SYNTHETIC ORGANIC ELECTROCHEMISTRY

Second Edition

Albert J. Fry

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PREFACE

While it should be of considerable use to specialists in the area of organic electrochemistry, this book is intended for the synthetic organic chemist who is unfamiliar with electrochemical methods—as indeed, most are—but wants to learn how they can be of use in a synthetic laboratory. It should be evaluated in this light. Any book of this type has to address a number of issues. Size is one: One would like to cover the enormous organic electrochemical literature exhaustively. This would, however, require a large and cumbersome volume, which would be of greater value to specialists than to those who are interested in electrochemistry as a synthetic tool. Emphasis is another: Much of the work reported in the organic electrochemical literature has been directed toward working out the mechanisms of electrode reactions. While this is a large and fascinating area in its own right, much of it is not particularly relevant to synthetic applications. In planning this book it was decided to keep it small enough that it would be accessible to the nonspecialist. This has been done by providing relatively complete coverage of the synthetic applications of organic electrochemistry. This has been done by emphasizing those aspects of the subject that are of synthetic interest, while de-emphasizing the mechanistic literature (and unfortunately also the large and growing area involving electrochemical generation of conducting polymers). This is not to say that mechanisms are ignored. Without a good appreciation of the major organic electrochemical reaction pathways, we would not be in a position to understand why it is, for example, that sometimes two relatively similar substrates react differently on electrolysis, or why a single substrate can afford several different products depending on the conditions of the electrolysis (solvent, pH, temperature, etc.). For every functional group whose electrochemistry is discussed here, I have outlined the essential features of its electrochemical behavior, including, in particular, presumed intermediates. However, throughout the book, the criterion for inclusion of such mechanistic discussions has always been their possible relevance to synthesis.

This point cannot be made too strongly. By the term "synthetic" in the title, *I imply a characteristic element of creativity*. Armed with a clear understanding of the mechanism of an organic electrode reaction, including possible intermediates in the reaction, one is in a position not only to use it most effectively, but also to divert it into new channels (for example, by trapping presumed intermediates inter- or intramolecularly) or even to devise entirely new chemistry suggested by it. This rational approach to electrosynthesis has led to much new organic electrochemistry in the last decade. Indeed, while the first edition (1972) attempted to make clear the enormous promise of electrochemistry as a synthetic tool, the story this second edition has to tell is that of promise fulfilled. Many useful electrochemical reactions, many of them superior to, and some without counterparts in, conventional chemical methodology, now exist and are presented herein. A laboratory involved in chemical synthesis can no longer afford to neglect electrochemistry. This does not mean that research groups should become full time specialists in the area. Rather, electrochemistry should be thought of as one more tool, like photochemistry, high pressure reactions, or gas and liquid chromatography, for which every synthetic laboratory is equipped, and that can be brought to bear in specific situations. In the last chapter I describe the necessary equipment, which is surprisingly simple, for developing routine capability in electrosynthesis.

In order to know best how to use this book, the reader should have an overall view of its organization. Chapter 1 contains a short introduction to electrochemical concepts and terms. Chapter 2 consists of a discussion of electrochemical principles. Although rather detailed for an introductory book stressing synthesis, it is far from comprehensive. The aim is to bring the reader up to a level where he or she has an understanding of the basic principles underlying electrochemical experiments. Chapter 3 discusses several common electrochemical techniques, and shows how each can be used to obtain information about the mechanism of a new organic electrode reaction. Chapter 4 illustrates the various ways in which the course of an electrochemical reaction can be influenced by changes in experimental parameters; the intent here is to suggest ways that one can control an electrode reaction to obtain improved yields or even new products. For many organic chemists, especially those unfamiliar with organic electrochemistry, the heart of this book will lie in Chapters 5 through 9. Chapters 5 through 8 summarize the electrochemical behavior of a wide variety of organic compounds, with emphasis on common mechanistic features, and organized according to structural types in order to stress these common features. The literature has been covered through early 1988 in these chapters, hence the book provides a very timely survey of the field. Chapter 9 is new in this edition. It discusses the many new applications that have appeared in recent years based on the use

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of electrogenerated reagents, some of which can be recycled to serve therefore as electrocatalysts. Chapter 10 provides an introduction to experimental methods, including recommendations for equipment for those beginning electrochemical investigations. An appendix provides names and addresses of suppliers of electrochemical equipment and materials.

Notice that the discussions of electrochemical principles and techniques (Chapters 1–3) precede the description of the electrochemistry of typical organic systems (Chapters 4–9). I prefer this organization, because it allows discussion of the voltammetric, coulometric, and other evidence that may have been used originally to deduce a given organic electrode reaction mechanism. However, many readers will want to know something about the kinds of reactions that can be carried out electrochemically. In this event, it is entirely possible, and in fact advisable, to begin with Chapter 4, using the earlier chapters as a reference where necessary.

I would like to take this opportunity to acknowledge the assistance of a number of individuals in the preparation of this book. I owe special thanks to my colleague Professor John Sease of Wesleyan University, who introduced me to the area of organic electrochemistry, and then, Southern gentleman to the core, suffered patiently through my many questions. Wesleyan University graduate students and now Dr. Richard Reed, Dr. Roberta Gable Reed, Dr. Marko Susla, and Dr. Wayne Britton all contributed to many early helpful discussions and contributed some of the illustrative material used herein. Dr. Britton especially has been a lifelong friend and continuing source of help and electrochemical insights. Unpublished preprints, information, and advice have been supplied by Professor Lennart Eberson, Professor Ronald Erickson, Professor Harry Mark, Professor Louis Meites, the late Professor Palle Iversen, and Professor Irving Shain. The hospitality of the Chemistry Department of the University of Arizona in the Spring of 1988, especially that of Professor Richard S. Glass and Mr. Kraig Steffen, during a sabbatical leave during which most of this book was written, is gratefully acknowledged. My family, especially my wife Melissa, was a constant source of good humor and encouragement, not to mention a great deal of patience and understanding, during completion of the manuscript.

ALBERT J. FRY

Middletown, Connecticut
March 1989

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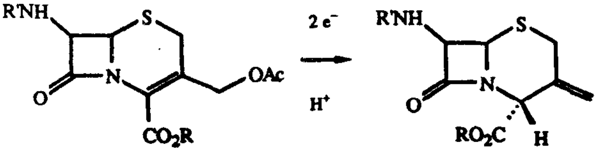
CHAPTER 1

INTRODUCTION

Although it should be of considerable use to practitioners in the field, this book is intended primarily for organic chemists who may have little or no prior knowledge of the field. There is great need for such a book. While there has been increasing interest in recent years in electrochemical methods in organic chemistry, it would still be fair to say that generally the real value of electrochemistry as a synthetic organic chemical tool is not widely appreciated by organic chemists. Even advanced textbooks and review series which lay claim to comprehensive coverage of the discipline of organic chemistry tend to pay little attention to the subject of organic electrochemistry. This is considered both unfortunate and surprising by those organic chemists who have developed an appreciation for the power of electrochemistry to effect useful chemical transformations. In point of fact, a wide variety of organic electrochemical chemical transformations can be carried out rapidly and in good yield, using relatively simple equipment, with the added advantage of avoiding hazardous or toxic reagents or by-products. Not only is it possible to carry out many reactions more efficiently electrochemically than with chemical reagents, there are in fact many reactions which can only be carried out electrochemically (this, ultimately, provides the major rationale for studying organic electrode processes). A few examples to support this statement include the following useful and representative electrochemical transformations:



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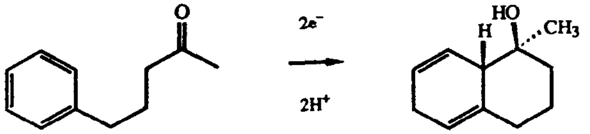

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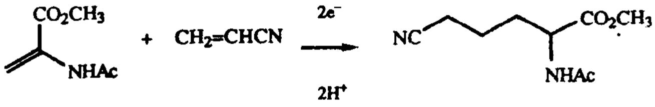

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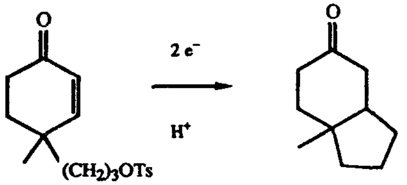

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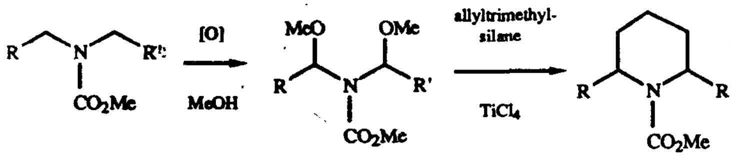

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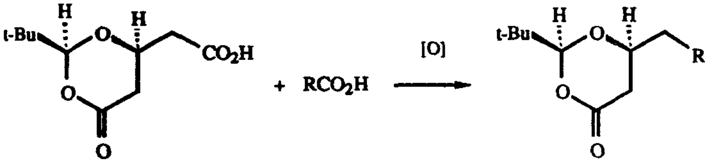

(Ref. 6)

[R = *i*-Pr , $CH_2CH_2CO_2Me$, $(CH_2)_3NHCHO$, etc.]

One of the primary aims of this book is to present an overview of the impressive number of useful organic electrochemical reactions which are already known. However, the mere fact that such chemistry is known is insufficient if it is not presented in a form accessible by the nonspecialist. It was therefore considered important in planning this book that the electrochemical reactions discussed be placed in a proper conceptual and mechanistic context, which requires a discussion of both electrochemical principles and organic electrode reaction mechanisms. It is hoped that with this background the reader will not only be able to predict with reasonable confidence the course of a previously untried organic reaction, but will be able to build creatively upon this knowledge to either design new reactions or divert existing ones in new directions. For this reason this book is not simply a compendium of reactions, though all major classes of organic electrochemical reaction are discussed and many examples are presented. Instead, the book is organized by the various modes of electrochemical behavior (reductive cleavage of single bonds, injection of electrons into π-electron systems, electrocatalytic processes, etc.). The objective of Chapters 5 through 9 is to extract useful generalizations concerning various types of electrochemical behavior, and detail what electrochemistry may be expected of a given functional group. A unique feature of this book can be seen in Chapter 4. This chapter is devoted to methods which can be used to influence the course of organic electrode reactions, which should provide the imaginative reader with useful hints as to ideas which can be tried in devising new electrochemical reactions. In addition, Chapters 2 and 3 contain an introduction to electrochemical principles and some techniques which can be used to carry out and interpret electrochemical reactions (electrochemical specialists will find these sections overly brief, but they are necessarily so in view of both the constraints of space and the overall orientation of the book). The final chapter discusses some of the practical aspects of electrochemical experimentation.

Organic electrochemistry is a very large field. In order to keep the size of the book manageable, the coverage of the synthetic electrochemical literature herein is selective. For the same reason, it has been necessary to exclude the area of physical organic electrochemistry, that is, the use of electrochemical methods and techniques to extract information concerning the thermodynamics of redox processes, rates of reaction of unstable intermediates generated electrochemically, mechanisms of organic electrode reactions, and so on. The reader will nevertheless find a great deal of mechanistic discussion throughout—indeed it is one of the central organizing themes of the book—but such material is always introduced not for its own sake but because of its synthetic implications.

1.1 DEFINITIONS

It is necessary at this point to introduce a few specialized terms and concepts used in electrochemistry. These relate to electrolysis and potential, and it will also be necessary to introduce a convention for graphical representation of electrochemical information.

1.1.1 Electrolysis

Examine the very simple electrochemical cell shown in Fig. 1.1. Two inert metallic electrodes *A* and *B* are immersed in a conducting salt solution. The electrodes *A* and *B* are connected to the positive and negative terminals of a direct current source *S*, which might be a battery or electronic power supply. An electrical circuit is thus completed: current flows as positive ions migrate

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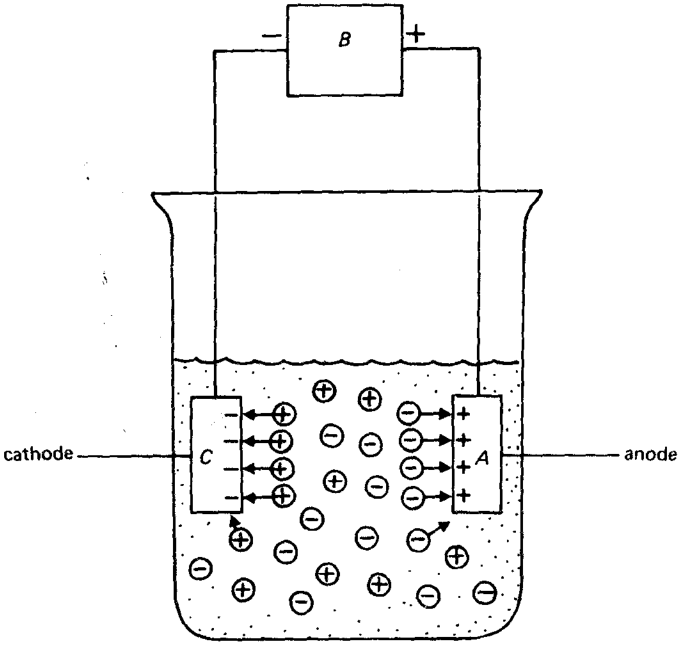


FIGURE 1.1 Undivided electrochemical cell. *B* is a source of direct current.

to the negative electrode (cathode) and are reduced, and negative ions migrate to the positive anode, give up electrons, and are oxidized. Because of the necessity for a complete circuit, every cell must of course have both an anode and a cathode, at which oxidation and reduction, respectively, occur simultaneously, but it may be that the anode and/or cathode reactions involve neutral species, not ions (in fact, this is usually the case in synthetic organic electrochemistry). Since current flow requires movement of ions, the electrolytic solution must then also contain a dissolved salt to provide electrical conductivity. Furthermore, the cell shown in Fig. 1.1 may often be inadequate on simple chemical grounds: If, for example, a reduction is being carried out, products formed at the cathode may migrate to the anode and be oxidatively destroyed there (and conversely for oxidations), or products formed at one electrode may be destroyed by other substances formed at the other electrode. For this reason, the anode and cathode are often placed in separate compartments, separated by a barrier which is porous enough to permit the passage of ions necessary for conduction of current, yet at the same time prevents mixing of the solutions in the two compartments (Fig. 1.2). These two requirements are somewhat incompatible, and place restrictions on the nature of materials to be used as cell barriers; this subject is taken up in more detail in Chapter 10. The solution in the cathode compartment is known as

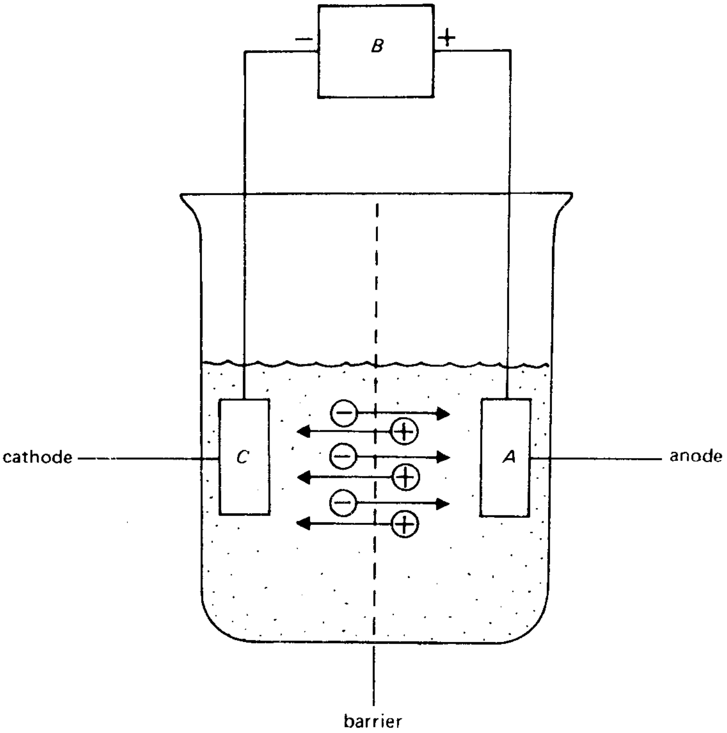
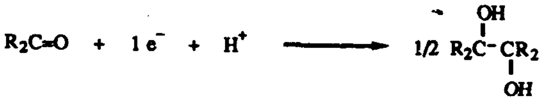


FIGURE 1.2 Divided electrochemical cell. *B* is a source of direct current.

the catholyte and that in the anode compartment is the anolyte; they need not have the same composition. The use of a divided cell introduces an element of experimental complexity, and prevents one from designing certain experiments which take advantage of some of the unique potentialities of electrochemical experimentation, for example, the possibility of effecting simultaneous oxidation and reduction of different components of the medium or of different functional groups in a single molecule. Attempts in recent years to address these issues have resulted in imaginative uses of undivided cells (Chapter 4).

The substance whose electrochemical behavior is being investigated is known as the electroactive substance, or substrate, or, in the older literature, depolarizer. The working electrode is the electrode at which the process of interest, that is, electrochemical conversion of the electroactive substance, is carried out. The cathode, then, is the working electrode for reductions, and the anode for oxidations. The counter electrode is the other current-carrying electrode, which must be included to complete the circuit—the anode is the counter electrode during reductions, and the cathode during reductions. These terms are useful when describing the design and construction of cells (Chapter 10).

The quantity of electricity necessary to change the oxidation state of one gram ionic weight of an ion or one gram molecular weight of a neutral substrate by one unit is called the faraday, and is given the symbol $\mathfrak{F}$. It is equal to 96,480 C/equiv; however, since it is also the proportionality factor between chemical and electrochemical free energy ($\Delta G = -n\mathfrak{F}\Delta E$), it is sometimes useful to express it in energy terms as 23.06 kcal/V/equiv (or 96.48 kJ/V-equiv). An oxidation or reduction process involving n faradays of electricity per mole of electroactive substance is said to be an n-electron process. Depending on experimental conditions, the same substrate may react by a variety of pathways involving different numbers of faradays. For example, benzophenone can be reduced in a 4-electron process to diphenylmethane, in a 2-electron process to benzhydrol, and in a net 1-electron process to benzpinacol (Chapter 6):



$$R_2C{=}O + 1\,e^- + H^+ \longrightarrow 1/2\ R_2\overset{OH}{\overset{|}{C}}-\underset{OH}{\underset{|}{C}}R_2$$

$$R_2C{=}O + 2\,e^- + 2\,H^+ \longrightarrow R_2CHOH$$

$$R_2C{=}O + 4\,e^- + 4\,H^+ \longrightarrow R_2CH_2 + H_2O$$

The fact of this diversity carries with it several important implications. The number of electrons involved in a reaction provides information about the oxidation state of the products and can therefore be of decisive importance in product identification; for this reason, it is often desirable to determine experimentally the quantity of electricity consumed in an electrochemical process. This is easily done; the experiment, known as coulometry, which is also capable of providing other useful mechanistic insights, is discussed in Chapter 3. Too, the fact that experimental conditions can substantially affect the course and products of electrolysis requires that we discuss the effects of changes in experimental parameters (pH, solvent, potential, etc.) on electrode reactions (Chapter 4). An understanding of the effects of such parameters is absolutely necessary for the design and interpretation of new electrochemistry.

In addition to the total amount of electricity consumed in an electrolysis, we are usually interested in the current flowing in the experiment. This can be expressed in the form of Faraday's law (Eq. 1.1), which states (for a reduction) that the current flowing in an electrochemical cell is proportional to the number of electrons involved in the process, the area of the electrode, and the concentration of the electroactive material (strictly speaking, its

$$i_{\mathrm{Red}} = n\mathcal{F}AC_{\mathrm{Ox}} \tag{1.1}$$

concentration at the electrode surface, C°).

Two other terms are often found in the literature. The *current efficiency* is the ratio (expressed as a percentage) of the theoretical amount of electricity required to effect a given reaction to the actual amount consumed. For example, for the benzophenone case just mentioned, if we were to carry out the reaction under conditions where the ketone is converted to the alcohol, and it was found that reduction of 1 mol of ketone consumed 2.5 $\mathcal{F}$ (241,250 C), the current efficiency would be 80% (2/2.5 [×] 100). Current efficiencies less than 100% can arise when other electrode reactions are occurring simultaneously with the desired process; current efficiencies greater than 100% are not common, but have been observed where catalytic chain processes are involved at the electrode (see Chapter 9 and Section 6.1.1). The *current density* is equal to the electrolysis current divided by the area of the working electrode. A high current density implies that a considerable number of molecules of the electroactive substance are being simultaneously destroyed within a relatively small area on the surface of the electrode. Reactions involving bimolecular reaction between reactive intermediates, for example, radical coupling processes, often are more efficient under conditions of high current density because the intermediates are formed in close proximity.

1.1.2 Potential

Consider the following simple redox couple:

$$\mathrm{O} + n\mathrm{e}^- \rightleftharpoons \mathrm{R}$$

where O and R represent the oxidized and reduced forms of a given species. From thermodynamic considerations,[7a] we may write

$$E = E^{\circ} - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\mathrm{Red}}}{a_{\mathrm{Ox}}} \tag{1.2}$$

from which we see that E°, the standard potential, is the potential at which the activities of R and O are equal. Notice that, knowing the standard potential, we may compute the ratio of R : O at any other potential. Equation 1.2 is doubtless already known to the reader as the Nernst equation.

It is common electrochemical practice to use a variant of the Nernst equation in which concentrations are used rather than activities. The potential where the concentrations of R and O are equal is known as the apparent standard potential, or formal potential, E'°:

$$E = E'^{\circ} - \frac{RT}{n\mathcal{F}} \ln \frac{[\text{Red}]}{[\text{Ox}]} \tag{1.3}$$

There are a number of reasons why the use of formal potentials is customary in electrochemical practice. The formal potential for a process may differ considerably from its thermodynamic standard potential because, for example, of surface adsorption or differential complexation or solvation of R and O, and hence we always actually measure E'°, not E°. The necessary data to correct E'° to E° are usually not available, nor is this necessary, as long as we recognize that potentials measured in different systems for the same substance may differ. Furthermore, we generally use data on potentials to make relative comparisons, for example, to determine the relative ease of oxidation or reduction of a series of compounds. The use of formal potentials is quite acceptable for such comparisons, as long as all are measured under the same experimental conditions and they are not used to compute absolute thermodynamic data directly. Because formal potentials depend on experimental conditions, the latter must always be specified as completely as possible.

Potentials are always defined relative to a generally accepted reference point. The reaction which serves as the fundamental reference for chemical measurements is reduction of the proton to hydrogen, and experimentally the fundamental reference point for potential measurements is the normal hydrogen electrode (NHE), which consists of a platinum electrode immersed in a solution whose proton activity is equal to unity and which is saturated with hydrogen gas at 760 mm pressure. By definition the potential of this electrode is 0.0 V. By convention, substances which are harder to reduce than a proton are assigned negative standard (or formal) potentials. For example, the reduction of sodium ion to sodium metal has an E° of −2.71 V versus NHE.

$$1/2\ H^{+} + e^{-} \rightleftharpoons 1/2\ H_2 \qquad E^{\circ} = 0\ V$$

Electrodes may be charged to positive or negative potentials. As the potential of a cathode is made increasingly negative, it becomes an increasingly powerful reducing agent, and conversely for anodic oxidations. When the working electrode potential exceeds that of one of the components of the medium, electron transfer between the electrode and that component takes place. This creates the need to know the potentials at which typical functional groups are oxidized or reduced. The NHE is inconvenient for routine use; hence, it is customary to measure potentials with a secondary reference electrode whose potential relative to NHE is accurately known. The most widely used reference electrode is the saturated calomel electrode (SCE), which is easily prepared; it consists of a paste of mercury(I) chloride (calomel) in contact with both a mercury pool and a saturated potassium chloride solution.

The potential of this electrode is constant (+0.2412 V relative to NHE) even when it passes small amounts of current, because oxidation and reduction merely interconvert mercury and mercury chloride, which as solids have unit activities; the electrode potential is therefore invariant (Eq. 1.2). Most potentials in the literature are reported relative to SCE, which simplifies comparisons between compounds studied in different laboratories. However, a number of other reference electrodes are in general use. These include, for example, electrodes based upon silver and its salts, such as Ag/AgX electrodes, which consist of a silver wire coated with the silver halide and immersed in a solution containing a soluble salt of the same halide, or Ag/Ag(I) electrodes, in which the silver wire is immersed in a solution of a soluble silver salt. The calomel electrode in fact cannot be used in all systems; for example, calomel is somewhat soluble in *N,N*-dimethylformamide (DMF), causing the potential of the SCE electrode to drift over time in this solvent. Extensive compilations of potentials of reference electrodes suitable for use in organic solvents are available.[8] While in principle any reference electrode that is stable in a given solvent system may be employed, it is customary when using an electrode other than SCE to state the potential of one's reference relative to SCE, in order to facilitate comparison with work in other laboratories.

Another term often encountered in the literature is overvoltage, particularly hydrogen overvoltage. Certain aspects of this phenomenon are not well understood, but it is essentially kinetic in origin. Reduction of protons to hydrogen is thermodynamically spontaneous at potentials negative of 0 V (versus NHE), when $[H^+] = 1\ M$. With a few metals, for example, platinum electrodes coated with finely divided platinum (so-called platinized platinum), observable hydrogen evolution does indeed occur at potentials negative of 0 V. At many other metallic electrodes, however, hydrogen evolution does not become detectable until considerably more negative potentials are reached. It is said that there is an overvoltage for hydrogen evolution at these metals. Typical value of hydrogen overvoltage in 1 N HCl are platinum, 0 V; copper, −0.19 V; cadmium, −0.39 V; lead, −0.40 V; and mercury, −0.80 V.[7b] These potentials are only approximate, since they depend on on a number of parameters such as pH and the history and physical composition of the electrode. It is generally believed that the overvoltage phenomenon arises because hydrogen formation on some metals is so slow at 0 V that it is simply not experimentally detectable. However, as will be seen in Chapter 2, rates of reduction increase rapidly as cathode potentials become more negative, and eventually a potential is reached where the rate of reduction of protons is high enough for hydrogen evolution to be apparent. This potential is different for different metals and even for the same metal pretreated in different ways, for example, by heat or even physical stress. The nature of the metal surface is clearly important; all metals which are good hydrogenation catalysts also have low hydrogen overvoltages. We shall not normally be concerned with hydrogen overvoltage, except insofar as it leads to a choice of a con-

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