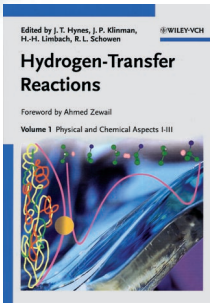
Hydrogen-Transfer Reactions



Vols. 1–4. Edited by *James T. Hynes, Judith P. Klinman, Hans-Heinrich Limbach* and *Richard L. Schowen*. Wiley-VCH, Weinheim 2006. 1559 pp., hardcover € 499.00.—ISBN 927-3-527-30777-7

Hynes, Klinman, Limbach, and Schowen present an impressive collection of short articles on fundamental aspects of hydrogen-transfer reactions and their applications in organic chemistry, biochemistry, and materials science. Experimental techniques and results, and their theoretical descriptions at different levels of complexity, are provided by key players in the field. The emphasis lies on the physical and chemical aspects and mechanistic details of the transfer of protons, hydrogen atoms, or hydride ions, with the latter two viewed as proton-coupled electron-transfer reactions. As hydrogen is the lightest element, protons are particularly subject to tunneling. Its experimental signatures are tunneling splitting of vibrational energy levels, characteristic kinetic isotope effects, and a non-Arrhenius temperature dependence of the reaction rate constants. The discussion of these topics is rounded off by chapters on hydrogen bonding and acid–base catalysis. Selected examples of applications in materials science, organic chemistry, and biochemistry are described.

Each of the four volumes is divided into two major sections, physical and chemical aspects in the first section and biological aspects in the second. Each of these sections is further split up into topic-specific parts and chapters, which are contributed by more than 80 different authors. The parts and sections are introduced by short statements by the editors, with descriptions of the contents of the individual chapters. Here the editors might have made more use of the opportunity to connect the different sections in order to develop a bigger picture. Each chapter is self-contained. As a consequence, definitions, introductory sequences, and key arguments are at times repetitive, but different ways of putting complex ideas also help one to understand them. While some authors focus on results from their own groups, the majority give a balanced introduction to a broader subsection of the field, with references to key articles from the original literature.

Kinetic isotope effects and tunneling are the lead ideas that connect the physicochemical and biological parts of the books. A second link is provided by the role of skeletal motion in proton and hydrogen atom transfer, as revealed by ultrafast spectroscopy, which is matched by the contribution of protein backbone motions in enzyme-catalyzed hydrogen transfer. Much space is devoted to the current controversy about whether enzymes employ and enhance tunneling to achieve their catalytic goals of rate increase and selectivity, and this is probably the most inspiring aspect of the books.

The fundamental aspects of hydrogen-transfer reactions are discussed comprehensively, although inevitably some relevant studies are not covered, in particular Carr–Parinello simulations of proton transfer in aqueous solution, proton diffusion in rare-gas matrices, and activation of C–H bonds by transition-metal ions in the gas phase. On the other hand, with regard to applications, the vast range of applications outside biochemistry is only superficially covered, and homogeneous organometallic catalysis is completely omitted. Heterogeneous catalysis is implicitly included in the chapters on zeolites and elemental hydrogen on metal surfaces.

Since few people will read all 1500 pages of the four-volume work, a 33-page alphabetical index helps to identify the chapters of interest. Given the heterogeneous character of the material, there seems to be no quick and easy way of accessing the full richness of the contents. There is a danger that the book goes back to the library shelf after browsing the first volume, as applications-oriented students will be discouraged by the ultrafast spectroscopy and tunneling-splitting chapters in the beginning, not realizing that "their" chapters are coming later. The strength of the books lies in their interdisciplinary nature, bringing together ultrafast spectroscopy of small molecules with enzyme kinetics, synthesis of complicated model compounds for enzyme catalysis and artificial enzymes, as well as the smallest molecules capable of intramolecular proton transfer. However, it takes significant time and effort to appreciate the deep thoughts voiced in the individual chapters.

The four-volume collection is indispensable for researchers working on kinetic isotope effects and tunneling, as might be expected from the names of the editors. Synthetic organic and inorganic chemists, as well as biochemists, are provided with readable short accounts of fundamental physicochemical ideas—which are not only relevant to hydrogen-transfer reactions—that have been developed and refined over the last 20 years. Teachers of physical chemistry will benefit from a treasure trove of first-hand treatises on a broad variety of up-to-date experimental methods and theoretical concepts. The links to modern applications in biochemistry, as well as to fuel cells, will be particularly appealing to students.

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