

PHOTOCHEMICAL TECHNOLOGY

André M. Braun

Marie-Thérèse Maurette

Esther Oliveros

Translation by

David F. Ollis

Nick Serpone



WILEY

JOHN WILEY & SONS

Chichester · New York · Brisbane · Toronto · Singapore

Originally published as *Technologie Photochimique*
© 1986 Presses polytechniques romandes, Lausanne

Copyright © 1991 by John Wiley & Sons Ltd
Baffins Lane, Chichester
West Sussex PO19 1UD, England



92/204

All rights reserved.

No part of this book may be reproduced by any means,
or transmitted, or translated into a machine language
without the written permission of the publisher.

Other Wiley Editorial Offices

John Wiley & Sons, Inc., 605 Third Avenue,
New York, NY 10158-0012, USA

Jacaranda Wiley Ltd, G.P.O. Box 869, Brisbane,
Queensland 4001, Australia

John Wiley & Sons (Canada) Ltd, 22 Worcester Road,
Rexdale, Ontario M9W 1L1, Canada

John Wiley & Sons (SEA) Pte Ltd, 37 Jalan Pemimpin 05-04,
Block B, Union Industrial Building, Singapore 2057

Library of Congress Cataloging-in-Publication Data:

Braun, André M.

[Technologie photochimique. English]

Photochemical technology / André M. Braun, Marie-Thérèse Maurette,
Esther Oliveros ; translation by David F. Ollis, Nick Serpone.

p. cm.

Translation of: Technologie photochimique.

Includes bibliographical references and index.

ISBN 0 471 92652 3

1. Photochemistry—Industrial applications. I. Maurette, Marie
—Thérèse. II. Oliveros, Esther. III. Title.

TP249.5.B7313 1991

660'.295—dc20

90-46482

CIP

British Library Cataloguing in Publication Data:

Braun, André M.

Photochemical technology.

1. Photochemistry

I. Title II. Maurette, Marie-Thérèse III. Oliveros,

Esther IV. [Technologie Photochimique. English]

541.35

ISBN 0 471 92652 3

Phototypeset by Thomson Press (India) Ltd., New Delhi
Printed and bound in Great Britain by Biddles Ltd., Guildford, Surrey

TABLE OF CONTENTS

TABLE OF CONTENTS	v
FOREWORD TO THE ENGLISH TRANSLATION	ix
FOREWORD	xi
TRANSLATORS' PREFACE AND ACKNOWLEDGEMENT	xiii
INTRODUCTION	xv
CONVENTIONS	xvii
ACKNOWLEDGEMENTS	xix
1 SUMMARY OF PHOTOCHEMISTRY PRINCIPLES	1
1.1 Introduction	1
1.2 Absorption of light	1
1.3 Electronically excited states	5
1.4 Absorption spectra	10
1.5 Photophysical processes of excited state deactivation	16
1.6 Energy transfer	23
1.7 Photochemical transformations	29
1.8 Quantum yield	33
1.9 Electron transfer	43
Notes	48
References	49
2 RADIOMETRY AND ACTINOMETRY	51
2.1 Introduction	51
2.2 Principles of radiometry	51
2.3 Radiometers	61
2.4 Actinometry	70
2.5 Quantum yields	93
Notes	104
References	104
3 LIGHT SOURCES AND FILTERS	107
3.1 Introduction	107
3.2 Light sources	107

3.3	Optical materials and filters	146
	Notes	150
	References	150
4.	PHOTOCHEMICAL REACTORS	152
4.1	Introduction	152
4.2	Photochemical reactors irradiated by a light beam	154
4.3	Photochemical reactors with an irradiation zone of large dimension	164
4.4	Solar reactors	195
	Notes	198
	References	199
5.	PHOTONITROSYLATION	202
5.1	General	202
5.2	Photooxidation of alkanes	203
5.3	Photooxidation of cyclohexane	208
5.4	Photooxidation of cyclododecane	221
5.5	Other photonitrosylation reactions	223
	Notes	228
	References	229
6.	PHOTOCHLORINATION	231
6.1	Introduction	231
6.2	Photochlorination by chlorine addition	234
6.3	Photochlorination by radical substitution	242
6.4	Photochlorination of methane and its chlorinated derivatives	252
6.5	Photochlorination of ethane and its chlorinated derivatives	255
6.6	Photochlorination of various alkanes and cycloalkanes	262
6.7	Photochlorination of fluorinated and brominated alkanes	269
6.8	Photochlorination of carboxylic acid and their derivatives	273
6.9	Photochlorination of various organic compounds	279
6.10	Photochlorination of alkylbenzenes	283
6.11	Photochlorination in the presence of oxygen	300
6.12	Photochlorination of polymers	302
	Notes	310
	References	310
7.	PHOTOBROMINATION	316
7.1	Introduction	316
7.2	Photobromination by bromine addition	318

TABLE OF CONTENTS

vii

7.3	Photobromination by radical substitution	322
7.4	Photobromination using initiators	342
7.5	Methods of removal of hydrobromic acid formed during photo- bromination reactions	348
	Notes	350
	References	350
8	SULFOCHLORINATION AND SULFOXIDATION	354
8.1	General	354
8.2	Photochemical sulfochlorination	356
8.3	Experimental conditions for the photochemical sulfochlorina- tion using the gas mixture SO_2/Cl_2	367
8.4	Photochemical sulfochlorination of polymers	375
8.5	Sulfoxidation	376
8.6	Production of sulfonic acid derivatives of paraffins	384
8.7	Other photochemical methods of sulfonation	392
	Notes	393
	References relating to sulfochlorination	393
	References relating to sulfoxidation	395
9	PHOTOCHEMICAL DESULFONATION AND DESULFONYLATION	397
9.1	General	397
9.2	Photodesulfonation	398
9.3	Photodesulfonylation	406
	References	417
10	PHOTOHYDRODIMERIZATION	419
10.1	Introduction	419
10.2	Primary process in the intermolecular photoreduction of carbonyl compounds	421
10.3	Competitive reactions	429
10.4	Photohydrodimerization	433
10.5	Photohydrodimerization of miscellaneous compounds	439
	Note	441
	References	441
11	PHOTOOXIDATION	445
11.1	Introduction	445
11.2	Singlet oxygen: history	445
11.3	Electronic states of oxygen	446

11.4	Lifetime of singlet oxygen	449
11.5	Production of singlet oxygen	452
11.6	Sensitized photooxidations	456
11.7	Characteristic reactions of singlet oxygen	463
11.8	Applications of singlet oxygen reactions in synthesis	472
11.9	Superoxide anion	484
	Notes	494
	References	495
12	VITAMINS	500
12.1	Photochemical production of vitamins	500
12.2	Electrocyclic reactions	501
12.3	<i>Cis-trans</i> photoisomerization	509
12.4	Industrial preparation of previtamin D	515
	Notes	522
	References	522
	CONCLUSION	524
	LIST OF SYMBOLS	529
	INDEX	537