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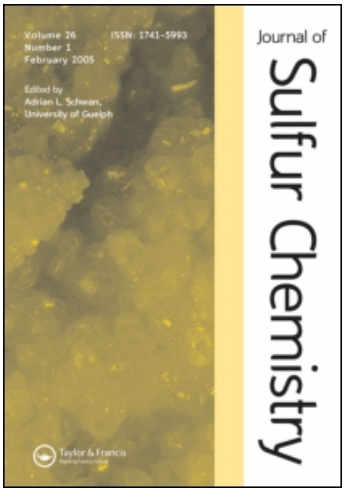

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BOOK REVIEWS

Nucleophilicity, Edited by J. Milton, Harris and S. P. McMarcus. Adv. in Chemistry Series 215, American Chemical Society, Washington DC, 1987, clothbound, xiii + 494 pp, US and Canada $94.95, export $113.95, ISBN 0-8412-09. LC 86-28843.

The book is an outgrowth from a symposium on nucleophilicity held in Chicago in September 1985. It consists of 31 chapters which have been divided into 5 sections. (1) Marcus Theory, Alkyl Transfer, and Gas-Phase Reactions; (2) Brønsted Equation, Hard-Soft Acid-Base Theory, and Factors in Nucleophilicity; (3) Linear Free-Energy Relationship for Solvent Nucleophilicity; (4) Novel Nucleophilic Reactions; and (5) Enhancement of Nucleophilicity.

In the first chapters the editors give an introduction to the subject and review the current study of nucleophilicity by describing the chapters in the book and giving a brief survey of the literature leading up to these works.

In chapter 2 J. I. Brauman *et al.* discuss nucleophilic displacement reactions of anions with alkyl halides in the gas phase by using mass spectrometric technique. On the basis of Marcus theory the energies of the self-exchange reaction, $Y^- + CH_3Y \rightleftharpoons CH_3Y + Y^-$, are suggested as a measure for the intrinsic nucleophilicity of Y. Some supposedly good nucleophiles are found to be rather poor nucleophiles by this definition.

E. S. Lewis *et al.* describe nucleophilic substitutions in sulfolane. They find that the quadratic term in Marcus equation is of minor importance and a simple equation can be used for methylations which relate the rate constant to a property of the methylating agent and the properties of the nucleophile. These properties can be obtained from the equilibrium constant with a reference compound and the self-exchange reaction.

Reactions in the gas-phase are also discussed by R. N. McDonald *et al.*, M. C. Caserio *et al.*, and M. Henchman *et al.* using different techniques to study several nucleophilic reactions, including addition to carbonyl groups, acylation reactions, and nucleophilic displacement reactions involving solvated nucleophiles.

Ando *et al.* measure the carbon and nitrogen kinetic isotope effect (KIE) of methyl transfer; the KIE of carbon was large and indicates the importance of the Walden inversion motion in methyl transfer in which transition states hold total bonding constant.

In chapter 8 C. F. Bernasconi employs the principle of non-perfect synchronization and uses well-known concepts in combination with Marcus theory to predict changes in nucleophilic reactivity.

The application of the Brønsted equation and other linear free energy relations is discussed in chapters by F. G. Bordwell *et al.*, W. P. Jencks, and C. D. Ritchie, and the influence of, *inter alia*, basicity, oxidation potential, and solvation on the rate of nucleophilic reactions is considered. Although a linear relationship may be found within

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different families of reactions, it has not been possible to find equations which permit a quantitative prediction of rates for a variety of substrates.

The nature of transition states of nucleophilic reactions with low and high energy LUMO has been discussed by S. Hoz. It is concluded that lowering of the energy of LUMO results in an increased diradicaloid character of the transition state. The α-effect is also discussed in this connection and also in the chapter by R. F. Hudson.

The relationship between reactivity of a nucleophile with an electrophile and the distance separating them is treated in the chapter by F. M. Menger. It is shown by means of rigid molecular frameworks bearing two functionalities at well-defined distances that the reactivity is very sensitive to distance and the angle of attack.

The HSAB principle of R. G. Pearson is applied by K. Fuji for designing nucleophilic reagents for cleaving C–X bonds, and the HSAB classification is discussed by R. G. Pearson in connection with rates of reaction of transition metal nucleophiles. It is found that the rates correlate both with the oxidation potentials of the nucleophile and with the pK_A of the corresponding acid, so these are not independent properties.

The influence of solvents on nucleophilic reactions is treated in several papers; nucleophilic and electrophilic solvent assistance, different solvent parameters, and the various equations relating them are discussed. Predictions about the influence of solvents are reliable only within rather closely related systems.

In the chapter on single electron transfer (SET) in nucleophilic reactions A. Pross argues that nucleophilic reactions, both polar and SET, involve a single-electron shift. The physical meaning of "shift" in relation to "transfer" is not clearly defined. The configuration mixing model is used to make qualitative predictions on the influence of parameters such as donor-acceptor pair ability, steric hindrance, bond strength, and radical delocalization.

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Reactions involving electron-transfer are also discussed in the chapters of G. Sorrano *et al.* and G. A. Russell *et al.* In the first one the competition between reduction and substitution in the reaction of 4-chloronitrobenzene with alkoxide is examined and in the other one the reaction between alkyl radicals and enolate ion is discussed. The reactivity of t-Bu radical decreases with an increase in basicity of the nucleophile, whereas for $PhCOCH_2$ the opposite trend is found.

The reactions of some ambident nucleophiles with nitro-aromatic electrophiles, the mechanism of the reaction of sulfonyl chlorides and of vinylic compounds with nucleophiles are discussed in chapters by E. Buncel *et al.*, J. F. King *et al.*, and Z. Rappoport.

Finally, micellar effects on nucleophilicity, the effect of cations on such reactions, and the manipulation of nucleophilic displacement reactions by means of host-guest complexes are treated.

A book based on contributions to a meeting has certain advantages and disadvantages. Among the advantages are that several points of view are presented in an authoritative way and all the subjects treated are discussed by specialists in the field; one of the disadvantages is that the book consists of 31 separate chapters, some have the character of a review, some are more like research papers.

Misprints are unavoidable, the book is relatively free of them; just to tease the editors, a couple of misprints could be mentioned from their introduction. On p. 10 the "lowest

occupied molecular orbital" should, of course, be "lowest unoccupied . . .", and on p. 19 occurs a reference 45 but this is not found in Literature Cited.

In summary, the book is interesting reading for all organic chemists, including graduate studients as well as experienced chemists; it maintains the high standard of the series and can be recommended for all libraries.

Henning Lund
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GINO J. MARCO, ROBERT M. HOLLINGWORTH, and WILLIAM DURHAM (Eds.), *Silent Spring Revisited*, American Chemical Society, Washington, DC, USA, 1987. xviii + 214 pp. Clothbound US $ 35.95 (in USA and Canada US $ 29.95), ISBN 0-8412-0980-4. Paperbound US $ 21.95 (in USA and Canada US $ 17.95), ISBN 0-8412-0981-2.

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This book, the proceedings of a 1984 symposium, contains the following chapters:

Rachel Carson: Her Vision and Her Legacy (by Shirley A. Briggs)

The Not So Silent Spring (by John A. Moore)

The Science and Politics of Pesticides (by C. F. Wilkinson)

Assessing the Toxicity of Pesticides to Aquatic Organisms (by D. R. Nimmo, D. L. Coppage, Q. H. Pickering, and D. J. Hansen)

Impact of Pesticides on Ground Water Contamination (by Robert F. Carsel and Charles N. Smith)

Impact of Pesticides on Bird Populations (by Russell J. Hall)

Human Health Effects of Pesticides (by J. E. Davies and R. Doon)

Analytical Chemistry of Pesticides: Evolution and Impact (by Joseph D. Rosen and Fred M. Gretch)

Pesticides: Global Use and Concerns (by Virgil H. Freed)

Agriculture, Pesticides, and the American Chemical Industry (by Gustave K. Kohn)

Is Silent Spring Behind Us? (by David Pimentel)

Many Roads and Other Worlds (by Gino J. Marco, Robert M. Hollingworth, and William Durham)

The book also contains appropriate indexes and glossaries.

While the 32 months production time of this volume must be considered excessive by any standards, this book contains useful factual information as well as expert opinions and predictions. By virtue of the editors' efforts and the production as a printed book the typical hotch-potch appearance of a symposium volume has been avoided.

However, on balance this reviewer doubts that this book's level corresponds to a legitimate readership. Off hand, it appears too difficult to grasp for the neophyte and too sketchy for the expert. Nevertheless, few private or institutional libraries with ecology among their subjects will wish to forego this addition to their collection.

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