

**PHOTOSENSITIZATION AND PHOTOCATALYSIS USING
INORGANIC AND ORGANOMETALLIC COMPOUNDS**

Catalysis by Metal Complexes

VOLUME 14

Editors:

R. UGO, *University of Milan, Milan, Italy*

B. R. JAMES, *The University of British Columbia, Vancouver, Canada*

Advisory Board:

J. L. GARNETT, *The University of New South Wales, Kensington, N.S.W., Australia*

S. D. ITTEL, *E. I. du Pont de Nemours Co., Inc., Wilmington, Del., U.S.A.*

P. W. N. M. VAN LEEUWEN, *Royal Shell Laboratory, Amsterdam, The Netherlands*

L. MARKÓ, *Hungarian Academy of Sciences, Veszprém, Hungary*

A. NAKAMURA, *Osaka University, Osaka, Japan*

W. H. ORME-JOHNSON, *M.I.T., Cambridge, Mass., U.S.A.*

R. L. RICHARDS, *The University of Sussex at Falmer, Brighton, U.K.*

A. YAMAMOTO, *Tokyo Institute of Technology, Yokohama, Japan*

The titles published in this series are listed at the end of this volume.

PHOTOSENSITIZATION AND
PHOTOCATALYSIS USING
INORGANIC AND
ORGANOMETALLIC COMPOUNDS

Edited by

K. KALYANASUNDARAM AND M. GRÄTZEL

*Institute of Physical Chemistry,
Swiss Federal Institute of Technology,
Lausanne, Switzerland*



SPRINGER-SCIENCE+BUSINESS MEDIA, B.V.

Library of Congress Cataloging-in-Publication Data

Photosensitization and photocatalysis using inorganic and organometallic compounds / edited by K. Kalyanasundaram and M. Grätzel.

p. cm. -- (Catalysis by metal complexes ; v. 14)

Includes bibliographical references and index.

ISBN 978-90-481-4265-1 ISBN 978-94-017-2626-9 (eBook)

DOI 10.1007/978-94-017-2626-9

1. Photocatalysis. 2. Inorganic compounds. 3. Organometallic compounds. I. Kalyanasundaram, K., 1949- . II. Grätzel, Michael. III. Series.

QD716.P45P46 1993

541.3'5--dc20

93-895

ISBN 978-90-481-4265-1

Printed on acid-free paper

All Rights Reserved

© 1993 Springer Science+Business Media Dordrecht

Originally published by Kluwer Academic Publishers in 1993

No part of the material protected by this copyright notice may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without written permission from the copyright owner.

Table of Contents

Preface	xiii
List of Contributors	xv
A.W. ADAMSON: <i>Evolution of Inorganic and Organometallic Photochemistry. Historical Perspectives and Commentary</i>	1
1. Introduction	1
2. Photochemistry	3
3. Bimolecular Excited State Processes	7
4. Things present and to come	9
References	11
V. BALZANI and M. MAESTRI: <i>Intermolecular Energy and Electron Transfer Processes</i>	15
1. Formation and Decay of Excited States	15
2. Energy Transfer	17
2.1 General considerations	17
2.2 Coulombic energy transfer	20
3. Electron Transfer and Exchange Energy Transfer	21
3.1 General considerations	21
3.2 Classical model	23
4. Quenching and Sensitization Processes	29
4.1 Excited state quenching	29
4.2 Sensitization by energy transfer	32
4.3 Sensitization in electron transfer processes	33
5. Examples and Applications of Quenching and Sensitization	39
5.1 Quenching process	39
5.2 Energy transfer processes	40
5.3 Electron transfer processes	42
References	47

H. HENNIG, R. BILLING and H. KNOLL: <i>Photocatalysis: Definitions and Classifications</i>	51
1. Introduction	51
2. Summary of recent discussions	53
3. Definitions and Examples	56
3.1 Definitions	56
3.2 Examples of photocatalytic reactions	60
4. Concluding Remarks	64
References	67
A. VOGLER AND H. KUNKELY: <i>Charge Transfer Excitation of Coordination Compounds. Generation of Reactive Intermediates</i>	71
1. Introduction	71
2. Charge Transfer Absorption Spectra	72
2.1 Ligand-to-metal charge transfer (LMCT)	73
2.2 Metal-to-ligand charge transfer (MLCT)	78
2.3 Metal-to-metal charge transfer (MMCT)	80
2.4 Ligand-to-ligand charge transfer (LLCT)	83
2.5 Intra-ligand charge transfer (ILCT)	84
3. Emission from Charge Transfer States	86
3.1 LMCT	86
3.2 MLCT	87
3.3 MMCT	87
3.4 LLCT	88
4. Charge Transfer Excitation	88
5. Reactivity of Charge Transfer States	89
5.1 LMCT	89
5.2 MLCT	94
5.3 MMCT	97
5.4 LLCT	99
5.5 ILCT	99
6. Reactive Intermediates Generated by CT Excitation	99
6.1 Coordinatively unsaturated complexes	100
6.2 Electrons	100
6.3 Atoms	100
6.4 Metal-based radicals	101
6.5 Ligand-based radicals	102
6.6 Other reactive intermediates	102
6.7 Redox isomers	102
7. Catalytically Active Species Generated by CT Excitation	103

8. Conclusions and Outlook	104
References	104
K. KALYANASUNDARAM: <i>Photoredox and Sensitization Processes involving Transition Metal Polypyridine Complexes</i>	113
1. Introduction	113
2. Excited States of Polypyridine Complexes	115
2.1 Excited states of homo and mixed ligand chelates	115
2.2 Tuning of the excited state	119
3. Principles of Photoredox Reactions	123
3.1 Excited state energy and redox potentials	124
3.2 Kinetic analysis and yield of redox products	127
3.3 Thermodynamic analysis	128
4. Photoredox Reactions of Polypyridine Complexes	130
4.1 Oxidative quenching	133
4.2 Reductive quenching	139
5. Sensitized Photoredox Processes and Their Applications	143
5.1 Photodecomposition of water	144
5.2 Photoreduction of CO ₂ and CO	147
6. Energy Transfer Reactions of the Excited State	149
6.1 Energy transfer quenching by metal complexes	149
6.2 Energy transfer quenching by organics	152
6.3 Applications of energy transfer processes	153
7. Concluding Remarks	154
References	155
F. SCANDOLA, C.A. BIGNOZZI and M.T. INDELLI: <i>Intramolecular Energy and Electron Transfer in Polynuclear Metal Complexes</i>	161
1. Introduction	161
1.1 Scope and limitations	161
1.2 Supramolecular systems	162
1.3 Intercomponent processes	168
1.4 Photochemical molecular devices	176
2. Charge Transfer Spectroscopy of Cyano-Bridged Complexes	178
2.1 Intercomponent perturbation of MLCT spectra	178
2.2 Intervalence transfer spectra	180
3. Covalently Linked Metal Polypyridine Complexes	185
3.1 Photoinduced electron transfer	186
3.2 Charge shift	189
3.3 Towards photoinduced charge separation	191

4. Cyano-bridged Ru(II)-Cr(III) Complexes	191
4.1 Chromophore-luminophore complexes	192
4.2 Perturbation of luminophore properties	194
4.3 Excited-state charge recombination	196
4.4 Towards more extended systems	199
5. Cyano-bridged Polychromophoric Complexes	200
5.1 Binuclear complexes	201
5.2 Trinuclear and polynuclear complexes	204
5.3 Spectral sensitization of semiconductors	208
6. Conclusions	210
References	211
R. ZIESSEL: <i>Photocatalysis: Reduction of CO₂ and Water-Gas-Shift Reaction Photocatalyzed by 2,2'-bipyridine or 1,10-phenanthroline Co(II), Ru(II), Re(I) and Ir(III) complexes</i>	217
1. Introduction	217
2. Photochemical Reduction of CO ₂ and HO to CO and H ₂ Catalyzed by Ru and Co Complexes	220
3. Photochemical Reduction of CO ₂ to HCOO ⁻ Catalyzed by Ru-bipyridine or Phenanthroline Complexes	223
4. Photoreduction of CO ₂ to CO Mediated by <i>fac</i> -Re(bpy)(CO) ₃ Cl	228
5. Photochemical Water-gas-shift Reaction Catalyzed by Novel Ir(III) Complexes	230
6. Conclusions	239
References	240
M. GRÄTZEL and K. KALYANASUNDARAM: <i>Metal Complexes as Photosensitizers in Photoelectrochemical Cells</i>	247
1. Introduction	247
2. Principles of Dye Sensitization	248
3. Early Studies of Dye Sensitization	249
4. Surface Chelation Effects	251
5. Sensitization of Polycrystalline TiO ₂ -based Photoelectrochemical Cells	253
6. Mechanism of Sensitization	259
6.1 Excited state decay on semiconductor surfaces	260
6.2 Studies of dye-colloidal semiconductor mixtures	262
6.3 Studies of dye-coated semiconductor electrodes	265
7. Other Systems that show efficient Dye Sensitization	267
References	268

A. HARRIMAN: <i>Photosensitization by (Metallo)porphyrins: Formation and Photophysical Properties of Porphyrin Assemblies</i>	273
1. Introduction	273
2. Covalently-linked Porphyrin Assemblies	274
2.1 Face-to-face porphyrin dimers	274
2.2 Adjacent bisporphyrins	278
2.3 Oblique bisporphyrins	281
2.4 Entwined bisporphyrins	283
2.5 Linear porphyrin dimers and trimers	285
2.6 Randomly-oriented porphyrin assemblies	287
3. Photon Antennae Assembled by Hydrogen Bonding	289
4. Assembling Porphyrin Arrays via Coordinative Bonding	296
4.1 Gold(III) bisporphyrins	297
4.2 Gold(III) tetrakisporphyrin/Copper(I) complex	298
5. Electrostatic Binding	300
References	302
C.L. HILL and C.M. PROSSER-McCARTHA: <i>Photocatalytic and Photoredox Properties of Polyoxometalate Systems</i>	307
1. Introduction	307
2. Properties of Polyoxometalates	307
3. Photocatalysis by Polyoxometalates. Background and General Features	309
4. Photocatalysis by Polyoxometalates. Energetic and Mechanistic Features	314
5. Survey of the Photoredox Activity of $Q_3PW_{12}O_{40}$ and $Q_4W_{10}O_{32}$	318
5.1 Reactivity of alkanes	321
5.2 Reactivity of alkenes	322
5.3 Reactivity of alcohols	323
5.4 Reactivity of ketones	323
5.5 Reactivity of other substrates	324
References	326
U. KÖLLE: <i>Photocatalytic Transformations of Organic Substrates Using Inorganic Salts and Complexes</i>	331
1. Introduction	331
2. Cu(I) Catalyzed Cycloadditions of Olefins	332
3. Cu(II) Catalyzed Photoreactions	340
4. Fe Salt Catalyzed Photoreactions	343
5. Emissive Species as Photosensitizers	345

6. Generation of Hydrogen by Photolysis of Organic Substrates	349
7. Hydrogenation Catalysts of the Wilkinson and Vaska Type	350
References	354
P.C. FORD, W. BOESE, B. LEE and K.L. MACFARLANE:	
<i>Photocatalysis Involving Metal Carbonyls</i>	359
1. Introduction	359
2. General Photochemical Properties of Metal Carbonyls	360
2.1 Spectroscopy	360
2.2 Photosubstitutions of mononuclear complexes	363
2.3 Photoreactions of polynuclear complexes	366
3. Photocatalytic Activation of Dihydrogen	370
4. Photocatalytic Hydrosilation and Isomerization of Alkenes	375
5. Photocatalytic Carbonylations	378
6. Other Photocatalytic Processes	382
6.1 The water gas shift	382
6.2 Photocatalyzed polymerization of alkynes	384
7. Summary	385
References	385
R.H. CRABTREE: <i>Photocatalysis in C-H Activation</i>	
1. Introduction	391
2. Stoichiometric Photochemical Studies	392
3. Catalytic Alkane Dehydrogenation	395
4. Photocarbonylation of Alkanes and Arenes	398
5. H-Atom Abstraction from a C-H Bond by Binuclear Complexes	400
6. Dehydrodimerization Reactions	401
7. Conclusion	403
References	404
T.M. BOCKMAN and J.K. KOCHI: <i>Electron Donor-Acceptor Interactions and Photo-induced Electron Transfer of Organometallic Compounds</i>	
1. Introduction	407
2. Organometallic Complexes as Electron Donors and Electron Acceptors	410
2.1 Ionization potentials and oxidation potentials of organometallic donors	410
2.2 Reduction potentials of organometallic acceptors	415
3. EDA Complexes and the Energetics of their Formation	416

Table of Contents

xi

3.1	Molecular complexes	417
3.2	Charge-transfer ion pairs	418
3.3	Strong charge-transfer complexes	421
4.	Spectroscopic and Structural Consequences of the Electron Donor-Acceptor Interaction	422
4.1	Charge-transfer absorption bands	422
4.2	Structural changes associated with electron donor-acceptor interactions	426
5.	Photophysical and Photochemical Activation of EDA Complexes upon Charge-Transfer Irradiation	428
5.1	Photophysics of (organometallic) EDA complexes	428
5.2	Photochemistry of organometallic EDA complexes	433
	References	438
	Index	449

PREFACE

Mankind has been intrigued for quite a long time by the effect of light on materials and the subject of photochemistry grew out of this curiosity. In all photochemical studies two terms "photosensitization" and "photocatalysis" appear again and again. Both refer to procedures by which permanent chemical transformations are induced on substrates (organic/inorganic) by radiation to which the substrates themselves are transparent. The light is absorbed by a donor/host molecule and the transformations are triggered by electron or energy transfer (in some cases by free radical) reactions of the electronically excited states. Such transformations on the acceptor/substrate can be highly specific and very efficient. Herein lies the power of the photochemical methods for possible applications. Often the two keywords are interpreted in many different ways and certainly no consensus exists on the definition of the second one. This arises whether the emphasis is placed on the substrate, host or energetics. An important variation is photoelectrochemical cells where the light energy is directly converted to electrical energy.

Obviously intelligent manipulation of the electronically excited states requires a good understanding of their properties (mode of production, lifetime, reactivity etc.). In the last two decades there have been intense activity and substantial progress in these areas. So when the publisher of the series "Catalysis by Metal Complexes" contacted us to contribute a volume on "photocatalysis" we decided to survey the progress with special emphasis on the above two keywords "photosensitization" and "photocatalysis". For inclusion in a series devoted to metal complexes, the scope was restricted to inorganic and organometallic compounds. We have been fortunate that a number of experienced researchers responded enthusiastically to our appeal and agreed to contribute.

The monograph is organized essentially in three parts. The first four chapters cover the basic materials. The book starts with a historical perspective and commentary followed by discussions on the principles governing electron, energy transfer, photocatalysis and the chemistry of the charge transfer excited state. Next five chapters deal with the photochemistry of classical/Werner-type coordination compounds and their applications. Polypyridine complexes by and large received major scrutiny. A survey of their photochemistry is followed by two key recent applications:

photoreduction of CO₂, CO and sensitization of large bandgap semiconductors. Currently major emphasis is being placed on larger polynuclear/supramolecular systems and this area is represented by chapters on the systems composed of polypyridine units and metalloporphyrins.

In the last five chapters attention is focused on a number of inorganic or organometallic systems where photocatalytic transformations of organic substrates have been demonstrated. Systems considered include polyoxometalates, metal carbonyls, organometallics, ground state complexes of inorganic salts and electron donor-acceptor complexes of organometallics such as metal alkyls or metallocenes. It is remarkable that a wide variety of chemical transformations have been achieved with some selectivity using these systems. The primary photochemical steps in many cases are yet to be unambiguously established. Certainly this is a very fertile area where a number of practical applications of photocatalysis will appear.

The authors have been encouraged to place emphasis on the basic principles and features of the system studied rather than a comprehensive survey. This is partly due to the evolutionary nature of the topic and our goals were to provide a broad introduction to the subject, easily assimilated by graduate students and researchers coming from very many disciplines. By putting together in a single volume photochemical systems that are purely inorganic and organometallic in nature, it is our earnest hope to bring together researchers working on these topics. A common working language should allow cross fertilization of ideas and approaches. In view of the diverse systems and topics covered, the volume should appeal to academic and industrial researchers in all sub-disciplines of chemistry, material science and catalysis.

It has been a pleasure and privilege to work with a distinguished collection of authors in putting together this volume and we would like to express our sincere appreciation for their enthusiastic collaboration.

Lausanne
February 1993

K. Kalyanasundaram
M. Grätzel

List of Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

- A. W. Adamson** (1) Dept. of Chemistry, Univ. of Southern California, California 90089, USA
- V. Balzani** (15) Dipartimento di Chimica G. Ciamician, Università di Bologna, I- 40126 Bologna, Italy
- C. A. Bigozzi** (161) Dept. of Chemistry, Univ. of Ferrara, I-44100 Ferrara, Italy
- R. Billing** (51) Sektion Chemie, Universität Leipzig, D/O-7010 Leipzig, Germany
- T.M. Bockman** (407) Dept. of Chemistry, Univ. of Houston, Texas 77204 , USA
- W. Boese** (359) Dept. of Chemistry, Univ. of California at Santa Barbara, California 93106, USA
- R.H. Crabtree** (391) Dept. of Chemistry, Yale Univ., New Haven, Connecticut 06511 , USA
- P.C. Ford** (359) Dept. of Chemistry, Univ. of California at Santa Barbara, California 93106, USA
- M. Grätzel** (247) Institut de Chimie Physique, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
- A. Harriman** (273) Center for Fast Kinetics Research, Univ. of Texas, Austin, Texas 78712, USA
- H. Hennig** (51) Sektion Chemie, Universität Leipzig, D/O-7010 Leipzig, Germany
- C.L. Hill** (307) Dept. of Chemistry, Emory Univ., Atlanta, Georgia 30322, USA
- M.T. Indelli** (161) Dept. of Chemistry, Univ. of Ferrara, I-44100 Ferrara, Italy
- K. Kalyanasundaram** (113, 247) Inst. de Chimie Physique, Ecole Polytech. Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
- H. Knoll** (51) Sektion Chemie, Universität Leipzig, D/O-7010 Leipzig, Germany
- J.K. Kochi** (407) Dept. of Chemistry, Univ. of Houston, Texas 77204 , USA

- U. Kölle** (331) Inst. für Anorganische Chemie, Tech. Hochschule, D-5100 Aachen, Germany
- H. Kunkely** (71) Institut für Anorganische Chemie, Universität Regensburg, D-8400 Regensburg, Germany
- B. Lee** (359) Dept. of Chemistry, Univ. of California at Santa Barbara, California 93106, USA
- M. Maestri** (15) Dipartimento di Chimica G. Ciamician, Università di Bologna, I- 40126 Bologna, Italy
- K. McFarlane** (359) Dept. of Chemistry, Univ. of California at Santa Barbara, California 93106, USA
- C.M. Prosser-McCartha** (307) Dept. of Chemistry, Emory Univ., Atlanta, Georgia 30322, USA
- F. Scandola** (161) Dept. of Chemistry, Univ. of Ferrara, I-44100 Ferrara, Italy
- A. Vogler** (71) Institut für Anorganische Chemie, Universität Regensburg, D-8400 Regensburg, Germany
- R. Ziessel** (217) Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, IPSCMS/GMI, F-67008 Strasbourg, France