Book Reviews

Organofluorine Chemistry: Principles and Commercial Applications. Edited by R. E. Banks (The University of Manchester), B. E. Smart (Dupont), and J. C. Tatlow (Journal of Fluorine Chemistry). Plenum Press: New York. 1994. xxv + 644 pp. $125.00. ISBN 0-306-44610-3.

As the editors state in the preface, the primary objective of this book is to provide an authentic and wide-ranging account of current commercial applications of fluoroorganic materials. With a team of almost 50 contributing authors, that goal has been achieved admirably. Interest in fluoroorganics has burgeoned in recent years due, in large part, to their increasing importance as agrochemicals, pharmaceuticals, medical diagnostic agents, polymers, fluids, and lubricants, as well as in the frenzied efforts to replace ozone-depleting CFCs and Halon fire extinguishers.

In Chapter 1, Banks and Tatlow offer an informal historical overview of the development of organofluorine chemistry. The reader will enjoy personal vignettes, such as the discovery of Teflon by Roy Plunkett and the use of "Joe's Stuff", the perfluorocarbons prepared by Simons for the secret Manhattan project. Chapter 2, by the same authors, features a fairly thorough tabular summary (through early 1992) of methods for the selective synthesis of C−F bonds. A second table lists useful examples of exhaustive fluorination of hydrocarbon feedstocks. In Chapter 3, Bruce Smart presents a superb, well-documented review of physical and chemical properties of C−F systems. Especially valuable are discussions on lipophilicity, acidity and basicity, reactive intermediates, and steric effects (F and O, *not* F and H, are nearly isosteric and the CF_3 group is much larger than CH_3 and at least as large as isopropyl!). Fundamental studies on perfluoroalkyl bromides and iodides (Chapter 8, Wakselman and Lantz) and the synthesis of benzotrifluorides (Chapter 10, Langlois) are well reviewed.

The remaining 23 chapters, varying in length from 4 to 38 pages, deal with a wide spectrum of commercial applications of fluoroorganics. The authors, almost all from industry, have "covered the waterfront" with a treasure trove of valuable information in clearly focused presentations on perfluorocarbon fluids, electrochemical fluorination, chlorofluorocarbons and alternatives, ring-fluorinated aromatics, agrochemicals, liquid crystals, dyes, surfactants and textile finishes, monomers and polymers from hexafluoroacetone, fluoropolymers (including plastics, elastomers, coatings, membranes, and perfluoropolyethers), and fluorinated carbon.

Chapter 24 on the uses of fluorine in chemotherapy (P. N. Edwards) is singled out for special mention. In this reviewer's opinion, the article is a tour-de-force and a major contribution by providing a long-needed, in-depth look at the *principles* behind the use of fluorine in drugs and in biochemical applications. For the first time, the subject is approached from a mechanistic and physicochemical viewpoint. Fluorinated inhalation anesthetics and biomedical applications of perfluorochemicals are well covered in separate chapters.

The book closes with an assessment of the fluorochemical industries in the United States, Western Europe, and Japan and a brief overview of CFCs and the environment.

The articles are well written, and the structures and diagrams are clearly illustrated. Most chapters cite references to 1990 or beyond. I recommend this book highly. It should be available in libraries or on the shelves of those working with or having an interest in organofluorine chemistry.

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Organic Reactions. Equilibria, Kinetics, and Mechanism. By F. Ruff (Eötvös University, Hungary) and I. G. Csizmadia (University of Toronto). Elsevier: Amsterdam. 1994. xviii + 464 pp. ISBN 0-444-88174-3.

The scope of physical organic chemistry is not clearly defined. Whereas initially the term was used by L. P. Hammett to deal with elucidation of reaction mechanisms based on information obtained from reaction kinetics (in particular, the reaction rate equation and effects of structure and medium on measured rate constants), it has been later extended to deal with other aspects of reactions, particularly equilibria and effects of structure on data obtained by physical chemical measurements. The reviewed monograph deals mostly with information obtained from kinetics but also with some equilibria, in particular, with solute−solvent interactions and acid−base equilibria.

The book is well organized, dealing first with nonkinetic information, then with principles of kinetics of both simple and complex reactions, substituent effects (based mostly on LFER), and isotope effects. This is followed by discussions of solvent effects, the role of ionic strength and the nature of neutral salts, effects of structure and solvents on acid−base equilibria, the use of acidity functions and superacids, and the reactivity of nucleophiles and electrophiles. Homogeneous acid−base and nucleophilic catalysis is discussed in the last chapter. Distribution of references with a predominance of older literature but inclusion of essential recent contributions corresponds to the historical development of this area.

Several aspects are particularly well presented—for example, the relationship between differential and integral forms of rate equations (pp 61 and 62) is very clearly explained as well as the principles of acid−base reactions (p 318 ff.) and the importances of isokinetic relationships (p 148). Good selections of problems accompany each chapter. As the authors—as all practitioners in the field—are unable to change the paucity of published primary kinetic data in chemical literature (reflecting since the 1950s strict editorial policies), most problems deal with reasoning rather than with practicing of real life data handling.

Perhaps less well explained is (pp 58−61) the distinction between stoichiometry (empirically obtained information dealing with ratios of the consumption of starting materials and yields of products), order of reaction (empirical value obtained from kinetics studies, which has well defined meaning only for simple reactions of the type $aA + bB + cC \rightarrow$), and molecularity (which is a theoretical concept, established *after* the mechanism has been elucidated).

The authors seemingly did not appreciate fully the impact and importance of the Kamlet−Taft treatment of solvent effects, particularly since many other semiempirical treatments of such effects can be correlated using this approach. The main limitation of the Kamlet−Taft treatment at present seems to be the lack of understanding of limits of its application.

In the interpretation of the dependences of rate constants on pH, the use of semilogarithmic plots of $k = f(\text{pH})$ is not mentioned, even when they are more informative than $\log k = f(\text{pH})$ plots. The former offer direct information about the pK_a values of acid−base reactions involved, their slopes indicate the number of transferred protons, and their use can prevent missing of trends of deviations, that can go unnoticed in the log−log plots.

This volume is strongly recommended as a useful text for upper level college courses and as an introduction to the discussed areas of physical organic chemistry.

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