Preface

As one of the simplest of chemical reactions, pervasive on this highly aqueous planet populated by highly aqueous organisms, yet still imperfectly understood, the transfer of hydrogen as a subject of scientific attention seems hardly to require defense. This claim is supported by the readiness with which the editors of this series of four volumes on *Hydrogen-transfer Reactions* accepted the suggestion that they organize a group of their most active and talented colleagues to survey the subject from viewpoints beginning in physics and extending into biology. Furthermore, forty-nine authors and groups of authors acceded, with alacrity and grace, to the request to contribute and have then supplied the articles that make up these volumes.

Our scheme of organization involved an initial division into physical and chemical aspects on the one hand, and biological aspects on the other hand (and one might well have said biochemical and biological aspects). In current science, such a division may provide an element of convenience but no-one would seriously claim the segregation to be either easy or entirely meaningful. We have accordingly felt quite entitled to place a number of articles rather arbitrarily in one or the other category. It is nevertheless our hope that readers may find the division adequate to help in the use of the volumes. It will be apparent that the division of space between the two categories is unequal, the physical and chemical aspects occupying considerably more pages than the biological aspects, but our judgment is that this distribution of space is proper to the subjects treated. For example, many of the treatments of fundamental principles and broadly applicable techniques were classified under physical and chemical aspects. But they have powerful implications for the understanding and use of the matters treated under biological aspects.

Within each of these two broad disciplinary categories, we have organized the subject by beginning with the simple and proceeding toward the complex. Thus the physical and chemical aspects appear as two volumes, volume1 on simple systems and volume 2 on complex systems. Similarly, the biological aspects appear as volume 3 on simple systems and volume 4 on complex systems.

Volume 1 then begins with isolated molecules, complexes, and clusters, then treats condensed-phase molecules, complexes, and crystals, and finally reaches

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treatments of molecules in polar environments and in electronic excited states. Volume 2 reaches higher levels of complexity in protic systems with bimolecular reactions in solution, coupling of proton transfer to low-frequency motions and proton-coupled electron transfer, then organic and organometallic reactions, and hydrogen-transfer reactions in solids and on surfaces. Thereafter articles on quantum tunneling and appropriate theories of hydrogen transfer complete the treatment of physical and chemical aspects.

Volume 3 begins with simple model (i.e., non-enzymic) reactions for proton-transfer, both to and from carbon and among electronegative atoms, hydrogen-atom transfer, and hydride transfer, as well as the extension to small, synthetic peptides. It is completed by treatments of how enzymes activate C-H bonds, multiple hydrogen transfer reactions in enzymes, and theoretical models. Volume 4 moves then into enzymic reactions and a thorough consideration of quantum tunneling and protein dynamics, one of the most vigorous areas of study in biological hydrogen transfer, then considers several specific enzyme systems of high interest, and is completed by the treatment of proton conduction in biological systems.

While we do not claim any sort of comprehensive coverage of this large subject, we believe the reader will find a representative treatment, written by accomplished and respected experts, of most of the matters currently considered important for an understanding of hydrogen-transfer reactions. I am enormously grateful to James T. (Casey) Hynes and Hans-Heinrich Limbach, who saw to the high quality of the volumes on the physical and chemical aspects, and to Judith Klinman, who gave me a nearly free pass as her co-editor of the volumes on biological aspects. We are all grateful indeed to the authors who contributed their wisdom and eloquence to these volumes. It has been a very great pleasure to be assisted, encouraged, and supported at every turn by the outstanding staff of VCH-Wiley in Weinheim, particularly (in alphabetical order) Ms. Nele Denzau, Dr. Renate Dötzer, Dr. Tim Kersebohm, Dr. Elke Maase, Ms. Claudia Zschernitz, and – of course – Dr. Peter Gölitz.

Lawrence, Kansas, USA, September 2006 *Richard L. Schowen*

Preface to Volumes 1 and 2

These volumes together address the subject of the physical and chemical aspects of hydrogen transfer, volume 1 focusing on comparatively simple systems and volume 2 treating relatively more complex ones.

Volume 1 comprises three parts, commencing with Part I, dealing with hydrogen transfers of polyatomic molecules and complexes in relatively isolated conditions. In the first three contributions, the transfer is a coherent tunneling process rather than a rate process, characterized by "tunnel splittings" or delocalized hydrogen nuclei, for which electronic and vibrational spectroscopies are common and potent tools. The molecular systems discussed are malonaldehyde and tropolone (Redington, Ch. 1), carboxylic acid dimers (Havenith, Ch. 2) and strongly hydrogen-bonded systems such as $(H_2O...H...OH_2)^+$ (Asmis, Neumark and Bauman, Ch. 3). Kühn and Gonzales (Ch. 4) consider theoretically the more active role of infrared radiation in controlling hydrogen dissociation dynamics in e.g. OHF^-.

The five contributions of Part II focus on condensed matter. If the barriers are large, the hydrogen transfer becomes a rate process which may involve incoherent tunneling. Ceulemans (Ch. 5) examines proton abstraction by alkanes from strongly acidic alkane radical cations in inert matrices. Limbach (Ch. 5) follows the kinetics of single and multiple hydrogen and deuteron transfers in liquids and solids via NMR. Optical methods are applied by Douhal (Ch. 6) to systems embedded in a nanocavity, and embedded in liquids and polymer matrices by Waluk (Ch. 7), with a contrast to coherent hydrogen transfer in supersonic jets. Finally, Vener (Ch. 9) compares theory and experiment for anharmonic vibrations of strong hydrogen bonds in crystals.

Part III, comprising four chapters, commences the examination of hydrogen transfer – here proton transfer – in polar environments. The strong electrostatic proton-environment interaction guarantees incoherent rate phenomena. Kiefer and Hynes (Ch. 10) lay out the theoretical description for such reactions. The next three chapters exploit the greatly enhanced acidity of aromatic acids in the excited electronic state. Lochbrunner, Schriever and Riedle (Ch. 11) focus on the role of the motion of the groups between which the proton transfers, Pines and Pines (Ch. 12) thoroughly examine the insight to be gained from Förster cycle and free

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energy analyses, while Tolbert and Solnstev (Ch. 13) pursue related themes for "super" photoacids in the concluding chapter of volume 1.

Volume 2 opens with Part IV dealing with hydrogen transfer in protic systems. Generally, a larger number of solvent molecules is involved, and hence multiple protons may be transferred. The first two chapters elucidate molecular details of proton transfer in solution via ultrafast infrared spectroscopy. Nibbering and Pines (Ch. 14) examine the transfer between acid-base pairs for the acid in the excited electronic state, while Elsaesser (Ch. 15) discusses coherent low frequency motions coupled to related proton transfers as well as in hydrogen-bonded complexes. The final two chapters in Part IV deal with proton transfer coupled to electron transfer, with Hammes-Schiffer (Ch. 16) expounding and illustrating the theory for these, while Hodgkiss, Rosenthal and Nocera (Ch. 17) discuss these reactions with a special emphasis on the connection to hydrogen atom transfer.

Part V, consisting of four chapters, opens with a discussion of the kinetics and mechanisms of proton abstraction from carbon in organic systems by Koch (Ch. 18) and then turns to a presentation by Williams (Ch. 19) on free energy relationships for proton transfer, as informed by various theoretical approaches. The final two chapters are devoted to hydrogen and dihydrogen mobility in the coordination sphere of transition metal complexes, where the transition from coherent to incoherent H-tunneling can be observed, with a review of the field given by Kubas in Ch. 20 and a discussion of insights from NMR studies presented by Buntkowsky and Limbach in Ch. 21.

In the first three of the five chapters of Part VI, hydrogen transfer is examined in assorted complex solids of importance in various applications: zeolites by Sauer in Ch. 22, fuel cells by Kreuer in Ch. 23 and ice bilayers by Aoki in Ch. 24. Attention is then turned to hydrogen transfer at metal surfaces in Ch. 25 by Christmann and in metals in Ch. 26 by Hempelmann and Skripov.

Volume 2 concludes in Part VII with contributions on the variational transition state theory approach to hydrogen transfer in various contexts (Truhlar and Garrett, Ch. 27), on experimental evidence of hydrogen atom tunneling in simple systems (Ingold, Ch. 28), and finally on a theoretical perspective for multiple hydrogen transfers (Smedarchina, Siebrand and Fernández-Ramos, Ch. 29).

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Boulder and Paris, September 2006 — *James T. Hynes*
Berlin, September 2006 — *Hans-Heinrich Limbach*