

CHEMICAL KINETICS

EDITED BY

C.H. BAMFORD

M.A., Ph.D., Sc.D. (Cantab.), F.R.I.C., F.R.S.
*Campbell-Brown Professor of Industrial Chemistry,
University of Liverpool*

AND

C.F.H. TIPPER

Ph.D. (Bristol), D.Sc. (Edinburgh)
*Senior Lecturer in Physical Chemistry,
University of Liverpool*

VOLUME 24

MODERN METHODS IN KINETICS



ELSEVIER SCIENTIFIC PUBLISHING COMPANY
AMSTERDAM — OXFORD — NEW YORK

1983

Contents

Preface	ix
-------------------	----

Chapter 1 (I.S. McDermid)

Modern photochemical techniques: the study of fluorescence decay	1
1. Introduction	1
2. General characteristics of a laser source	1
2.1 Power and coherence	2
2.2 Tunability	3
2.2.1 The dye laser	3
2.2.2 The pulsed dye laser	4
2.2.3 Synchronously pumped picosecond dye lasers	5
2.2.4 Passive mode-locking of dye lasers	6
3. Fluorescence decay	7
3.1 Introduction	7
3.2 Theory	8
3.3 Collisions and energy transfer	11
4. Experimental measurement of fluorescence decay	14
4.1 Single photon counting	14
4.1.1 Sampled single-photon detection	18
4.2 The boxcar integrator	19
4.3 Transient recorders	25
4.3.1 Biomation series waveform recorders	26
4.3.2 Potential errors caused by limitations of resolution	27
4.3.3 Tektronix transient digitizers	30
4.4 Streak cameras	31
4.5 Measurement of lifetimes $> 10 \mu s$	36
4.5.1 Geometrical considerations	36
4.5.2 Radiative lifetimes from integrated absorption	41
5. Time resolved spectroscopy	45
5.1 Multielement detectors	46
5.2 Intensification and gating of multielement detectors	46
Acknowledgements	48
References	48

Chapter 2 (P.J. Derrick and K.F. Donchi)

Mass spectrometry	53
1. Introduction	53
2. Theoretical background	55
2.1 Quasiequilibrium theory (QET)	55
2.1.1 Excited electronic states	56
2.1.2 Vibrational relaxation	58
2.1.3 Calculations of numbers and densities of states	60
2.1.4 Phase space theory	61
2.1.5 Product stability	63

2.2	Specific state theories.	63
2.2.1	Localised theory of mass spectra.	64
2.2.2	Charge distributions in molecular orbitals.	64
2.3	Angular momentum.	65
2.4	Ion structure	68
2.4.1	Stable ion structures.	69
2.4.2	Ion geometries	70
2.4.3	Reacting configuration	71
2.4.4	Energies and heats of formation	72
2.5	Relationship between experimental results and theoretical rate coefficients, $k(E)$	73
3.	Experimental techniques	76
3.1	Mass spectra	76
3.1.1	Photoion—photoelectron coincidence (PIPECO)	77
3.1.2	Electron impact coincidence	78
3.1.3	Charge exchange	79
3.1.4	Translational energy release	79
3.2	Metastable ions	82
3.2.1	Metastable ions by photoion—photoelectron coincidence (PIPECO).	83
3.2.2	Metastable ions following charge exchange	84
3.2.3	Translational energy release in the decomposition of metastable ions.	84
3.3	Field ionization (FI)	86
3.3.1	Field ionization mass spectra	86
3.3.2	Field ionization kinetics (FIK)	87
3.4	Nanosecond lifetimes	88
3.5	Lifetimes longer than microseconds	89
4.	Critical energies.	90
4.1	Determination of critical energies.	90
4.1.1	Kinetic shift	91
4.1.2	Competitive shift.	94
4.2	Significance of appearance energies.	94
5.	Photoion—photoelectron coincidence (PIPECO)	96
5.1	Diatomic and triatomic molecules.	96
5.2	Molecules containing one carbon atom	96
5.3	Molecules containing two carbon atoms.	97
5.4	Molecules containing three carbon atoms.	98
5.5	Molecules containing four carbon atoms	98
5.6	Pyridine and other molecules containing five carbon atoms	100
5.7	Benzene, halobenzenes and other molecules containing six carbon atoms	101
5.8	Benzonitrile and some molecules containing eight carbon atoms.	102
5.9	Polyatomic inorganic molecules	103
6.	Field ionization kinetics (FIK).	103
6.1	Internal energies of molecular ions formed by field ionization (FI)	103
6.1.1	Temperature effects.	103
6.1.2	Determinations of internal energy.	105
6.2	Hydrocarbons.	106
6.2.1	Aliphatic hydrocarbons.	106
6.2.2	Aromatic hydrocarbons	109
6.3	Nitrogen-containing molecules	110
6.4	Oxygen- and sulphur-containing molecules.	110

6.4.1 Alcohols	110
6.4.2 Aldehydes and ketones	112
6.4.3 Ethers	113
6.4.4 Acids and esters	113
6.4.5 Sulphur-containing molecules	115
6.5 Halogen-containing molecules	115
7. Isotope effects	115
7.1 Relationship between intramolecular isotope effects on ion abundances and intramolecular kinetic isotope effects	117
7.1.1 Mass spectra	119
7.1.2 Field ionization kinetics and metastable ions	119
7.1.3 PIPECO and charge exchange	120
7.2 Relationship between intermolecular isotope effects on ion abundances and intermolecular kinetic isotope effects	121
7.3 Significance of kinetic isotope effects	122
7.3.1 Intramolecular kinetic isotope effects	122
7.3.2 Intermolecular kinetic isotope effects	124
7.4 Primary and secondary isotope effects	125
7.5 Isotope effects on ion abundances	126
7.5.1 Primary hydrogen isotope effects on simple bond cleavage	127
7.5.2 Primary hydrogen isotope effects on loss of molecular hydrogen	132
7.5.3 Primary hydrogen isotope effects on eliminations and rearrangements	134
7.5.4 Secondary hydrogen isotope effects	143
7.5.5 Heavy atom isotope effects	147
8. Translational energy release	148
8.1 Theories of translational energy release	149
8.1.1 QET and translational energy	149
8.1.2 Dynamical extensions of QET	152
8.1.3 Partition of reverse critical energy, E_R	153
8.2 Translational energy releases from photoion-photoelectron coincidence (PIPECO)	155
8.3 Translational energy release in source reactions induced by electron impact (EI)	158
8.3.1 Positive ions	158
8.3.2 Negative ions	160
8.4 Metastable ions	161
8.4.1 Molecular orbital calculations of transition state geometries	163
8.4.2 "Early" and "late" transition states	165
8.5 Translational energy release data	168
8.5.1 Key to symbols used in the tables	221
Acknowledgements	223
References	223

Chapter 3 (G.M. Côme)

The use of computers in the analysis and simulation of complex reactions	249
1. Introduction	249
1.1 Pure chemical kinetics	249
1.1.1 Elementary processes	249
1.1.2 Reaction mechanisms	249
1.2 Applied chemical kinetics	250
1.2.1 Experimentation	251
1.2.2 Analysis of experimental results	251

1.2.3 Modelling	251
1.3 Chemical reaction engineering	252
1.4 Classification of models	252
1.5 Model reactions.	253
2. Reaction models	254
2.1 Stoichiometry.	255
2.1.1 Introduction.	255
2.1.2 Independent constituents and stoichiometries	256
2.1.3 Brinkley's criterion	256
2.1.4 Jouguet's criterion	257
2.1.5 Extents of reaction	258
2.1.6 Invariants.	259
2.1.7 Remarks	260
2.2 Thermochemistry	261
2.3 Empirical models.	262
2.4 Pseudo-kinetic models	263
2.4.1 Lumped constituent models.	263
2.4.2 Molecular reaction schemes	264
2.5 Mechanistic models	266
2.5.1 Definition	266
2.5.2 Rate laws	266
2.5.3 Building a reaction mechanism	268
2.5.4 Kinetic parameters.	272
2.6 Comparison of reaction models	278
2.6.1 Simulation	278
2.6.2 Kinetic analysis	279
3. Reactor models.	281
3.1 Ideal reactors	281
3.2 Batch reactors.	282
3.3 Continuous flow stirred tank reactors (CFSTR).	282
3.4 Plug flow reactors	283
3.5 Non-ideal reactors	284
4. Numerical analysis.	285
4.1 Rank of a matrix.	286
4.1.1 Linear combinations.	286
4.1.2 Singular value decomposition (SVD)	286
4.2 Systems of linear algebraic equations.	287
4.2.1 Direct methods	287
4.2.2 Iterative methods.	288
4.3 Systems of non-linear algebraic equations.	289
4.3.1 Newton's method	289
4.3.2 Direct iteration	290
4.4 Derivation	290
4.4.1 Graphical methods.	291
4.4.2 Interpolation	291
4.4.3 Model fitting.	292
4.5 Systems of ordinary differential equations with initial values	294
4.5.1 Stiffness.	295
4.5.2 Methods of integration	296
4.5.3 One-step algorithms	299
4.5.4 Linear multistep algorithms	300
4.5.5 Algorithms of singular perturbation type	301
4.5.6 General properties of integration methods	303
4.5.7 Control of step size	305

4.5.8	Choosing a method for numerical integration	307
5.	Model identification	308
5.1	Introduction	308
5.2	Parameter estimation	309
5.2.1	Least squares estimation	309
5.2.2	Linear estimation	311
5.2.3	Non-linear estimation	312
5.3	Confidence intervals and confidence regions	314
5.4	Quality of fit; comparison of models	316
6.	Computer assisted processing and design of reaction mechanisms	317
6.1	Introduction	317
6.2	Chemical notations	318
6.2.1	Linear notations	318
6.2.2	Two-dimensional input	320
6.2.3	Reaction mechanisms	320
6.3	Chemical compilers	320
6.4	Computer-assisted design of reaction mechanisms	321
7.	Conclusion	322
8.	Symbols	322
	References	325

Chapter 4 (A.B. Callear)

Basic RRKM theory	333
1. Introduction	333
2. Calculation of state densities	334
2.1 Partition functions	334
2.2 Classical equations	335
2.3 A system of s classical oscillators	336
2.4 Rotation	337
3. Early theories	339
3.1 The Lindemann type model	339
3.2 Kassel's theory	340
4. Marcus—Rice theory	342
4.1 The basic model	342
4.2 Reduction to the equations of Kassel and Eyring	345
4.3 Overall rotation	346
4.4 The low pressure fall-off	347
5. Application	348
5.1 State counting	348
5.2 Arbitrary choice of structure	350
5.3 Collisional energy transfer	353
5.4 Direct measurement of $k(\epsilon)$	355
References	356

Chapter 5 (J.C. Whitehead)

The distribution of energy in the products of simple reactions	357
1. Introduction	357
1.1 Experimental methods	359
1.1.1 Generation of reactive species	359
1.1.2 Systems for studying reactions	365
1.1.3 Detection methods	369
1.2 Theoretical methods	374

1.2.1	Potential energy surfaces	374
1.2.2	Quantum calculations of energy disposal	376
1.2.3	Semi-classical calculations of energy disposal	377
1.2.4	Classical calculations of energy disposal	378
1.2.5	Statistical calculations	379
1.2.6	Model calculations	380
1.2.7	Information theory	382
2.	Some factors governing the disposal of energy in reaction products.	383
2.1	The effect of the nature of the potential-energy surface on energy disposal	383
2.2	Dynamical effects	386
2.3	The effect of reagent energy	388
3.	A review of measured product energy distributions for some simple chemical reactions	391
3.1	Reactions of atoms	392
3.1.1	Reactions of hydrogen atoms	392
3.1.2	Reactions of alkali atoms	407
3.1.3	Reactions of ground-state alkaline earth atoms	415
3.1.4	Reactions of electronically excited alkaline earth atoms	427
3.1.5	Reactions of other metal atoms	430
3.1.6	Reactions of nitrogen atoms	440
3.1.7	Reactions of oxygen atoms	440
3.1.8	Reactions of halogen atoms	456
3.1.9	Reactions of metastable inert gas atoms	476
3.2	Reactions of diatomic molecules	479
3.2.1	Reactions of hydrogen halides	479
3.2.2	Reactions of alkali dimers	481
3.2.3	Reactions of alkaline earth metal dimers	481
3.2.4	Reactions of alkali halides	482
3.2.5	Reactions of C ₂	482
3.2.6	Reactions of NO	483
3.2.7	Reactions of OH	484
3.2.8	Reactions of O ₂ [*] (¹ Δ _g)	484
3.2.9	Reactions of halogen molecules	484
3.2.10	Miscellaneous diatomic reactions	485
3.3	Reactions of polyatomic species	485
3.3.1	Reactions of alkaline earth dihalides	485
3.3.2	Reactions of CH ₂	485
3.3.3	Reactions of methyl radicals	487
4.	Conclusions	488
5.	Acknowledgements	489
	Appendix 1	489
	References	491
	Index	507