the rather short distance of the thickness of the double layer, and hence this is an extremely steep gradient, in the order of 10^6 V cm^{-1} or greater, which is an electrical field of considerable intensity. This is the driving force for the electrochemical reaction at electrode

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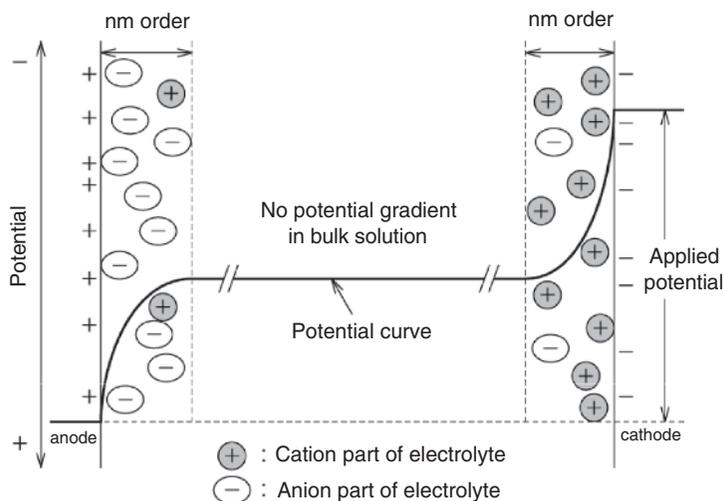


Figure 1.1 Electrical double-layer model and potential distribution in the double layer

interfaces, therefore when the polarization between anode and cathode is increased gradually, the potential gradient in the vicinity of the anode and cathode is also increased and consequently the most oxidizable and reducible species in the system are subject to an electron-transfer reaction at the anode and cathode, respectively. Because a charge imbalance in the vicinity of an electrode takes place after the electron-transfer reaction, ions are transferred to the electrode interface to neutralize the imbalance, and consequently the continued Faradic current is observed. Thus, the electrolyte in a solution plays a role in the formation of the electrical double layer and the neutralization of a charge imbalance after electrolysis.

1.2 ELECTRODE POTENTIALS (REDOX POTENTIALS)

In all electrochemical experiments the reactions of interest occur at the surface of the working electrode therefore we are interested in controlling the potential drop across the interface between the surface of the working electrode and the solution. However, it is impossible to control or measure this interfacial potential without placing another electrode in

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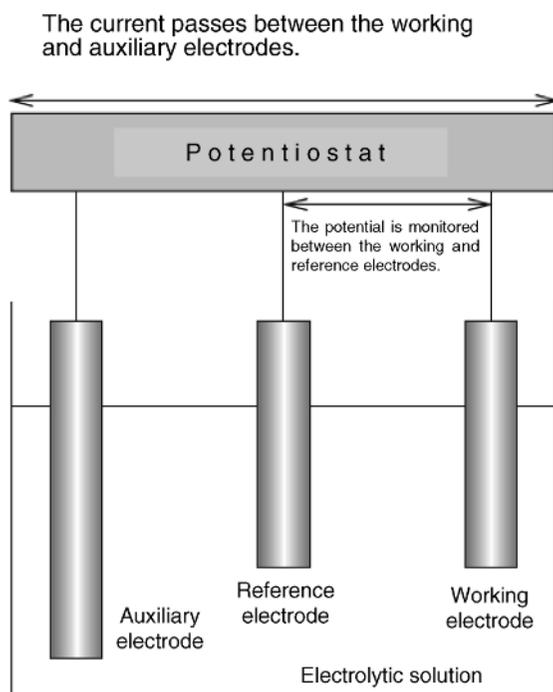


Figure 1.2 Experimental setup for the three-electrode system

the solution. Thus, two interfacial potentials must be considered, neither of which can be measured independently. Hence, one requirement for the counter electrode is that its interfacial potential remains constant so that any changes in the cell voltage produce identical changes in the working electrode interfacial potential. An electrode whose potential does not vary with the current is referred to as an ideal non-polarizable electrode, but there is no electrode that behaves in this way. Consequently, the interfacial potential of the counter electrode in the two-electrode system discussed above varies as the current is passed through the cell. This problem is overcome by using a three-electrode system in which the functions of the counter electrode are divided between the reference and auxiliary electrodes (Figure 1.2) [2]. This ensures that the potential between the working and reference electrodes is controlled and the current passes between the working and auxiliary electrodes. The current passing through the reference electrode is further diminished by using a high-input impedance operational amplifier for the reference electrode input.

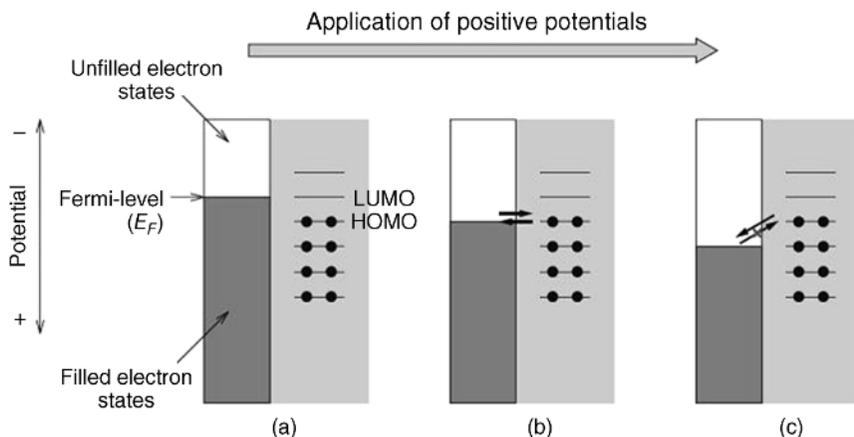


Figure 1.3 Fermi-level within a metal along with the orbital energies (HOMO and LUMO) of a molecule (Red) in solution

By employing the three-electrode system we can control or measure the working electrode potential. We then consider the essential meaning of the potential control using the following simple redox couple (Eq. 1.1):



where Red and Ox represent the reduced and oxidized forms of a given species.

It is helpful to focus on the energy of electrons in the working metal electrode and in the Red species in the electrolyte solution, as depicted in Figure 1.3. The behaviour of electrons in a metal electrode can be partly understood by considering the Fermi-level (E_F) [3]. Metals are composed of closely packed atoms that have strong overlap between one another. A piece of metal therefore does not possess the individual well-defined electron energy levels that would be found in a single atom of the same material. Instead a continuum of levels exists, with the available electrons filling the states from the bottom upwards. The Fermi-level corresponds to the energy of the highest occupied orbitals (HOMO). This level is not fixed and can be moved by supplying electrical energy (see Figure 1.3). We are therefore able to alter the energy of the Fermi-level by applying a potential to an electrode (when a negative potential is applied, the Fermi-level moves to higher energy; when a positive potential is applied, it moves to a lower energy.). Depending on the position of the

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Fermi-level it may be thermodynamically feasible to reduce/oxidize species in solution. Figure 1.3 shows the Fermi-level within a metal along with the orbital energies (HOMO and LUMO) of a molecule (Red) in solution.

As shown in Figure 1.3a, the Fermi-level has a higher value than the HOMO of Red. It is therefore thermodynamically unfavourable for an electron to jump from the HOMO to the electrode. However, as shown in Figure 1.3c, when the Fermi-level is below the HOMO of Red it is thermodynamically favourable for the electron transfer to occur and we can observe current for the oxidation of Red. The critical potential at which this electron-transfer process occurs identifies the standard potential, E° , of the redox couple Red/Ox (see Figure 1.3b).

1.3 ACTIVATION ENERGY AND OVERPOTENTIAL

As mentioned in section 1.2, depending on the relative position of the Fermi-level to the orbital energies (HOMO and LUMO) of a substrate molecule in solution, it may be thermodynamically feasible to reduce/oxidize the molecule. However, in general electrochemical reactions possess energy barriers that must be overcome by the reacting species. This energy barrier is called the activation energy (see Figure 1.4). Hence, the potential difference above the equilibrium value (the standard potential, E°) is usually required to produce a current. This potential difference

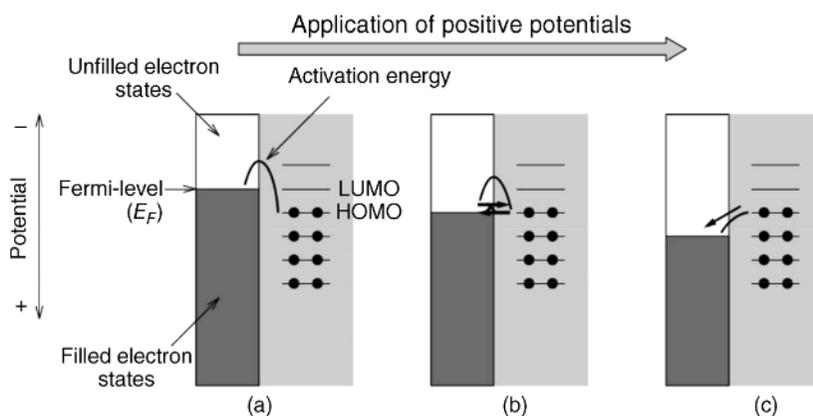


Figure 1.4 The activation energy in the electron transfer process at an electrode

between the standard potential and the potential at which the redox event is experimentally observed is called the overpotential [4].

1.4 CURRENTS CONTROLLED BY ELECTRON TRANSFER AND MASS TRANSPORT

Although electrode potential is an extremely important experimental parameter for manipulation of electrochemical reaction rates, other parameters such as mass transport can also affect reaction rates. We now consider the simplest electrochemical model, which is composed of the electron transfer process and the mass transfer process, as shown in Figure 1.5. In this case, depending on the electrode potential, the rate-determining step might be either the electron transfer rate or the rate of mass transport of the substrate to the electrode surface. To examine the quantitative and semiquantitative interrelationships between potential, electrochemical reaction rates and mass transport, a wide variety of voltammetric experiments are commonly used [5].

We will now consider the factors affecting the relative heights and shapes of voltammetric waves such as those in Figure 1.6. As the electrode potential is scanned during a voltammogram (to more negative potentials for a reduction or more positive potentials for an oxidation), the electron transfer rates are dramatically increased and a voltammetric curve passes through a mixed region in which the rates of mass transport and electron

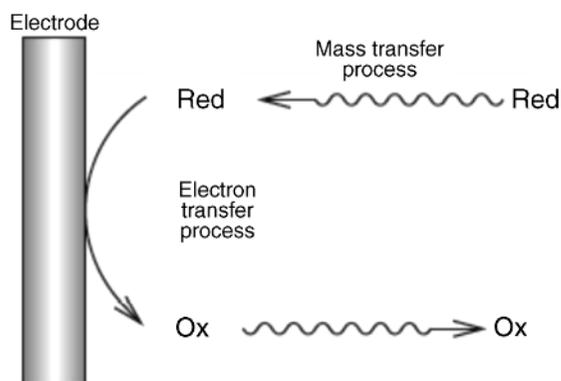


Figure 1.5 Electrochemical model showing the electron transfer process and the mass transfer process

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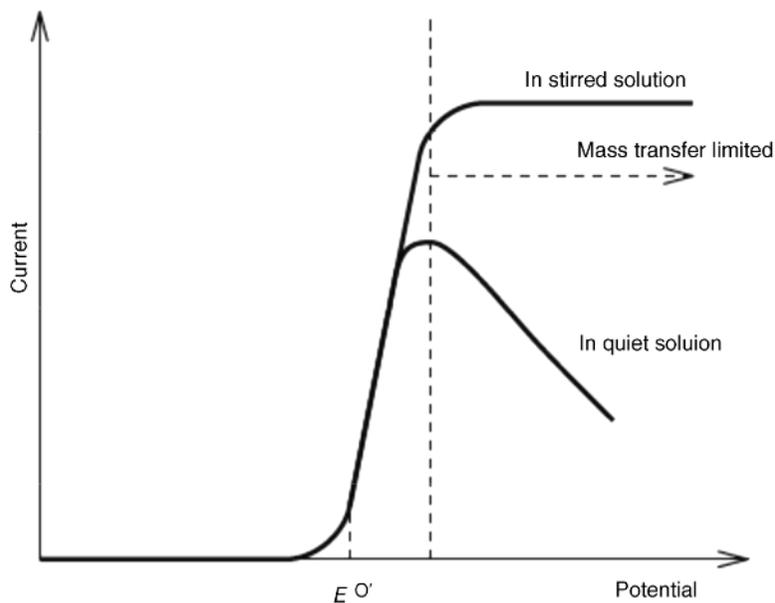


Figure 1.6 Voltammetric waves in quiet and stirred solution

transfer both limit the electrolysis current. Finally, the electron transfer rate eventually reaches a high enough rate that the currents are purely mass transfer limited, and the mass-transport-limited voltammetric peak and plateau currents are observed in quiet and stirred solution, respectively. For this reason the equations dealing with the electrolysis current are different for each rate-determining step.

When the electrochemical reaction is controlled by the electron transfer step, the net electrolysis current density (i) is represented by the Butler–Volmer equation (Eq. 1.2) [4]. This equation describes how the current density (i) on an electrode depends on the overpotential (η), considering that both a cathodic and an anodic reaction occur on the same electrode:

$$i = i_a - i_c = i_0 [\exp(\alpha n F \eta / RT) - \exp\{-(1 - \alpha) n F \eta / RT\}] \quad (1.2)$$

where i_a and i_c are the individual anodic and cathodic current densities, respectively, i_0 is the exchange current density, α is the charge transfer coefficient (its value lies between 0 and 1, frequently being about 0.5 at lower overpotentials), n is the number of electrons involved in the electrode reaction, F is the Faraday constant and η is the overpotential.

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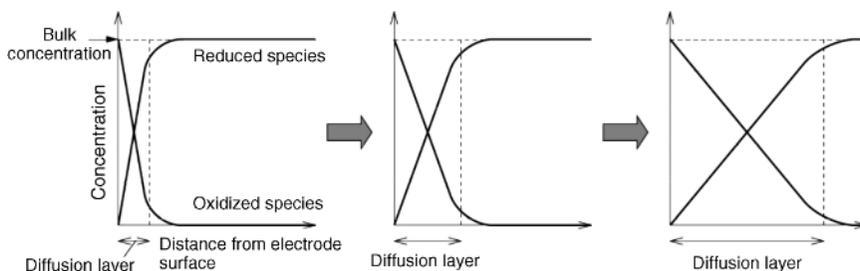


Figure 1.7 Change in the diffusion layer thickness with electrolysis time

As indicated by the Butler–Volmer equation, the net current density is the difference between the cathodic and anodic current densities. In addition, the exchange current density is that current in the absence of net electrolysis and at zero overpotential.

When the electrochemical reaction is controlled by the mass transfer step, the electrolysis current density relates to the magnitude of the gradient of the substrate molecule concentration at the electrode surface, represented by Eq. 1.3 [6]:

$$i = nFD(dc/dx)_{x=0} \quad (1.3)$$

where n is the number of electrons involved in the electrode reaction, F is the Faraday constant, D is the diffusion coefficient (the rate constant for motion of the substance through the given medium by diffusion), c is the substrate molecule concentration, x is the distance from the electrode surface and hence $(dc/dx)_{x=0}$ represents the gradient of the substrate molecule concentration at the electrode surface. The concentration profiles for the substrate and product in quiet solution are shown in Figure 1.7. Since the thickness of the diffusion layer and hence the concentration gradient change as electrolysis proceeds in quiet solution, the decrease in electrolysis current is observed in its voltammogram, as illustrated in Figure 1.6a.

In the presence of convection, for example stirring, the variation of the diffusion layer with time is inhibited and hence the concentration gradient is constant. In this case, a limiting current density (i_d) related to the diffusion layer thickness (δ) would be observed [5]:

$$i_d = nFDc/\delta \quad (1.4)$$

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Equation 1.4 describes the current density at the plateau of a voltammogram measured in stirred solution (Figure 1.6b), provided that the potential is scanned rapidly, so the concentration of the substrate in the bulk of the solution is not significantly depleted during the time needed to measure the voltammogram. In addition, since δ is reduced by more efficient stirring, the limiting current densities in stirred solution increase with the stirring rate. They are of course much larger than the current densities in quiet solution because convection is so much more efficient than diffusion at transporting the substrate molecule to the electrode surface.

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