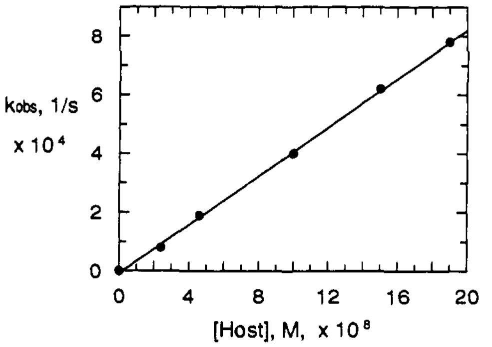
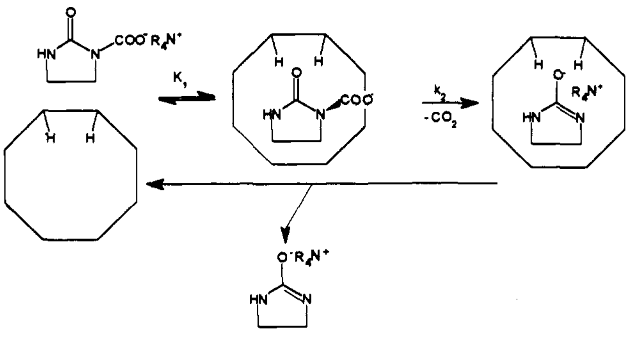
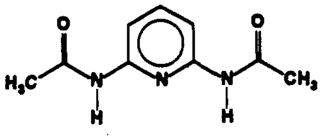


**Figure 1.** Observed first-order rate constant for decarboxylation of *N*-carboxyimidazolidinone (**5**) as a function of the concentration of host **H**.

**Scheme II**



2,6-Pyridinediylbis(acetamide) (**6**)[12] binds both **5** and **1**, but there is no decarboxylation of **5** detected (3 days, THF).



**6**

Addition of aqueous base leads to hydrolytic decomposition, presumably via an addition intermediate.[13] Concentrations of **5** above $10^{-7}$ M produce nonlinear response in UV absorbance, indicating that aggregation is occurring. The observed first-order rate constant for decarboxylation of **5** was measured as a function of the concentration of **H** (Figure 1). The slope gives an apparent second-order rate constant ($k_{obs}/[\mathbf{H}]$) of $4.15 \pm 0.05 \times 10^3$ $M^{-1}$ $s^{-1}$. Kinetic saturation could not be observed under conditions where **5** does not aggregate.

A schematic mechanism of decarboxylation of **1** in the presence of **H** is shown in Scheme II based on the array seen using computer modeling of the host-guest complex. The rate expression for the reaction is

$$v = k_{obs}[\mathbf{5}] = k_2[\text{complex}] = K_1k_2[\mathbf{H}][\mathbf{5}]$$

and

$$k_{obs}/[\mathbf{H}] = k_2K_1$$

If $K_1 \approx 10^3$ $M^{-1}$ (see Table I), then $k_2 = 4$ $s^{-1}$.

Since decarboxylation of **5** was too slow to detect in the absence of **H**, its half-life must be at least 10 days under the reaction conditions, giving an upper limit for the rate constant of the uncatalyzed process of $10^{-6}$ $s^{-1}$, corresponding to an acceleration in the complex of over $10^6$. The actual acceleration could be much larger. The results are consistent with the proposal of distortion upon binding as a means of altering the biochemical reactivity of *N*-carboxybiotin.[2,3]

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada for continued support through an operating grant.

**Supplementary Material Available:** Spectral data for **H** (1 page). Ordering information is given on any current masthead page.

---

(12) Feibush, B.; Figueroa, A.; Charles, R.; Onan, K. D.; Feibush, P.; Karger, B. L. *J. Am. Chem. Soc.* **1986**, *108*, 3310.

(13) Caplow, M.; Yager, M. *J. Am. Chem. Soc.* **1967**, *89*, 4513.

# *Book Reviews*

**Advances in Chromatography. Volume 31.** Edited by J. Calvin Giddings (University of Utah), Eli Grushka (Hebrew University of Jerusalem), and Phyllis R. Brown (University of Rhode Island). Marcel Dekker, Inc.: New York. 1992. xix + 393. $150.00 (U.S. and Canada), $172.50 (elsewhere). ISBN 0-8247-8568-1.

This series, initiated in 1965, reviews topics which are important to separation scientists. Authors are encouraged to be selective of material, evaluate information, and be critical as their experience dictates. Reviewers are not encouraged to merely assemble an annotated bibliography. The editors have accomplished this goal very well for nearly three decades, and this volume continues the tradition.

Elution gas-liquid and liquid-liquid chromatographies have dominated separation methods, largely due to the linearity of the solute distribution; that is, the distribution coefficient is constant over an appreciable range of solute concentration and the solute species are independent of one another in both phases. Groups intent on establishing standard nomenclature and preferred methods of reporting data such as the retention index, number of theoretical plates, and plate height have based their recommendations on linear systems. If a system is non-linear, efforts are made to make it linear or a different system is sought which is linear. In so doing, powerful gas-solid and liquid-solid separation systems and techniques such as frontal and displacement analysis became obscure diversions. The review (188 pages, 220 references) by A. Katti and G. Guiochon (University of Tennessee) attacks the subject. The review, which is highly mathematical, selects the most successful models and presents those equations which best describe solute behavior in the system, for example, Langmuir-type sorption isotherms and solute competition for sorption sites. Results and conclusions based on the mathematics are presented in more easily understood graphical form to give a balance between mathematical formalism and interpretation. Frontal and displacement methods are discussed. Applications include displacement separations of nucleotides and proteins. The review ends with a discussion of remaining mysteries. This is an excellent review of a difficult subject prepared by knowledgable and experienced workers. It is not light reading, however.

P. L. Dubin (Indiana-Purdue University) treats problems in aqueous size exclusion chromatography (32 pages, 95 references). The author presents valuable tables of commercial packings which include the number of theoretical plates to be expected, upper molecular weight limits, and maximum mobile flow rates. Aqueous solutions of high molecular weight compounds are complicated by both solvation and charge interactions, as these depend on the ionic strength. Dubin treats both effects and presents some dramatic graphs summarizing the dependence of retention on ionic strength and possible explanations. The search for a universal calibration curve is the Holy Grail of the polymer chemist. There is an excellent section devoted to this problem. The chapter should also interest those doing hydrodynamic chromatography and field-flow fractionation with aqueous solutions where ionic strength also plays a part.

Too often high performance liquid column chromatography with expensive instrumentation and columns is employed at the outset of an investigation. The chapter by J. Gasparic (Charles University, Czechoslovakia) (99 pages, 650 references) dealing with thin-layer chromatography on stationary phases impregnated with organic substances is most welcome to those interested in reverse phase systems; HPLC is not the only way. A discussion of principles is followed by an extensive table (42 pages) listing the stationary phase, the support, the method of impregnation of the support, the mobile phase, and the solutes chromatographed. Investigators weary of waiting for an HPLC to become available or with a limited library of columns or with a limited budget or with all of the above should seek respite in this chapter.

M. Knight (Peptide Technologies Corp.) reviews the countercurrent chromatography, CCC, of peptides (39 pages, 48 references). She summarizes the limitations of HPLC systems, for example, the limited number of solvent systems currently available for use. Countercurrent chromatography with no solid support is very "gentle" with solutes. Knight compares countercurrent distribution with CCC and then discusses the theory and methods of the latter. There is a discussion of equipment, particularly of extended techniques, for example, multi-coil CCC. Applications are discussed. Countercurrent distribution was understandably abandoned because the apparatus is a beast. Its advantages are forgotten. It is refreshing to see its rebirth with simpler and more compact equipment.

Boronates, fixed to a stationary support, retain solutes which are *cis*-diols where the hydroxyl groups are on adjacent carbons and are in the same plane. A very large number of biologically important molecules quality for this specific interaction (affinity chromatgraphy). If phenyl boronates are used, the retention properties can be controlled by substituents on the phenyl group. Electronic effects are transmitted across the ring to the retentive groups. The chapter (42 pages, 112 references) by R. P. Singhal and S. S. M. DeSilva (Wichita State University) discusses the method, the retention mechanism, chemical modification of the boronate to produce a variety of effects, and applications. Their discussion of what needs to be done is a stimulus for future research, as only one boronate derivative is commercially available.

The chapter (45 pages, 101 references) by N. Motohashi (Meiji College of Pharmacy, Japan), K. Kamata (Tokyo Metropolitan Research Laboratory of Public Health, Japan), and R. Meyer (Herbert Laboratories) summarize chromatographic methods (column, paper, thin-layer, HPLC, and gas-liquid) for determining carcinogenic benz(*c*)acridine. Their survey (1956–87) is frequently presented in tabular form, to make a very efficient summary. Their efforts will save someone frustrating hours in the library.

**Roy A. Keller,** *State University of New York, College at Fredonia*

---

**Principles of Nuclear Magnetic Resonance Microscopy.** By Paul T. Callaghan (Massey University). Clarendon Press: Oxford, England. 1991. xvii + 492 pp. $125.00. ISBN 0-19-853944-4.

Imaging by nuclear magnetic resonance has burgeoned almost beyond belief in the last 15 years. The bulk of the advances have been made in medical imaging, with extraordinary improvements in resolution, in sensitivity, and in different procedures for producing contrast. Microscopy by magnetic resonance was only demonstrated in 1986 but has also experienced very rapid development, and currently many models of pulse-Fourier transform spectrometers can be fitted with commercial units to allow microscopic examination of suitable materials.

NMR spectroscopy has led to the creation of many books with a variety of levels of sophistication. The classics of super-sophistication surely include Abragam's *Principles of Nuclear Magnetism* and Ernst, Bodenhausen, and Wokaun's *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*. Now, Oxford University Press strikes again with *Principles of Nuclear Magnetic Resonance Microscopy*.

As with its predecessors in the Oxford series, the emphasis in Callaghan's book is indeed on principles and, if you are looking for a manual covering experimental techniques and hardware, you will need to look elsewhere. Mathematical rigor starts early with a rapid introduction to principles of imaging; this is followed by an introduction to NMR including spin manipulation and multiple-quantum coherences in homogeneous magnetic fields. Then comes the real test of the reader's determination and background, an all-out foray into the key element of NMR imaging, the influence of magnetic-field gradients on the behavior of nuclear spin systems and its formulation in terms of Mansfield's k-space. The explanations for selective excitations and two-dimensional reconstructions are reasonably qualitative and well illustrated.

Following these general principles of imaging, which occupy about a third of the book, the focus turns to microscopy with detailed discussions of the physics of resolution, alternative contrast techniques, use of nuclei other than protons, liquid vs solids, diffusion, q-space imaging, and finally, a brief chapter (20 pages) describing the elements of the instrumentation and gradient-coil design.

The book is not for the faint-hearted in mathematics. However, if you understand the general principles of NMR spectroscopy, you should be able to read around the equations to gain further understanding of NMR imaging techniques in general, as well as those important in microscopy.

**John D. Roberts,** *California Institute of Technology*

---

**Advances in Electron Transfer Chemistry: A Research Annual. Volume 1.** Edited by Patrick S. Mariano (University of Maryland—College Park). JAI Press Inc.: Greenwich, CT, and London, England. 1991. xi + 197 pp. $78.50. ISBN 1-55938-167-1.

Two recent Nobel prizes have been awarded for work on electron transfer related chemistry. It is only fitting that this first of a series of volumes on electron transfer (ET) chemistry be published in the 1990s for critical, lively, and relevant recent essays by experts in fields that embody electron transfer, irrespective of whether it be in the field of organic, inorganic, physical, or analytical chemistry or biochemistry and regardless of whether electron transfer is thermally induced or photoassisted. This series of volumes is also a good addition to the recent set of four volumes edited by M. A. Fox and M. Chanon and published by Elsevier (1988) which addressed the specific area of photo-induced ET phenomena.

This first volume contains four critical and enlightening essays that are a "must be read" by the disciples and novices of electron transfer chemistry. The first, written by M. A. Fox, addresses the photo-induced ET phenomena that occur on irradiated semiconductor surfaces, an area where the Texas school (Austin) has made significant contributions. Specifically, the chapter looks at the mechanisms of photocatalyzed organic transformations. After a brief introduction and a discussion on the factors (adsorption, potential, current, kinetics, and the nature of solvent and cocatalysts) that control electron transfer on semiconductor surfaces, the body of the essay examines some of the details of such organic transformations as photo-oxidations, photo-oxidative cleavage of olefins, functional group oxidative reactivity, and organic photoelectrochemical reductions, to end with a brief treatment of transformations with reversible ET as the activation step. (254 references.)

The second chapter is titled Thermal and Photochemical Activation of Aromatic Donors by Electron Transfer, by Amatore and Kochi (University of Houston). These authors lay the basic groundwork for the various mechanistic aspects of aromatic activation by electron transfer; they have selected and rigorously treated a few examples to illustrate the viability of the electron transfer mechanism. Conventional wisdom has dictated that nitration of an arene is a simple addition of the electrophile to the ring to produce the Wheland intermediate; the alternative possibility considered here is a two-step process in which electron transfer occurs first to form an ion radical pair, which is subsequently followed by rapid collapse to give the same Wheland intermediate. Evidence for the formation of the radical pair by thermally driven processes has not been forthcoming; the photochemical activation route is explored. Aficionados of radical ion chemistry will be delighted with this essay. (106 references.)

The distance and angle effects on electron transfer rates in chemical and biological molecules are addressed in a very brief essay by McLendon and Helms (University of Rochester). The essay focuses on the role of wave function overlap, as modified by the donor–acceptor distance and angle, in governing the electron transfer process; examples from systems of biological importance are treated. The brevity of the essay and the small number of references (15) indicate this particular field of electron transfer chemistry has yet to mature in our collective understanding of ET in complex systems.

The volume ends with an essay by Schuster (University of Illinois), who examines bond cleavage following from, or leading to, an electron transfer event; in particular the essay after a brief introduction into the theory of electron transfer where terms of importance are defined, looks at the intra-ion-pair electron transfer reaction of cyanine borates, a process relevant in the photoinitiation of polymerization with visible light. Another example, among others, that is treated is the thermally initiated ET to an organic peroxide which results in the rupture of an O–O bond and eventually to the generation of light: chemiluminescence. (30 references.)

These four essays have emphasized each author's recent work without neglecting the work of others. The topics covered are of current interest, and although the list of references is by no means comprehensive and exhaustive, the seasoned researcher and the novice will find it a good starting source to amplify their understanding of electron transfer phenomena. This volume is affordable and is a must in anyone's laboratory.

**Nick Serpone,** *Concordia University*

**Molecular Design of Electrode Surfaces.** Edited by Royce W. Murray. Techniques of Chemistry, Volume XXII. John Wiley & Sons: New York. 1992. xi + 427 pp. $135.00. ISBN 0-471-55773-0.

This volume is the latest in the series Techniques of Chemistry, founded by Arnold Weissberger and presently edited by William H. Saunders, Jr. It follows the tradition of the series in exploring in moderate detail a subject in which the power of modern techniques of chemical research has helped bring forward a new and promising area of science, in this case the preparation and characterization of chemically complex electrochemical interfaces. Professor Murray is well positioned to edit a volume on this subject, as he has been actively involved in both the birth and development of this field.

The book consists of nine chapters, each written by a specialist in a particular subdiscipline of the title subject. Professor Murray begins the volume with an overview chapter to "...set the stage with some of the motivations for molecular electrode design." He proceeds to review selected examples of immobilized monomolecular and polymeric layers on electrodes and discusses the range of electrochemical reactivity commonly exhibited by such layers. The introductory chapter is heavily referenced (over 400 citations) and will serve both as an excellent introduction to the subject of designed electrode surfaces for the nonspecialist and as a resource to the original literature for the specialist.

The remaining chapters might best be thought of as a series of review articles on different aspects of the title subject. Specific subjects covered in these chapters, along with the authors, are as follows: Adsorbed Molecules on Well-defnied Electrode Surfaces (Salaita and Hubbard); Self-organized Electroactive Microstructures (Facci); Electron Transport in Redox-active Polymeric Assemblies (Majda); Catalysis at Redox-polymer-coated Electrodes (Andrieux and Saveant); Electrodes Modified with Clays, Zeolites, and Related Microporous Solids (Bard and Mallouk); Electron-transfer Mediation at Redox-polymer-coated Electrodes (Leidner); Voltammetric Diagnosis of Charge Transport in Polymer-coated Electrodes (Oyama and Ohsaka); and Mass and Charge Transport in Electronically-conductive Polymers (Martin and Van Dyke). Most of these chapters include an introduction, a discussion of relevant theory, and an overview of examples of specific chemical systems, usually with some emphasis on work from each author's laboratory. The chapters are in general not comprehensive in the sense of covering all the material on each subject; however they do provide insights that are possible only from authors who are active participants in the research endeavor. The book is universally well written and well referenced, including over 1400 literature citations and a comprehensive index. Nearly all of the citations are less than 15 years old; most chapters include references that are current through at least 1990, though some are more current.

The book is not without its characteristic biases and omissions. For example, electron conduction in redox-active polymers is discussed in some depth in at least five of the nine chapters. Application of designed electrodes in electrochemical sensing is however not covered at all. Readers interested primarily in electronically conducting polymer films will also be disappointed; the subject is mentioned in only one chapter, and then in only a very specific context. There is a systematic bias against material focusing only on electrode surface characterization; Murray has clearly made the chemistry of the designed interfaces, and not their characterization, the main focus of the book.

This volume is certain to be a valuable resource for specialists interested in chemically designed and modified electrode surfaces and for other scientists interested in learning about how this subdiscipline of electrochemistry has developed in the last fifteen years. Any science library which serves people interested and involved in the modern practice of electrochemistry should obtain this volume. Specialists in the field may wish to consider obtaining their own copy for ready reference.

**Stephen E. Creager,** *Indiana University*

**Surfactant Science Series. Volume 41. Light Scattering by Liquid Surfaces and Complementary Techniques.** Edited by Dominique Langevin (Ecole Normale Supérieure). Marcel Dekker: New York, Basel, and Hong Kong. 1992. ix + 451 pp. $150.00. ISBN 0-8247-8607-6.

Light scattering provides a useful means of studying collective dynamics of liquid surfaces and liquid–liquid interfaces. This ambitious volume presents a relatively comprehensive overview of surface light scattering and its applications, along with a short survey of related techniques.

The book is divided into four sections, the first of which deals with the general principles of surface light scattering in liquids. A brief history of the technique is presented, and then the basic mathematics of the scattering process are developed in detail. Following this are two short chapters on the practical aspects of performing surface light scattering experiments.

The second section of the book is devoted to the discussion of the most important applications of surface light scattering. The chapters in this section cover simple liquids, surface critical opalescence, liquid crystals, polymeric solutions, monolayers, lipid bilayers, multiphase microemulsions, thin liquid films, and nonequilibrium crystal-melt interfaces. Each chapter in this section is similar in format: first the relevant mathematics are introduced; then specific examples are presented, and practical problems with the particular application are discussed.

The third section of the book deals with complementary techniques for studying liquid surfaces, including externally-excited surface waves, light reflectivity and ellipsometry, X-ray and neutron scattering, and fluorescence methods. The fourth section consists of a short chapter on light scattering from solid surfaces.

Because of the wide scope of material covered in this volume, none of the topics is discussed in great detail; indeed, entire books can and have been written on the subjects of single chapters. As such, this book serves best as reference material for scientists performing surface light scattering experiments. Most of the chapters have thorough and up to date reference lists that would be of great value to the practitioner of this technique. On the flip side, however, the scientist from another field who is interested in using surface light scattering to solve a particular problem may have difficulty with this volume. The information in this book is not, for the most part, presented in such a way that the neophyte could quickly find necessary details. Along these lines, most of the chapters would have benefited from a quick discussion of the sort of information that can be obtained in a particular application before launching into the mathematics involved. Nevertheless, considering the ambitious scope of the material presented, this book does a good job of covering all the bases and will be of value to anyone considering doing surface light scattering experiments.

**John Fourkas,** *University of Texas at Austin*