



INTRODUCTION TO ORGANIC ELECTROCHEMISTRY

Techniques and Applications in Organic Synthesis

M. R. Rifi and Frank H. Covitz

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Organic Electrochemistry

by M. R. Rifi and Frank H. Covitz

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EDITOR'S INTRODUCTION

The synthetic organic chemist, must, of necessity, be well versed in the applications and subtleties of a wide variety of reactions. As time goes on, and the volume of literature expands, it becomes increasingly difficult for the practicing organic chemist to be aware of all of the applications of a given reaction. It also becomes much more difficult for him to select the conditions which are most suitable for each particular application of a given reaction. It is the purpose therefore of this series on techniques and applications in organic synthesis to provide chemists with concise and critical evaluations of as many reactions of synthetic importance as possible.

While the use of electrolysis in organic chemistry is not new, its synthetic application is usually limited to the Kolbe reaction on carboxylic acids. In recent years, the apparatus required for electrolysis has become more readily available and, as a result, more synthetically useful reactions have been developed. This technique unfortunately, is but one of an increasing number of synthetically useful procedures. It is the purpose of this book to provide the practicing organic chemist with a practical guide to the synthetic utility of organic electrochemistry.

Included in this book is a discussion of the various types of apparatus used, a consideration of the important reaction parameters, and a presentation of the types of reactions which can be run electrochemically. Specific experimental procedures are given for a number of these reactions.

It is hoped that by the use of this book, the synthetic organic chemist will not only become aware of the practical utility of electrochemistry but also be relieved of the necessity of surveying the original literature in the field, and, thus, have more time to spend in the pursuit of his ultimate goal.

Robert L. Augustine

PREFACE

Organic electrochemistry is a field that represents a challenge both in its theoretical as well as in its practical aspects. The researcher who is well versed in both areas has the opportunity to make significant contributions. In the past, the practical art outstripped the ability of theory to account for the observations. The opposite appears to be the case today. Electrochemical theory has been developed to the point where most mechanistic hypotheses can be put to the test of experimental verification. Sophistication in instrumentation has also undergone a recent revolution; with respect to organic synthesis, this means that the researcher has access to most of the "eyes" he needs to "see" what is really going on when a current passes between electrodes through an electrolytic medium. Electroorganic processes are "scale-up-able," a contention we hope will not escape the eyes of the industrialist.

The ideal organic electrochemist should first and foremost be a top-notch organic chemist. He also needs to understand and appreciate the fundamentals of electrochemistry and its unique advantages with respect to synthesis. He needs the ability to sort the electrochemistry from the organic chemistry and to put them back together in a realistic way. He must be able to tap on many disciplines -- besides straight organic synthesis and electrochemistry, he needs to be knowledgeable in analytical techniques, instrumentation, design of apparatus, heterogeneous and homogeneous catalysis, surface physical chemistry, and analysis of multivariable systems. Creativity and ingenuity of course are also essential to success.

The authors themselves, both of whom are organic chemists by training, recognized the desirability of being knowledgeable in the above areas when they first became involved in organic electrochemistry. At that time, however, we were unable to find a modern text which covered the subject in an introductory, yet comprehensive manner. Having acquired our knowledge the hard way, we felt a need existed for a text to serve as a guide for organic chemists interested in initiating and expanding projects in organic electrochemistry. With this thought in mind, we undertook

the task of writing this book. We sincerely hope that this book will in fact help to fulfill that need, and that similar books will appear in the future to update the rapidly expanding technology in this field.

M. R. Rifi

Frank H. Covitz

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INTRODUCTION

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1.1. HISTORICAL PERSPECTIVE

Organic electrochemistry is not a new field of endeavor. On the contrary, it was among the first general techniques to be employed at a time when organic chemistry itself was in its infancy. The foundation of electrochemistry, as laid down by Faraday and Nernst in the nineteenth century, was well recognized by organic electrochemists of the late nineteenth and early twentieth centuries. The importance of the electrode potential in controlling the course of an electrolytic reaction was also understood and was expounded in quite definite and succinct terms by Haber (1) in 1898. The early twentieth century saw a flurry of activity in organic synthesis using electrochemical techniques by such prolific individuals as Haber, Fichter, Thatcher, Kolbe, and many others who recognized the promise of electrolysis as an important synthetic tool for both laboratory and industrial reactions. In fact, industrial electrochemical processes to produce anthraquinone, benzidine, and other intermediates were practiced within the German dye industry

on a small scale in the early 1900s (2). And yet, from these early promising beginnings, interest and activity in organic electrochemistry declined in the 1930s and 1940s, a period when organic chemistry was flourishing and expanding in many directions.

What can we point to in order to understand the reasons for a decreasing influence during this time? For one, organic electrochemistry became, to a considerable extent, a victim of the inadequacy of the theory of reversible electron transfer to describe the irreversible events occurring in the electrode when large currents are passing, the typical situation required for convenient synthesis. The Nernst equation, which works so well for highly reversible systems, is not applicable to most organic synthetic systems because of their general irreversibility and the complexity of the chemical and electrochemical processes occurring. Phenomena such as polarization, overvoltage, and even electrode potential were not well understood in their connection with organic systems. The terms were so misused during the early days of organic electrochemistry that one cannot help but gain the impression of "black magic art" from reading the literature of that time. The predominant use of aqueous or partially aqueous media, with concomitant limited solubility for organic materials, also contributed to the disenchantment with organic electrochemistry. The remarkable ionizing ability of water for inorganic salts which is largely responsible for the considerable success of electrochemistry in producing workhorse inorganic chemicals such as sodium, chlorine, and many metals and in the battery field, is not necessary and is unduly restrictive for organic systems. In many cases the evolution of hydrogen and oxygen from electrolysis of water limits the range of accessible potentials, or causes many reported electroorganic reactions to resemble catalytic hydrogenation or oxygenation, and would thus tend to dampen the enthusiasm of the potential researcher in electrochemistry. The overworked terms "hydrogen

carrier" and "oxygen carrier," found in the early literature point out the obsession with aqueous media. The need to unravel the complexity of reaction products, common to many organic systems under uncontrolled conditions, coupled with the added desire to understand the electrochemical aspects, had to remain largely unfulfilled without the powerful analytical and electrochemical tools of today.

The typical introduction to electrochemistry, to which an aspiring organic chemist is subjected, is usually made within a predominantly physical chemical framework. Normally, little or no connection with organic synthesis is made. On the other hand, until recently, the only reference to electrochemistry made in organic chemistry courses was the timeworn Kolbe reaction (3) of carboxylic acids. Can the reader recall any other "name" reactions of electrochemistry?

The organic electrochemists of yesterday thus were improperly equipped--both because of inadequacies in the theory and in their instrumentation--to stimulate growth of electroorganic research and to achieve the still largely unexploited potential of electrochemistry in organic synthesis. (The "potential" of electrochemistry is a standard pun used by electrochemists!) Perhaps starting with the extensive work of Tafel (4) on the phenomenological description of irreversible electron-transfer reactions, and continuing on with the more advanced theoretical studies of Frumkin, Temkin, Delahay, Bockris, and others, the understanding of the electrochemical aspects of irreversibility and the effect of the so-called "double layer" and adsorption is now much deeper and on firmer ground than previously. Although the synthetic organic chemist will probably not be able to take direct advantage of these theoretical developments, the much sounder and more quantitative, although admittedly complex, description of electrochemical events occurring at the electrode/solution interface allows progress to be made from a solid theoretical base.

Perhaps more important has been the development of electrochemical techniques and instrumentation, initially developed for analytical uses, but capable of providing much deeper information concerning the electrode process itself, and which have finally given the organic electrochemist the "eyes" to examine properly the electrode reactions he is dealing with. By far the most immediately useful technique is that of polarography, with which we associate the names of Heyrovsky (5) and Ilkovic (6). This technique involves a recording of the current-potential relationship at a dropping mercury electrode and is normally employed for the investigation of reduction processes, since mercury itself is easily oxidized. Polarography is covered in more detail in Chap. 3. More recent developments, covered in detail in an excellent book by Adams (7), have allowed solid electrode voltammetry to be equally useful, although requiring considerably more experimental skill. A host of instrumental techniques permit the present-day worker in organic electrochemistry to study, in as sophisticated a manner as he requires, the details of organic electrochemical reaction mechanisms. Of course, the importance of the newer analytical techniques to identify the reaction products is not to be underestimated; a detailed knowledge of the identity and amounts of the products still provides the least ambiguous information about the course of the reaction.

The activity devoted to development of organic fuel cells and high-energy-density batteries using organic electrolytes has also contributed to the awakening of interest in electroorganic synthesis.

Finally, one should acknowledge the devoted efforts of people like S. Wawzonek (8) and S. Swann (9) to promote and encourage activity and interest in organic electrochemistry. The field is, in fact, on the upswing, and a definite enthusiasm and feeling of newness is evident among the workers in organic electrochemistry, even though the report of Michael Faraday (10) that ethane is produced by electroly-

tic oxidation of aqueous acetate solutions occurred well over 100 years ago.

1.2. ADVANTAGES AND DISADVANTAGES

As in most specialized synthetic techniques, organic electrochemistry has intrinsic advantages and disadvantages which should be recognized and understood by the potential and actual practitioner. Let us dispose of the disadvantage first:

1. Of primary concern to the experimentalist is the fact that organic electrochemical reactions are usually relatively slow, i.e., high current densities (current per unit electrode area) cannot routinely be used, when compared to typical inorganic electrolyses or conventional homogeneous reactions. The inherent rate is often related to a rate-limiting electron-transfer or adsorption/desorption step. More practically, the reputed slowness can usually be attributed to the low surface-to-volume ratio of most preparative electrochemical cells described in the literature.

2. Cell designs for synthetic usage are not standard, nor is such apparatus generally available from commercial sources. In practice, the experimenter is faced with a compromise between designing a cell with maximum flexibility (electrode replacement, reference electrode accessibility, cell divider, temperature control, and agitations) and one which maximizes electrode area and minimizes electrode spacing. The cell divider, when needed, gives rise to experimentally awkward construction, can be a maintenance problem, and usually results in high voltage drops. Also, the number of available types of dividers are limited.

3. The requirement that the solvent be inert as well as capable of ionizing a suitable electrolyte and dissolving the organic substrate, is restrictive, although several

choices, such as DMF, dioxane, acetonitrile, ethanol, pyridine, and others have been used extensively. Choices of electrolytes in nonaqueous media are usually also limited, tetraalkylammonium salts being the most generally used in organic systems; they are quite soluble and have sufficient conductivity and inertness for a wide variety of electrochemical syntheses. Also, the electrolyte must be separated from the product in the work-up.

4. Finally, in oxidative studies, the number of stable anode materials are limited, since most metals are themselves easily oxidized. The noble metals, such as platinum and gold, carbon and graphite, and lead dioxide, are the only ones which had heavy usage in anodic reactions.

The advantages of electrochemical syntheses are even more formidable:

1. Precise control of the electrode potential, and hence of selectivity, is easily attainable when required. The equivalent of a continuum of oxidizing and reducing agents, all equally accessible, is an attractive (although admittedly not precise) analogy.

2. Electrochemical reactions do not require thermal energy to overcome activation barriers, and hence are applicable to thermally sensitive compounds. The driving force is the electrode potential.

3. Stoichiometric amounts of oxidants and reductants are not required, and their by-products are thus avoided. This has interesting implications when one considers the current pressure to avoid pollution by discarded by-products. In this connection, many conventional redox reactions have the possibility of being "catalytic" if the redox product can be easily reconverted in situ to the starting reagent by electrolysis.

4. It should be generally recognized that although the cost of most materials has increased steadily over the years, the cost of electricity has remained remarkably stable, and is thus becoming an ever more attractive reagent for large-

scale reactions. The use of breeder reactors for the industrial generation of electricity is foreseeable in the not-too-distant future (11), and should further enhance the availability and utility of this highly desirable "reagent."

5. Electrochemical synthesis, by its very nature, and by ease of instrumentation, is eminently suitable for continuous and automatic operations, another industrially attractive feature.

6. The ease of quantitatively monitoring the course of the reactions by coulometry (integral of current with time), using electronic or electrochemical coulometers, is unsurpassed compared to most other general synthetic techniques. The current itself is the measure of the rate of reaction. Just as conveniently, polarography or related techniques can generally be employed to follow the disappearance of starting material and, in some cases, the appearance of product. Of practical convenience is the ease by which the reaction can be instantly stopped--by turning off the switch!

In many cases one is tempted to reflect on some analogies between organic electrochemistry and photochemistry. Consider the electrode potential and the current in the same vein as the wavelength and intensity, respectively. The energies involved in electrochemistry are of the order of 1 to 3 volts (V) [25 to 75 kcal/mole]; in photochemistry energies of the order of 2 to 6 V [50 to 150 kcal/mole] are encountered. The primary "reagent" is quantized (electron vs photon) and neither contributes materially to the mass of the product. In both techniques, novel syntheses with no conventional counterpart are often uncovered. The recently investigated cases of electrochemiluminescence (12) where the product of an electrolytic oxidation ($E \sim 2$ V) and that of a reduction ($E \sim -2$ V) are allowed to react in the bulk of the solution where light is emitted, is a rather neat demonstration of the overlap in the energy ranges accessible. Of course, the reader will draw the

appropriate conclusion when he considers the form of energy required to power most light sources.

A much more intimate connection exists between electrochemistry and heterogeneous catalysis. The importance of adsorption and orientation of molecules on surfaces is obvious in both fields. Heterogeneous catalysis has also suffered in the past from the aura of "black magic" surrounding processes that are not well understood. In both cases, many mysteries concerning the nature of the adsorbed species remain to be solved, and only recently have the tools become available to study these difficult problems in detail.

Finally, one should consider the relationship that organometallic chemistry has toward electroorganic chemistry. In many cases, evidence has been found for the formation of intermediate organometallics in both oxidative and reductive electrochemistry. In fact, an impressively wide array of organometallics has been synthesized electrolytically, mainly through the efforts of Dessy and co-workers (13). Since metals are employed almost exclusively as electrodes in electrolytic processes, one should always consider the possibility of specific organometallic interactions; indeed, such interactions are difficult to disprove.

1.3. SCOPE OF THE BOOK

This book is primarily intended to be used by organic chemists in academic and industrial environments who wish to start a program of laboratory work in the field of electroorganic synthesis. Although little or no previous knowledge of electrochemistry is required, a general knowledge of organic reactions and laboratory procedures is assumed. The basic information needed to initiate such a study is provided. This book contains the elements of electrochemical theory, but is specifically geared to avoid

a requirement of advanced mathematics. Extensive use is made of analogies between the more familiar concepts in chemistry to which the reader has undoubtedly been exposed. It contains experimental procedures, including specific examples of syntheses, electrode preparation, cell construction, etc., trying to foster an appreciation of the types and varieties of equipment needed, and lists commercial sources where such equipment may be purchased if available at all. Emphasis is placed on reactions which have the possibility of general application, and on the effect of variables on the course of reactions. Literature sources are provided and references suggested for more complete coverage of the subject material.

The book does not include detailed information on the more sophisticated techniques available, but rather, will refer the reader to more advanced texts. It is not meant to be used as a reference manual, nor is it exhaustive in coverage. Although most of the examples presented are taken from literature sources, no attempt will be made to review critically the literature with respect either to experimental procedures or conclusions. On the contrary, a conscious effort will be made to exclude highly controversial subjects and to include only information which is generally agreed upon by leaders in the field of electroorganic chemistry.

Within this framework, we apologize to those who may feel we have underemphasized certain aspects or have presented analogies which are somewhat naive. To the extent that these analogies have been helpful in assisting electroorganic chemists understand electrochemical reactions and predict their results, they will, in fact, be emphasized.

Organic electrochemistry has had an unusual past--the early workers recognized the promise but were improperly equipped to fulfill it. The latter cannot be said today. Many unique reactions remain to be discovered; the time is ripe--let's use it.