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Book review

Comprehensive chemical kinetics, 39: Unimolecular kinetics, Part 1. The reaction step. Nicholas J.B. Green (Ed.); Elsevier Science B.V., Amsterdam, 2003, 246 pages, EUR 155 (US$ 155) ISBN 0-444-50893-7

This book is a further volume in the Comprehensive Chemical Kinetics series and deals with what must be one of the most conceptually simple reactions in chemistry, the unimolecular reaction. We are told in the preface that the book is the result of a project that has grown so much that it now occupies two volumes. In this first volume, the editor focuses attention on the reaction step whilst volume 2 presents a detailed description of the energy-transfer step.

Do not be fooled by the title of this volume. The apparent simplicity of the unimolecular reaction, in the eyes of most chemists, is because they do not appreciate the complexities that underlie the unimolecular process. This is a scholarly volume in which a small group of authors shows the development of understanding of the unimolecular reaction, from the failures of the Lindemann theory to up to the contemporary problems associated with quantum mechanical descriptions of the dynamics of unimolecular dissociation. It is perhaps not surprising that this is not an easy book to read. It is certainly a volume for the aficionado, and is clearly aimed at researchers in the area of chemical kinetics. Nevertheless, the persistent non-specialist reader will learn much about the unimolecular reaction, even if not appreciating all the detail. The text is remarkably free of errors, and so it is a little unkind to highlight the obvious "typos" in which RRK and RRKM theories are referred to as RKK and RKKM, right at the front in the Contents page. I suspect the authors have now noticed this mistake. However, I am sure that the audience that will read this book will not be misled by the error.

The volume is divided into three chapters. In the first chapter (Introduction), Nicholas Green gives an historical perspective and outlines the salient features of unimolecular reactions. The reader is taken from the failures of the Lindemann theory through to the development of the RRK and RRKM theories. Certainly, as a non-specialist I found this chapter the most easy to digest and having read Chapter 1 I felt more confident in tackling the subsequent specialist chapters.

In Chapter 2 (RRKM Theory and its Implementation) Stephen Klippenstein takes us through the various forms of the RRKM theory, which is still the method of choice for calculating rate coefficients for gas phase dissociation and isomerisation reactions. The problems of applying the theories to reactions without barriers and also with well-defined barriers are presented in an easily understood manner.

In Chapter 3 (State Specific Dynamics of Unimolecular Dissociation), S.Yu. Grebeshchikov, R. Schinke and W.L. Hase discuss the major quantum mechanical effects inherent in dynamic unimolecular dissociation, notably the fact that there are discrete metastable states (resonances) in the dissociation continuum. There are fluctuations in the rate coefficients for states with quite similar energies. For many states the rate coefficients are close to the statistical rate coefficients, but some are a long way from this and the reasons are discussed.

As a chemist who uses kinetics all the time in his work, I was embarrassed at my lack of understanding of the details of unimolecular reactions. This volume is an education. I don't pretend to understand everything that is presented, but I do have a better understanding of the unimolecular process after reading it. I would recommend this text to anyone involved in research involving kinetics. For those of us studying complex reaction systems, this volume is a real eye-opener to the elegant work and sophisticated level of understanding that researchers have accomplished in looking at one of the simplest of all chemical reactions.

R.A. Henderson [1]
Department of Chemistry, School of Natural Sciences
Bedson Building, University of Newcastle
Newcastle upon Tyne NE1 7RU, UK

[1] Fax: +44-191-222-6929.

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