Chemical Kinetics

Fast Reactions and Primary Processes in Chemical Kinetics. Proceedings of the 5th Nobel Symposium, Stockholm, Aug.–Sept. 1967. STIG CLAESSON, Ed. Interscience (Wiley), New York; Almqvist and Wiksells, Stockholm, 1967. 487 pp., illus. $27.50.

The Nobel Symposium on fast reactions and primary processes in chemical kinetics is a testimonial to the impact of the work of R. G. W. Norrish, G. Porter, and M. Eigen on the advancement of this field in the last two decades.

What the techniques of these distinguished kineticists have in common is the rapid input of energy, via light, heat, or electric field, followed by an appropriate method for the fast recording of the subsequent events. The flash-photolysis research of Norrish and Porter enables the initiation of reactions in systems far from equilibrium and the study of the chemistry of excited states.

The temperature-jump and high-field techniques of Eigen make possible the rapid displacement of systems from equilibrium followed by measurement of the relaxation rate. These techniques, with the addition of the more recently available laser light sources, enable measurement of reaction rates covering many orders of magnitude in time, from picoseconds to minutes. Rate processes covering this range are discussed in this volume.

The participants in the symposium, in addition to the Nobel laureates, included a group of outstanding scientists interested in chemical kinetics per se, or in using it as a means for study of rates and mechanisms of reactions of chemical and biological importance. The contributions include papers ranging in subject matter from reactions involving species such as atoms and diatomic molecules to reactions in complex biological systems. In spite of this great variation in system complexity, most of the chapters, with the exception of the review of flash initiation of gas-phase reactions by Norrish, treat dynamics involving simple species—electrons and protons, vibrational and electronic excited states, and monoenergetic hydrogen atoms.

In addition to the techniques advanced by the Nobel laureates, other recent experimental and theoretical advances in fast-reaction kinetics are included. Two papers by Prigogine summarize recent contributions of his group on the statistical mechanics of rate processes. Especially challenging is his conclusion that in dissipative processes, for example, in a system in which diffusion and chemical reactions are coupled, chemical instabilities can arise. Although the existence of such an instability was suggested by Chance with respect to his experiments on a specific enzyme reaction, the need for experimental confirmation remains.

Nine of the 24 papers discuss the application of flash photolysis in chemical and biological systems. Three papers, two of them by Eigen, discuss the application of the jump methods to proton transfer in solutions and to reactions in biological systems. Among other topics treated are the chemistry of the electron in aqueous and gas phase and the use of the stopped-flow technique to study rates of biochemical processes, and there are papers summarizing the mechanisms of proton transfer and of nerve action. In addition to these contributions, some of the discussions of specific papers and summarizing statements by Porter and Eigen are included. The latter are especially noteworthy for the challenge they present to future chemical kineticists by discussing needed techniques and problems to be solved. One of the more interesting discussions is that between B. Chance and H. T. Witt on the interpretation of the latter's research on photosynthesis.

In spite of the high caliber of the contributors and contributions, the book cannot be considered to be a complete summary of the current status of chemical kinetics. It will be of greatest interest to those desiring a summary of the influence of the Nobel laureates on the science of chemical kinetics, to scientists interested in energy-exchange processes, and, especially, to those desiring information on the application of kinetics to the understanding of biological phenomena. It has less to offer on the theory and measurements of the kinetics of gas-phase reactions than does *Molecular Dynamics of the Chemical Reactions of Gases*, volume 44 of the Discussions of the Faraday Society.

The clarity of print and figures, especially the reproduction of spectra, is excellent. However, the reviewer found the frequency of misspelled words high for a book of this overall quality.

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Coordination Complexes

Reactions of Transition-Metal Complexes. J. P. CANDLIN, K. A. TAYLOR, and D. T. THOMPSON. Elsevier, New York, 1968. xvi + 483 pp., illus. $30.

This book represents a significant attempt to bring to the attention of the synthetic organic chemist an area which is likely in the future to have a major impact on investigations of organic synthesis. However, interest in this volume will by no means be confined to synthetic organic chemists. Transition-metal complexes are taken in their largest definition to include organometallic compounds (containing metal carbon bonds) as well as more classical coordination complexes. This review of reactions of transition-metal complexes consists of three parts. The first is a discourse and review of the types of reactions which these complexes undergo. This section is quite extensive (210 pages) and covers substitution reactions, combination reactions, and redox reactions as the main types. Mechanistic aspects are stressed, and extensive examples and literature references are given. The second section (206 pages) deals with the reactivity of classes of reagents with transition-metal compounds. The six chapters in this section are headed: "Hydrocarbon reactions"; "Reactions of organic halogen compounds"; "Reactions of carbon monoxide and isonitriles"; "Reactions of OR^-, OH^-, and CN^-"; "Reactivity of H^-, H_2 and H^+"; and "Reactions of inorganic compounds." Each chapter is extensive, consisting of several sections each with its own list of literature references. For instance, the chapter on reactions of inorganic compounds has sections dealing with the following classes of reagent: group IV elements; nitrogen compounds; nitric oxide; phosphines, arsines, and stibenes; group VI elements; halogens; and mercury compounds. The third and final part of the book, entitled Preparation of New Organic Systems, is extremely brief (19 pages) and may be disappointing to some readers. Instead of outlining the preparation of new organic compounds via transition-metal-containing intermediates, it discusses some classes of novel organometallic compounds: metallocenes, π-bonded heterocycles, and cyclobutadiene derivatives, among others. The heading of the chapter that constitutes this section, "Stabilized organic systems," seems to describe the contents more accurately.