Book Reviews

Thermochemical Kinetics. Methods for the Estimation of Thermochemical Data and Rate Parameters. By SIDNEY W. BENSON, Chairman, Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, Calif. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1968. xii + 223 pp. 15.5 × 23.5 cm. $9.95.

When I completed graduate work and tried to estimate the changes I could expect to see in chemistry during my professional career, I hoped that by the time I retired a bright young chemist with a slide rule and a few empirical parameters could predict the occurrence of about three-quarters of the reactions presented in an elementary course in organic chemistry, including optimum conditions of temperature and solvent and approximate values for rates and yields. Over a quarter of a century later, I am willing to allow that chemist the fastest digital computer that technology can produce, but I no longer expect him to do his thing by the time I retire.

Dr. Benson has restricted himself to gas reactions but has attempted to show how to estimate the position of equilibrium and the rate for any hypothetical reaction involving reasonably conventional compounds. Although the heroic effort does not quite come off, the failure is due to the difficulty of the subject rather than to lack of ability of the author; probably nobody today could do better.

The first of the four major sections attempts to summarize theories of chemical kinetics in 17 pages. Such a summary is useful for reference, but no student should attempt to learn the subject from this brief discussion.

The second section deals with estimating thermochemical data for equilibrium systems. The approach is very empirical, but the group parameters presented here permit good estimates of enthalpy, entropy, and heat capacity changes for a large number of hypothetical reactions. The tables connected with this section would justify the purchase of the book by anybody interested in gas reactions.

The third major section attempts to provide rules for estimating Arrhenius parameters for elementary processes in gas phase. The results of A-factor estimations are rather impressive, although it is not always clear how well the rules would work when not accompanied by Dr. Benson's exceptional intuition. Activation energies are another story, and the book makes little attempt to show how to estimate them for any reactions except single bond dissociations and atom abstractions. We badly need a good method to estimate activation energies for reactions involving four or more reaction centers. Dr. Benson and I have both tried our hands at this problem, and neither has much reason to feel satisfied with his accomplishments.

The fourth section considers a number of complex reaction systems. The examples chosen are interesting, but many other complex systems also exist. Treatments of general utility are very hard to develop.

This review can be summarized as follows. This book has lots of useful information if you want to estimate changes in thermodynamic properties due to a gas reaction. It can also help you to make an educated estimate of the Arrhenius A factor for an elementary process. It offers keen insights into a number of complex reaction types that may include systems of interest to you. Its failure to go much further points up how much more we must know before we can do a really good job of predicting reaction mechanisms from the properties of individual molecules.

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The Principles of Heterocyclic Chemistry. By ALAN R. KATRITZKY, M.A., D.Phil., Ph.D., Sc.D., Dean of the School of Chemical Sciences, University of East Anglia, Norwich, England, and J. M. LAGOWSKI, B.S., M.S., Ph.D., Research Scientist, Genetics Foundation, The University of Texas, Austin, Texas. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1968. xiv + 183 pp. 16 × 23.5 cm. $6.75.

This is a somewhat streamlined and updated version of the book which in 1960 pioneered in presenting heterocyclic chemistry in a unified mechanistic fashion.

The general plan of presentation is to discuss heterocycles which are subject to similar chemical influences together in a chapter. Each discussion begins with mention of a few compounds that the reader might have heard about and some brief comments on nomenclature. The emphasis in the ring-synthesis sections is on general methods, of which specific examples are also given. Next are presented the reactions of the rings: the very frequent and often reversible electrophilic reactions at the heteroatom, electrophilic and then nucleophilic substitutions at ring carbon atoms, radical reactions at ring carbons, and rupture of the rings. Variation of behavior in all these reactions is shown to be determined by the number and nature of the heteroatoms, the ring size, electron density, etc. A convenient and clear exposition of the results of multisite reactions is made with short heavy arrows and the per cent reaction at the ring positions involved. As is reasonable, the saturated heterocycles are dealt with only briefly since their reactions are mostly aliphatic in nature.

Chapters 2–5, covering the various heterocyclic classes, are arranged exactly the same, thus facilitating comparison of the synthesis and reactivity of heterocyclic types. Preparation of one heterocyclic compound from another is inserted at the logical reactivity point rather than at a point governed by the expected importance of product or reactant. Ring closures are discussed on the basis of reaction mechanism and the activating and deactivating effects of substituents. The authors adhere to the important but frequently ignored principle that reactions should be presented using the actual reacting species, *e.g.*, the pyridinium ion in nitration or sulfonation of pyridine. This approach leads to some incisive differences in evaluation of certain phenomena. For instance, the apparent activating effect of chlorine in 2,6-dichloropyridine toward nitration is properly classified not as activation by the substituents but as a change in the reacting species. With this dihalopyridine, the *base* is involved in this reaction which is quite facile relative to that of unsubstituted *pyridinium ion*. Further indication of the high quality of the book is given by the fact that the authors emphasize in several places the dangers of deducing the structure of tautomers (or other interconvertible compounds) from their reaction products. Such deductions can be seriously in error depending on the actual reaction rates of the possible structures, the reversibility of their reactions, and the interconvertibility of their products.

Typographical and other errors seem to be very rare. The structures are clear and realistically drawn; however, structure 29 could be improved. The notations at the tops of the pages enable one to flip quickly to any desired section; the table of contents is thorough enough to locate reaction or compound types. The text is made quite readable by the generous use of structures for all the types of reagents and products as well as for many specific compounds and reaction products.

"Principles of Heterocyclic Chemistry" should provide the student with a modern approach to the most important and fastest growing section of organic chemistry. In addition, research workers will find a well-organized framework on which to add recent work of others or from which to develop ideas for work of their own.

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