

Advances in Physical Organic Chemistry

Volume 32

Edited by

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Advances in Physical Organic Chemistry

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Editor's preface

Thirty six years after the appearance of the first volume of *Advances in Physical Organic Chemistry*, the subject reaches the last year of the century in good shape. New methodologies and exciting discoveries continue to appear both in purely academic research areas, but also increasingly in applied areas such as the development of novel materials with useful chemical and physical properties. The broad definition of physical organic chemistry used in the series has allowed the inclusion in this volume of reviews on topics that would scarcely have been regarded as appropriate when Victor Gold first saw the need for the series. Thus, the importance of organic electrochemistry as a branch of physical organic chemistry, first recognised in this series in Volumes 5 (1967) and 12 (1976) and discussed in several subsequent reviews, is revisited in a fairly fundamental way with an account of developments in the underlying technique of voltammetry and their implications for studies of chemical kinetics. The relationship between organic structures and nonlinear optical properties is dealt with in a thorough and truly physical organic way in the second contribution, which emphasises that both the physical and organic components of the research must be done to the highest standards if results are to be meaningful. Recent advances in the study of the role of hydrogen bonding on structure in the organic solid state are reviewed in the third contribution. In the final section of this volume, Professor Yuho Tsuno, after a distinguished career in physical organic chemistry spanning more than forty years, has contributed to a review of the part played in the study of the relationship of structure and reactivity by the four-parameter equation that bears his name. I want to express my thanks to all the contributors for the time, effort and enthusiasm that has gone into their reviews and my belief that the scientific community will find this volume just as useful as they have found previous ones in the series.

With the coming of the millennium, *Advances in Physical Organic Chemistry* will have a new Editor. After being associated with the editorial side of the series since 1975, first as Associate Editor, then as Co-Editor and finally, after the sad, premature death of Victor Gold in 1985, as Editor, it seemed to me that it was an appropriate time to pass on the baton to a younger pair of hands. Academic Press have been fortunate to secure the services of Professor Thomas Tidwell of the University of Toronto to lead the series into the next century. I leave the series confident that he will command the support of the whole physical organic chemical community and further extend its appeal. My thanks go to the members of my Editorial Advisory Board, the ever-changing editorial staff at Academic Press, the many contributors who,

over the years, have coped patiently with my comments, queries and grammatical eccentricities, but most of all to the readers who have loyally supported and used the series from its inception and by their citations made it the success that it is today.

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Contents

Preface	vii
Contributors to Volume 32	ix
Perspectives in Modern Voltammetry: Basic Concepts and Mechanistic Analysis	1
JOHN C. EKLUND, ALAN M. BOND, JOHN A. ALDEN AND RICHARD G. COMPTON	
1 Introduction	2
2 General concepts of voltammetry	6
3 Cyclic voltammetry	27
4 Hydrodynamic voltammetry	44
5 Microelectrodes	63
6 Sonovoltammetry	69
7 Theoretical modelling	83
8 A comparison of voltammetric techniques	96
9 Current and future direction of voltammetry	104
Appendix	110
References	113
Organic Materials for Second-Order Non-Linear Optics	121
J. JENS WOLFF AND RÜDIGER WORTMANN	
1 Introduction	122
2 Basics of non-linear optics	124
3 Quantum-chemical basis for second-order polarizabilities	136
4 Non-linear optical susceptibilities and experimental methods to evaluate $\chi^{(2)}$ and β	153
5 Optimization of second-order polarizabilities: applications to real molecules	168
6 Conclusion	206
Acknowledgements	208
References	208
Tautomerism in the Solid State	219
TADASHI SUGAWARA AND ISAO TAKASU	
1 Introduction	219

2	Proton tautomerism in an isolated system	222
3	Proton tautomerism in the solid state	229
4	Photochromism and thermochromism derived from proton tautomerism	244
5	Photochemical hole-burning	250
6	Dielectric properties derived from proton tautomerism in crystals	252
7	Concluding remarks	261
	Acknowledgements	261
	References	262

The Yukawa-Tsuno Relationship in Carbocationic Systems 267

YUHO TSUNO AND MIZUE FUJIO

1	Introduction	267
2	Applications of the Yukawa-Tsuno equation	272
3	Yukawa-Tsuno correlations for benzylic sololyses generating carbocations	276
4	Carbocation formation equilibria	315
5	Yukawa-Tsuno correlations for electrophilic addition of	322
6	Structure-reactivity relationship in polyarylcarbocation systems	334
7	Stabilities of carbocations in the gas phase	343
8	Theoretically optimized structures of carbocations	362
9	Reaction mechanisms and transition-state shifts	365
10	Concluding remarks	378
	Acknowledgements	379
	References	379

Author Index 387

Cumulative Index of Authors 405

Cumulative Index of Titles 407

Perspectives in Modern Voltammetry: Basic Concepts and Mechanistic Analysis

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- 1 Introduction 2
 - Historical aspects 2
 - Scope of the review 3
 - Basic definitions 4
 - The two major classes of voltammetric technique 4
 - Evaluation of reaction mechanisms 6
- 2 General concepts of voltammetry 6
 - Electrodes: roles and experimental considerations 8
 - The overall electrochemical cell: experimental considerations 12
 - Presentation of voltammetric data 14
 - Faradaic and non-Faradaic currents 15
 - Electrode processes 17
 - Electron transfer 22
 - Homogeneous chemical kinetics 22
 - Electrochemical and chemical reversibility 25
- 3 Cyclic voltammetry 27
 - A basic description 27
 - Simple electron-transfer processes 29
 - Mechanistic examples 35
 - Examples of complex mechanisms commonly encountered in organic electrochemistry 38
 - Examples of electrode reaction mechanisms consisting of extensive combinations of E and C steps 42
- 4 Hydrodynamic voltammetry 44
 - Rotating-disc electrodes 46
 - Channel electrodes 48
 - Wall jet electrodes 52
 - Electron-transfer processes 53
 - Combinations of electron transfer and homogeneous chemical steps 55
- 5 Microelectrodes 63
 - General concepts 63

	Mass transport to microelectrodes	64
	Microelectrodes and homogeneous kinetics	66
	Microelectrodes and heterogeneous kinetics	68
	Convective microelectrodes	69
6	Sonovoltammetry	69
	The effect of ultrasound on electrochemical processes	69
	Sonovoltammetric experiments: practical considerations	70
	Mass transport effects: a simple description	71
	Sonotrodes	77
	Sonovoltammetry: mass transport effects – further aspects	80
	Electrode cleaning and activation	81
	Electrode kinetics	82
	Coupled homogeneous chemical reactions	82
7	Theoretical modelling	83
	The four components of an electrochemical model	83
	Analytical solutions	85
	Numerical solutions	86
	Finite difference simulations	88
	Two-dimensional simulations	93
	Chemical kinetics	94
	Boundary conditions	94
	Current integration	95
	Optimization	95
8	A comparison of voltammetric techniques	96
	A quantitative comparison of the kinetic discrimination of common electrode geometries at steady state	97
	Steady-state vs. transient experiments	102
9	Current and future directions of voltammetry	104
	Instrumentation	104
	Electrodes	105
	Voltammetric simulations	108
	Investigations in alternative chemical environments	109
	Appendix	110
	References	113

1 Introduction

HISTORICAL ASPECTS

The transfer of electrons between species in the solution phase and solid electrodes was known to result in interesting reaction pathways as long ago as the early 19th century, the pioneer in this field being undoubtedly Michael Faraday (James, 1989). However voltammetric techniques have only become popular since the 1940s when instrumentation required to conduct such experiments became readily available. The early studies invariably used a linear sweep DC technique. In the last 50 years, a wide range of techniques of interest in this review have emerged. Thus, Sevcik (1948) reported the first cyclic voltammetric studies, while the fifties and sixties saw the common use of hydrodynamic techniques such as rotating-disc electrode voltammetry (see for

example, Hogge and Kraichman, 1954). The seventies and early eighties then witnessed the widespread use of microelectrodes (see for example, Wightman, 1981), initially under near steady-state conditions, and subsequently, when advances in instrumentation occurred, extremely fast-scan voltammetric techniques were introduced (see for example, Howell and Wightman, 1984). Recent studies have reported combinations of voltammetry, microelectrodes and convective transport (see for example, Compton *et al.*, 1993a) and voltammetry in the presence of ultrasound (see for example, Compton *et al.*, 1997a). Thus at the end of this century a wide range of voltammetric techniques are available which utilize DC type waveforms.

SCOPE OF THE REVIEW

This review describes a range of voltammetric techniques based on the use of inherently simple DC waveforms (linear, cyclic or staircase). The description of the techniques begins at a level which presupposes only limited prior knowledge and is suitable for those unfamiliar with the application of voltammetric techniques for the elucidation of electrode reaction mechanisms. As a result, the first two sections of this review aim to provide a sound fundamental basis to build upon when more advanced concepts are described in later sections, thus serving to initiate the novice and refresh the memory of the more experienced electrochemist. The article focuses on typical solution-phase reaction mechanisms encountered in organic and organometallic electrochemistry. For details of important bioelectrochemical processes the reader is advised to consult such texts as Dryhurst and Niki (1988). For details on surface-related processes such as adsorption and corrosion as well as solid state voltammetry and AC, square-wave and pulsed techniques, the interested reader is directed to more general texts (such as Bard and Faulkner, 1980; The Southampton Electrochemistry Group, 1990; Bockris and Kahn, 1993; Brett and Oliveira-Brett, 1993; Bruce, 1995; Kissinger and Heineman, 1996). In addition, there are a number of review articles available in this series on topics related to those described here (Fleischmann and Pletcher, 1973; Ebersson, 1976; Parker, 1984; Savéant, 1990). In the remainder of this introductory section, the basic definitions of terms associated with voltammetry are presented and the scope of applications of the technique are summarized. Section 2 provides a basic general introduction to the practical and theoretical concepts of voltammetric experiments of interest, while Sections 3–6 describe the voltammetric techniques: cyclic, hydrodynamic, microelectrode and sono-voltammetry. A range of examples of mechanistic studies is given for each technique. There is obviously a wealth of such examples in the recent literature and it is impossible to be fully comprehensive. Therefore, we focus primarily upon studies from our own laboratories, but a sample of excellent illustrative examples from the recent literature is also provided. Section 7

summarizes the general principles associated with the simulation of voltammetric responses, while Section 8 compares the relative merits of the voltammetric methods considered. In addition there is an appendix of the symbols and abbreviations used at the end of this review.

BASIC DEFINITIONS

Voltammetric techniques considered in this review involve monitoring the current when a time-dependent potential is applied to an electrochemical cell. The measured current results from frequently complex combinations of heterogeneous (in which an electron is transferred at the solution-electrode interface) and homogeneous processes (which occur in the solution phase). Comprehensive information concerning a particular electrode reaction mechanism of interest can be obtained from examining how the current varies as a function of time and the applied electrode potential. For kinetic studies, it is the variation of this current-potential response as a function of time that is commonly crucial for the qualitative and quantitative determination of a reaction mechanism. The processes that are probed by voltammetry occur at or in the region of working electrode(s). Thus these electrode(s) are the electrode(s) of critical interest. The reference electrode merely provides a fixed reference potential and the counter electrode completes the electrical circuit (see Section 2). A host of processes and species may be probed by voltammetric techniques. Some examples are given in Table 1 of which the first four are considered in this review.

THE TWO MAJOR CLASSES OF VOLTAMMETRIC TECHNIQUE

As noted above, the time element, which is critical for kinetic studies, may be introduced in two ways.

Steady-state voltammetry

In this form of voltammetry, the concentration distributions of each species in the electrode reaction mechanism are temporally invariant at each applied potential. This condition applies to a good approximation despite various processes still occurring such as mass transport (e.g. diffusion), heterogeneous electron transfer and homogeneous chemical processes. Theoretically it takes an infinite time to reach the steady state. Thus, in a practical sense steady-state voltammetric experiments are conducted under conditions that approach sufficiently close to the true steady state that the experimental uncertainty of the steady-state value of the parameter being probed (e.g. electrode current) is greater than that associated with not fully reaching the steady state. The

Table 1 A range of processes that may be probed by voltammetric techniques.

Process type	Example (reference)
Redox chemistry	Reduction of pyridine and benzene-substituted <i>n</i> -alkyl esters (Webster <i>et al.</i> , 1996). For further examples refer to texts such as Pombeiro and McCleverty (1993)
Homogeneous reactions coupled to electron transfer	Reduction of α -substituted acetophenones (Andrieux <i>et al.</i> , 1997)
Photoelectrochemical	Photochemical halide expulsion from halogenated aromatic radical anions (Compton <i>et al.</i> , 1995a)
Sonoelectrochemical	The oxidation of $\text{Mo}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ (Compton <i>et al.</i> , 1995b)
Bioelectrochemical	Electron-transfer processes in metalloproteins (Bond, 1994)
Quantitative determination of trace species in solution	Trace metal ions (Wang, 1985)
Transfer of species between immiscible phases	$\text{Ru}(\text{bpy})_3^{2+}$ transfer between water and 1,2-dichloroethane (Ding <i>et al.</i> , 1996)
Adsorption/desorption/deposition	Absorption/desorption of hydrogen on platinum electrodes (Will and Knorr, 1960). Adsorption of palladium onto platinum (Attard <i>et al.</i> , 1994)
Electroplating	Copper electroplating (Pletcher, 1982)
Dissolution	Dissolution of calcite in the presence of sulphuric acid (Booth <i>et al.</i> , 1997)

time-scale of a near steady-state process is determined by the rate at which material reaches the electrode surface. This time-scale may be varied in a number of ways:

- Altering the convective rate of transport, e.g. by changing the rotation frequency of a rotating-disc electrode. Experiments in which the convective rate of transport can be altered are known as hydrodynamic techniques.
- Decreasing the size of the electrode so that the rate of radial diffusion of material to the electrode surface is enhanced as is the case for microelectrodes.
- Applying ultrasound to the electrochemical system of interest. This forms the basis of the sonovoltammetric approach.

Transient voltammetry

In these experiments, a potential perturbation to the working electrode is applied to the system of interest and the resulting current response is measured as a function of time. Transient techniques include cyclic, linear

sweep, square-wave, pulsed, AC, etc. voltammetries (see for example Bard and Faulkner, 1980). In the former two cases the potential at the working electrode is scanned in a linear (or staircase) fashion and the current is continuously monitored. The temporal aspect arises from the rate at which the potential is ramped, known as the scan-rate, ν . When the potential is swept in only one direction the technique is known as linear sweep or staircase voltammetry. If the potential is swept in one direction, and then reversed this technique is known as cyclic voltammetry. Cyclic voltammetry is the prime transient technique discussed in this review.

EVALUATION OF REACTION MECHANISMS

The kinetics of voltammetrically relevant heterogeneous and homogeneous reactions may be examined by varying the critical time parameter of the experiment and monitoring its effect on some voltammetric feature (e.g. half-wave potential, see Section 4 for definition) associated with the process being investigated. The general procedure for obtaining quantitative kinetic data related to an electrode reaction mechanism using a voltammetric technique is schematically shown in Fig. 1.

The basic concept is that the experimental voltammetric data are collected and a mechanism for the electrode reaction mechanism is postulated. The proposed mechanism may be theoretically simulated by solving the appropriate mathematical problem. Satisfactory agreement between experiment and theory is used to suggest a quantitative description for a particular mechanism, but as with most kinetic studies ideally the identity of proposed reaction intermediates must be confirmed by an independent technique, e.g. a spectroscopic technique. It is inherently dangerous to assume the structure of a reaction product or intermediate solely on the basis of a voltammetric response.

2 General concepts of voltammetry

As is the case with all experimental methods, the application of voltammetry requires a knowledge of the relevant techniques and protocols that are most appropriate for the particular system being investigated. In order to assist the novice user of the technique to choose an optimal procedure for their particular circumstances, a brief survey of all the relevant facets of the technique that need to be considered when undertaking a voltammetric experiment and interpreting the resulting voltammogram are presented below with reference to stationary solutions and electrodes in the absence of any form of forced convection. Experiments involving additional forms of mass transport will be discussed in Sections 4, 5 and 6.

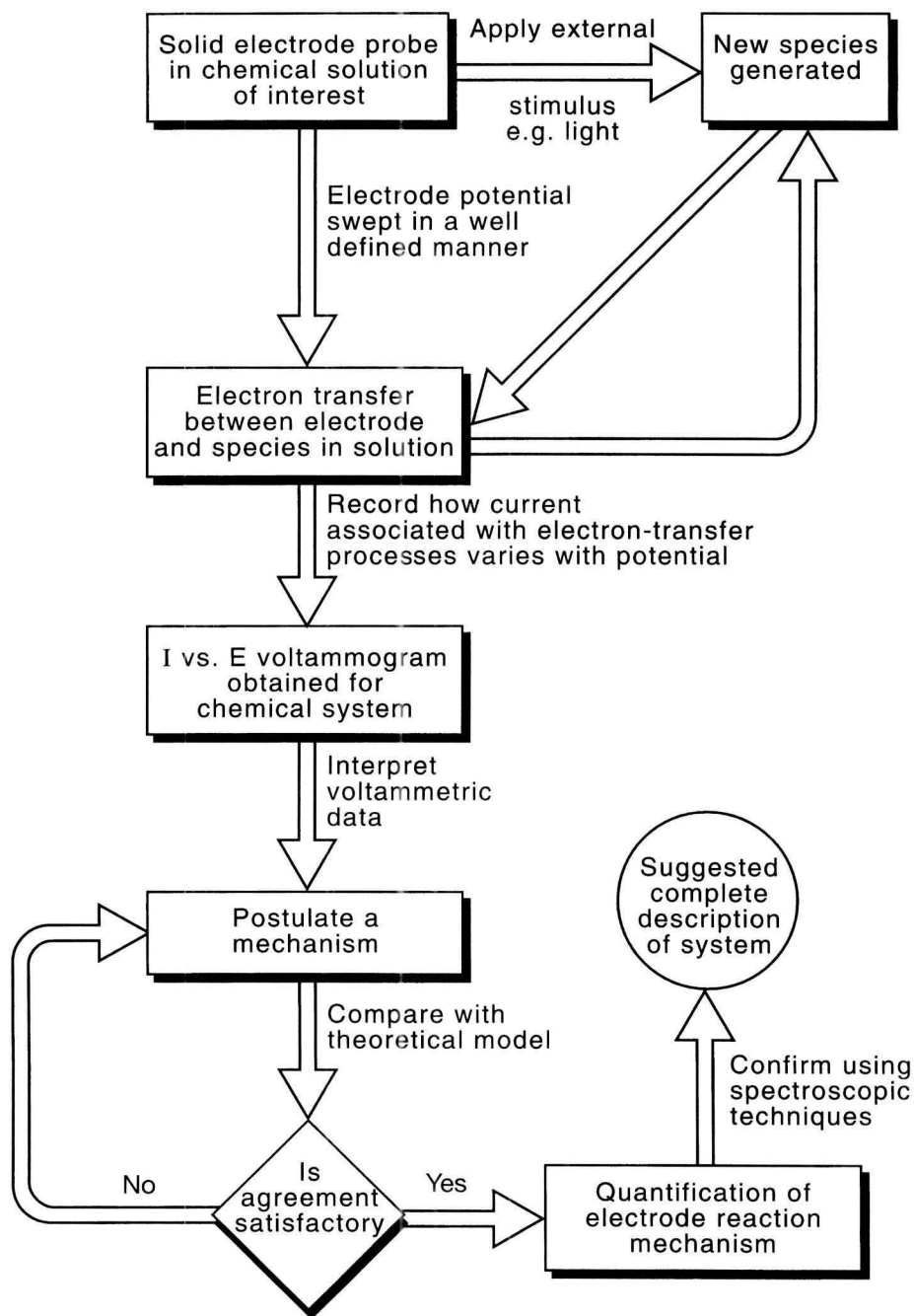


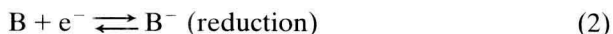
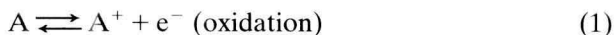
Fig. 1 Schematic diagram representing the process of examining an electrode reaction mechanism using voltammetric techniques.

ELECTRODES: ROLES AND EXPERIMENTAL CONSIDERATIONS

As alluded to in the introduction a typical voltammetric experiment utilizes three types of electrode.

Working electrode (Fig. 2)

This is the electrode at which the reaction of interest takes place, e.g. the simple one-electron oxidation–reduction processes given in equations (1) and (2).



Typically these electrodes are fabricated from an inert and electrically conducting material. Common examples would range from liquid mercury to solid platinum and some forms of carbon (i.e. glassy carbon or graphite). Mercury electrodes (Bond, 1980) are used in the form of dropping electrodes in which the surface is continuously renewed or a hanging mercury drop electrode. Recently diamond film electrodes have been utilized for studies that require wide potential windows (Tenne *et al.*, 1993). Typically, the solid

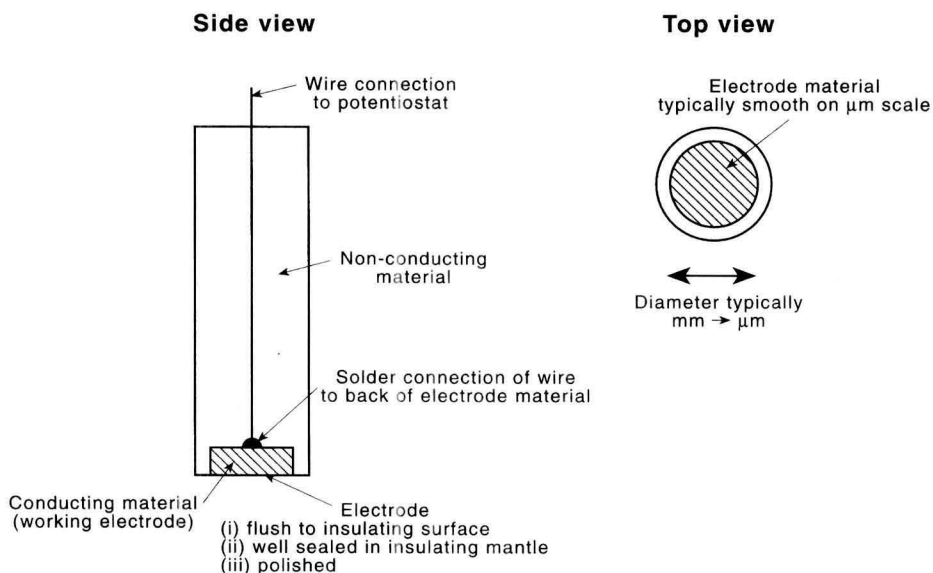


Fig. 2 Schematic diagram of a typical disc working electrode.