

Postgraduate Chemistry Series

Photochemistry
of Organic
Compounds

From Concepts to Practice

Petr Klán and Jakob Wirz



WILEY

Contents

Special topics	xi
Case studies	xiii
Foreword	xv
Preface	xvii
1 Introduction	1
1.1 Who's afraid of photochemistry?	1
1.2 Electromagnetic radiation	8
1.3 Perception of colour	11
1.4 Electronic states: elements of molecular quantum mechanics	13
1.5 Problems	23
2 A crash course in photophysics and a classification of primary photoreactions	25
2.1 Photophysical processes	25
2.1.1 State diagrams	25
2.1.2 Beer–Lambert law	29
2.1.3 Calculation of fluorescence rate constants from absorption spectra	30
2.1.4 Dipole and transition moments, selection rules	32
2.1.5 Rate constants of internal conversion; the energy gap law	35
2.1.6 Rate constants of intersystem crossing, El Sayed rules	38
2.1.7 Quantum yield: definition	39
2.1.8 Kasha and Vavilov rules	40
2.1.9 Franck–Condon principle	41
2.2 Energy transfer, quenching and sensitization	44
2.2.1 Diffusion-controlled reactions in solution, spin statistics	44
2.2.2 Energy transfer	47
2.2.3 Excimers and exciplexes	60
2.2.4 Delayed fluorescence	63
2.2.5 Dioxygen	64
2.3 A classification of photochemical reaction pathways	67
2.4 Problems	71

3 Techniques and methods	73
3.1 Light sources, filters and detectors	73
3.2 Preparative irradiation	82
3.3 Absorption spectra	85
3.4 Steady-state emission spectra and their correction	87
3.5 Time-resolved luminescence	91
3.6 Absorption and emission spectroscopy with polarized light	92
3.7 Flash photolysis	94
3.7.1 Kinetic flash photolysis	95
3.7.2 Spectrographic detection systems	97
3.7.3 Pump–probe spectroscopy	98
3.7.4 Analysis of kinetic data	99
3.7.5 Global analysis of transient optical spectra	102
3.8 Time-resolved IR and Raman spectroscopy	109
3.9 Quantum yields	110
3.9.1 Differential quantum yield	110
3.9.2 Actinometry	112
3.9.3 Spectrophotometric determination of the reaction progress	114
3.9.4 Reversible photoreactions	117
3.9.5 Luminescence quantum yields	118
3.9.6 Polychromatic actinometry and heterogeneous systems	119
3.9.7 Relating quantum yields to rate constants	119
3.9.8 Stern–Volmer analysis	121
3.9.9 Quantum yields of triplet formation	127
3.9.10 Experimental arrangements for quantum yield measurements	128
3.10 Low-temperature studies; matrix isolation	130
3.11 Photoacoustic calorimetry	131
3.12 Two-photon absorption spectroscopy	133
3.13 Single-molecule spectroscopy	133
3.14 Problems	134
4 Quantum mechanical models of electronic excitation and photochemical reactivity	137
4.1 Boiling down the Schrödinger equation	137
4.2 Hückel molecular orbital theory	140
4.3 HMO perturbation theory	144
4.4 Symmetry considerations	148
4.5 Simple quantum chemical models of electronic excitation	151
4.6 Pairing theorems and Dewar's PMO theory	156
4.7 The need for improvement; SCF, CI and DFT calculations	159
4.8 Spin–orbit coupling	172
4.9 Theoretical models of photoreactivity, correlation diagrams	173
4.10 Problems	179
4.11 Appendix	180
4.11.1 First-order perturbation	180
4.11.2 Second-order perturbation	180

5 Photochemical reaction mechanisms and reaction intermediates	183
5.1 What is a reaction mechanism?	183
5.2 Electron transfer	184
5.3 Proton transfer	192
5.4 Primary photochemical intermediates: examples and concepts	198
5.4.1 Carbenes	198
5.4.2 Nitrenes	201
5.4.3 Radicals and radical ions	204
5.4.4 Biradicals	206
5.4.5 Carbocations and carbanions	217
5.4.6 Enols	218
5.5 Photoisomerization of double bonds	221
5.6 Chemiluminescence and bioluminescence	223
5.7 Problems	225
6 Chemistry of excited molecules	227
6.1 Alkenes and alkynes	227
6.1.1 Alkenes: <i>E</i> – <i>Z</i> isomerization	229
6.1.2 Alkenes: electrocyclic and sigmatropic photorearrangement	241
6.1.3 Alkenes: di- π -methane rearrangement	247
6.1.4 Alkenes and alkynes: photoinduced nucleophile, proton and electron addition	251
6.1.5 Alkenes and alkynes: photocycloaddition reaction	256
6.1.6 α,β -Unsaturated ketones (enones): photocycloaddition and photorearrangement	267
6.1.7 Problems	273
6.2 Aromatic compounds	274
6.2.1 Aromatic hydrocarbons and heterocycles: photorearrangement and phototransposition	276
6.2.2 Aromatic hydrocarbons and heterocycles: photocycloaddition	279
6.2.3 Substituted benzenes: photosubstitution	287
6.2.4 Problems	292
6.3 Oxygen compounds	293
6.3.1 Carbonyl compounds: photoreduction	296
6.3.2 Carbonyl compounds: oxetane formation (Paterno–Büchi reaction)	300
6.3.3 Carbonyl compounds: Norrish type I reaction	305
6.3.4 Carbonyl compounds: Norrish type II elimination	310
6.3.5 Carbonyl compounds: photocyclization following <i>n</i> , ₁ -hydrogen abstraction	316
6.3.6 Carbonyl compounds: photoenolization	323
6.3.7 Quinones: addition and hydrogen/electron transfer reaction	327
6.3.8 Carboxylic acids and their esters: photofragmentation and rearrangement	331
6.3.9 Transition metal carbonyl complexes: photodecarbonylation	337
6.3.10 Problems	338

6.4	Nitrogen compounds	340
6.4.1	Azo compounds, imines and oximes: <i>E</i> - <i>Z</i> photoisomerization	343
6.4.2	Azo compounds, azirines, diazirines, diazo compounds, diazonium salts, azides, <i>N</i> -oxides, nitrite esters and heteroaromatic compounds: photofragmentation and photorearrangement	351
6.4.3	Nitro compounds: photofragmentation and photoreduction	362
6.4.4	Amines, aromatic nitriles, metallocorganic complexes: photoinduced electron/charge transfer	369
6.4.5	Problems	380
6.5	Sulfur compounds	381
6.5.1	Thiocarbonyl compounds: hydrogen abstraction and cycloaddition	383
6.5.2	Sulfones, sulfonates and sulfoxides: photofragmentation	386
6.5.3	Problems	389
6.6	Halogen compounds	390
6.6.1	Halogen compounds: photohalogenation	390
6.6.2	Organic halogen compounds: photofragmentation, photoreduction and nucleophilic photosubstitution	395
6.6.3	Problems	403
6.7	Molecular oxygen	404
6.7.1	Molecular oxygen: ground state and excited state	405
6.7.2	Singlet oxygen: [2 + 2] and [4 + 2] photooxygenation and related photoreactions	412
6.7.3	Singlet oxygen: ene reaction	419
6.7.4	Problems	422
6.8	Photosensitizers, photoinitiators and photocatalysts	423
6.8.1	Organic photosensitizers, photocatalysts and photoinitiators	424
6.8.2	Transition metal photocatalysts	440
6.8.3	Problems	452
7	Retrosynthetic photochemistry	455
8	Information sources, tables	467
	References	471
	Index	549