Book Reviews

Solvolysis Mechanisms. By EDWARD R. THORNTON, University of Pennsylvania. The Ronald Press Co., 15 East 26th St., New York 10, N. Y. 1964. viii + 258 pp. 14 × 21 cm. $7.00.

The exact way in which alkyl halides, sulfonates, and similar compounds undergo displacement reactions in solution has intrigued organic chemists for decades. The terms *solvolysis*, analogous to *hydrolysis*, was introduced as a general term to include all reactions in which these substrates react with nucleophilic solvent molecules. Frequently, those concerned with the mechanisms of such reactions have cast wider nets to take in reactions of the substrate with solute molecules and ions. Professor Thornton, in the present book, casts a very wide net, indeed.

The first third of the book deals with theory and includes discussions of chemical kinetics, partition functions, steric effects, and molecular orbital calculations. These sections are well done, but much of this material could have been omitted without harming the subsequent discussion. The next two chapters, accounting for approximately half of the pages in the book, deal with many aspects of solvolysis mechanisms including bridge-head ions, internal and external return, ion pairs, neighboring groups, nonclassical ions, nucleophilicity, and leaving-group ability. In addition such fundamental relations as the Hammett equation are derived and discussed in general terms before being applied to solvolysis reactions. A curiosity in this part of the book is a seven-page section bearing the same heading as the title of the book itself. The final chapter deals with isotope effects and there are three appendices which provide additional theoretical material.

The book is free from errors and the typography is good (except that S_N2 appears as SN2 throughout). As with other books in this series, "Modern Concepts of Chemistry," the references do not appear at the bottom of the page and one must do considerable page-flipping to trace a particular piece of work. This is more noticeable in the present volume because authors are almost never referred to by name in the text. A very good feature, however, is the brief discussion of pertinent references which concludes each chapter. These sections do include authors' names.

Inevitably one must compare this book with Streitwieser's *Chemical Reviews* article "Solvolytic Displacement Reactions" which first appeared in 1956 and was updated and placed between hard covers in 1962. The books are comparable in length but Streitwieser includes much more "hard" news. There is possibly four times as much data in tables and figures and about four times as many references in Streitwieser as in Thornton. In addition, the discussion of neighboring-group effects is much more extensive in Streitwieser. Thornton's strong point is his perceptive treatment of the subtleties of mechanistic variation in S_N1 and S_N2 reactions. In addition many readers will find this a useful introduction to the more theoretical aspects of organic chemistry. However, those interested only in solvolysis mechanisms, *per se*, will feel that extensive editing could have drastically cut the size of the book without affecting its principal message.

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Principles of the Theory of Solids. By J. M. ZIMAN, Professor of Theoretical Physics, University of Bristol. Cambridge University Press, 32 East 57th St., New York, N. Y. 1964. xii + 360 pp. 16 × 23.5 cm. $8.50.

Ziman's book is well organized, accomplishing admirably its objective of treating in a readable way the physical processes associated with perfectly regular crystal lattices. To quote from the preface, ". . . there is no serious discussion of alloys, dislocations, F-centres, impurity centres, etc. There is nothing about magnetic resonances associated with single atoms or nuclei, and no attempt to interpret essentially macroscopic phenomena as ferromagnetic domains, p–n junctions or the intermediate state of a superconductor. The exclusion of all except simple, perfect, crystalline solids is artificial, but it is convenient, for it gives some unity to the discourse, which is centred on the mathematical consequences of lattice periodicity . . . ." This is indeed an accurate appraisal. The topics which *are* discussed include magnetism, superconductivity, transport, the Fermi surface, electron–electron interactions, and standard introductory material on phonons and Bloch electrons. There is no undue emphasis on crystallography, and no group-theoretical background is assumed. The treatment is at approximately the second-year graduate level in physics or chemistry, though among chemists it will be appreciated mainly by those with rather formal inclinations. The drawings are of high pedagogical merit and are large in number (174). Because of its readability and reasonable price, this book is likely to become quite popular as a first-semester solid-state text.

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