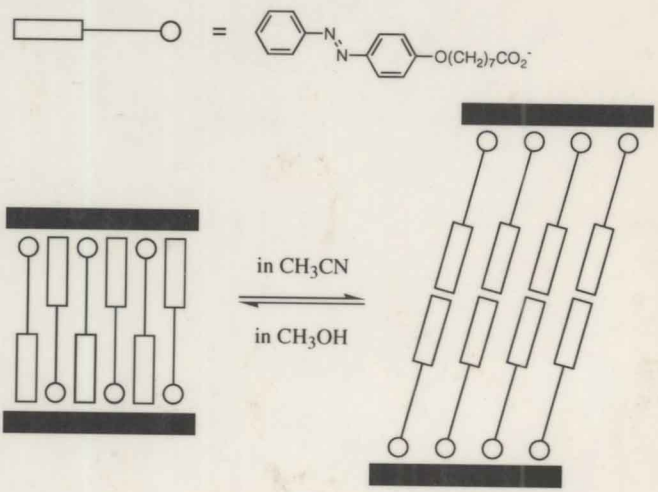
MOLECULAR AND SUPRAMOLECULAR PHOTOCHEMISTRY

VOLUME 5

Solid State and Surface Photochemistry



edited by
V. Ramamurthy
Kirk S. Schanze

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edited by

V. Ramamurthy
Tulane University
New Orleans, Louisiana

Kirk S. Schanze
University of Florida
Gainesville, Florida

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Series Editors

V. RAMAMURTHY
Professor
Department of Chemistry
Tulane University
New Orleans, Louisiana

KIRK S. SCHANZE
Professor
Department of Chemistry
University of Florida
Gainesville, Florida

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ADDITIONAL VOLUMES IN PREPARATION

Preface

Organic photochemistry has grown over a period of four decades from a relatively unknown to a well-developed discipline. A large number of photoreactions have been discovered, excited-state behavior of a number of chromophores has been understood, and several applications of photochemistry have been developed. Yet controlling the excited-state behavior of a molecule to the desired photochemical and photophysical end is a challenging task. An approach in this context has been the use of solids and surfaces as media for photoreactions. Three surfaces—silica, clay, and zeolite—continue to play a key role as media for photochemical and photophysical studies. For over a century, the interest of photochemists has also been attracted to organic crystals. In this volume we present six chapters written by experts covering recent developments in photochemistry and photophysics on surfaces and crystals. Five of the six chapters deal with chemistry and the sixth focuses on photoreactions of crystals.

In the first chapter, Dabestani and Sigman, two significant contributors to the area of surface photochemistry, summarize the photochemistry and photophysics of arenes on silica surfaces. This complements the chapter by L. J. Johnston in *Photochemistry in Organized and Constrained Media* (V. Ramamurthy, ed., VCH Publishers, New York, 1991, pp. 359–386). The two articles together give a good overview of photochemistry and photophysics on silica surfaces.

Takagi and Shichi, who have pioneered the use of clays in their own research, provide in Chapter 2 an exhaustive summary of the use of clay as a

medium for photochemistry and photophysics. Extensive literature references and critical presentation of the progress in this area make this chapter a valuable resource for anyone wishing to use clay as a reaction medium.

Irie has been instrumental in the development of photochromic crystals. In Chapter 3, he summarizes the work carried out in his laboratory on photochromism of diarylethylenes in crystalline state. The in-depth summary provided in this chapter is a valuable resource to every photochemist. Photochromism is only a small part of research activity that occurs in crystalline-state photochemistry. Photoreactions in crystalline state have also been covered in Volumes 2 and 3 of this series.

The last three interrelated chapters deal with the use of zeolite as a reaction medium for photochemical and photophysical phenomena. Overlap between the chapters has been kept to a minimum. The three chapters provide an in-depth view of electron transfer and charge transfer chemistry within zeolites and are an excellent resource for references. The authors of the three chapters—Yoon, Hashimoto, and Vasenkov and Frei—are pioneers in the use of zeolites as reaction media and have made important contributions to photochemistry within zeolites. The exhaustive chapter by Yoon deals primarily with charge transfer interactions within zeolites. This chapter is a must for those who wish to pursue studies of this topic. Hashimoto's chapter on electron transfer processes within zeolites complements the chapter by Yoon. The chapter focuses mostly on transient studies from his own, as well as other, laboratories. Vasenkov and Frei, a leader in the use of zeolites to oxidize alkanes, alkenes, and aromatics, have nicely summarized the work in this area.

We thank all the contributors for the in-depth coverage of the literature, for adherence to the deadlines, and for their patience in dealing with us. We enjoyed interacting with them and reading their contributions. It is our hope that this volume will serve not only as a valuable resource for experts but also as supplementary reading material for graduate students.

V. Ramamurthy
Kirk S. Schanze

Contributors

Reza Dabestani, Ph.D. Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Heinz Frei, Dr.sc.nat. Physical Biosciences Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, California

Shuichi Hashimoto, Ph.D. Department of Chemistry, Gunma College of Technology, Maebashi, Gunma, Japan

Masahiro Irie, Ph.D. Graduate School of Engineering, Kyushu University, Fukuoka, Japan

Tetsuya Shichi, Ph.D. Department of Crystalline Materials Science, Nagoya University School of Engineering, Nagoya, Japan

Michael E. Sigman, Ph.D. Oak Ridge National Laboratory, Oak Ridge, Tennessee

Katsuhiko Takagi, Ph.D. Department of Crystalline Materials Science, Nagoya University School of Engineering, Nagoya, Japan

Sergey Vasenkov, Ph.D.* Lawrence Berkeley National Laboratory, University of California, Berkeley, Califoria

Kyung Byung Yoon, Ph.D. Department of Chemistry, Sogang University, Seoul, Korea

**Current affiliation*: Fakultät für Physik und Geowissenschaften, Universität Leipzig, Leipzig, Germany.

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Volume 2. Organic and Inorganic Photochemistry

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Spectroscopy and Photochemical Transformations of Polycyclic Aromatic Hydrocarbons at Silica– and Alumina–Air Interfaces

Reza Dabestani and Michael E. Sigman
Oak Ridge National Laboratory, Oak Ridge, Tennessee

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), also known as polynuclear aromatic hydrocarbons or polyarenes, constitute a large class of organic compounds. These toxic and sometimes carcinogenic compounds are formed and released into the environment through natural and man-made sources. Natural sources include volcanoes and forest fire, while the man-made sources come from wood burning, automobile exhaust, industrial power generators, incinerators, production of coal tar, coke, asphalt, and petroleum, incomplete combustion of coal, oil, gas, garbage, tobacco, and char-broiled meat. These ubiquitous environmental contaminants are found in significant levels in our drinking water, food, and the air we breathe. Anthropogenic sources account for the major portion of atmospheric PAH pollution [1]. For example, vehicle emissions are believed to account for 35% of the total PAH emission in highly populated and industrialized urban areas of the United States [2]. The concentrations of PAHs found in soil around urban and industrialized areas are sometimes up to two orders of magnitude higher than those in less developed areas. Deposition of PAHs in surface waters and groundwaters can take place from a variety of sources such as airborne PAHs,

municipal wastewater discharge, effluents from wood treatment plants and other industries, oil spills, and petroleum processing. Accumulation of PAHs in soils is believed to result from atmospheric deposition after long-range transport. Once released into the environment, PAHs can partition between air, water, soil, or sediments. An extensive body of work on this subject has appeared in the literature in recent years. Representative examples include partitioning of PAHs between the gas and suspended particle phase [3,4], air–water interface [5], water–sediment interface [6–9], soil–air interface [10], soil–sediment interface [11], and dissolved organic matter from different soils [12]. There are more than 100 different PAH compounds known, but only 17 have been classified by EPA as priority pollutants [13], shown in Scheme I. The EPA selection of these compounds has been based on a number of factors, including toxicity, more available information, greater chance of human exposure, and frequent presence at hazardous sites.

During their residence time in the environment, PAHs can undergo chemical and photochemical transformation to other products that may or may not be biologically more inert than the parent compound. The fate of PAHs in the environment depends to a large degree on the media to which they are exposed. Thus, their transformation rate (with and without light) in air, water, and soil may vary as each media impacts the physical properties of PAHs differently.

In the past several years, we have been studying the photochemistry and photophysics of many PAHs, including eight that are on the Environmental Protection Agency (EPA) priority pollutant list at silica–air and liquid–air interfaces. These studies have focused on product analysis and in situ steady-state and transient spectroscopic measurements, coupled with conventional quenching, sensitization, and reactive intermediate trapping techniques, to gain a better understanding of their behavior and fate under conditions that mimic environmental settings. These methodologies have provided us detailed mechanistic information with regard to photo-oxidation pathways that operate under these conditions. We have identified two distinct photo-oxidation routes that participate in the photodegradation of these PAHs. One oxidation path (type II) involves the addition of singlet molecular oxygen to the sorbed PAH to form a thermally unstable dioxetane or endoperoxide intermediate, which decomposes to give oxidized PAH products. The second oxidation pathway (type I) involves an electron transfer from the excited PAH to the surface active sites or oxygen (to produce superoxide or oxy radicals) to form the PAH cation radical that can react with physisorbed water to give oxidized PAH products. In this chapter, an overview of the photophysical and photochemical behavior of PAHs at the solid–air interface of silica and alumina studied in our laboratory will be presented.