Organic Molecular Photochemistry

Organic Molecular Photochemistry

edited by

V. Ramamurthy
Tulane University
New Orleans, Louisiana

Kirk S. Schanze
University of Florida
Gainesville Florida

Organic Molecular Photochemistry

MOLECULAR AND SUPRAMOLECULAR PHOTOCHEMISTRY

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

ADDITIONAL VOLUMES IN PREPARATION

Preface

The third volume in the Molecular and Supramolecular Photochemistry series focuses on organic molecular photochemistry. This volume presents six chapters in the general area of photochemical and photophysical studies of organic molecules. Although the thrust of the individual chapters vary, each deals with the excited-state behavior of organic molecules in their molecular form.

Tremendous activity in photochemical studies over the past 40 years has resulted in a reasonable understanding of the photobehavior of a large number of organic molecules, in the discovery of innumerable reactions, and in establishing the basic mechanistic framework for a large number of photoreactions. Such a rapid development has resulted in photoscience becoming a tool in the hands of chemists who want to exploit light for useful ends. Because of this, there is a need to periodically consolidate and critically evaluate the information that becomes available through the tireless efforts of our colleagues. The Molecular and Supramolecular Photochemistry series aims to serve this role.

In Volume 3 of this series, *Organic Molecular Photochemistry*, eight active photochemists summarize and critically evaluate the literature in their area of expertise. Chapters 3 and 4 deal with a well-investigated and important reaction in photochemistry: geometric isomerization. Arai (Chap. 3) deals with the one-way cis-trans isomerization of aryl-substituted alkenes. Rao (Chap. 4) summarizes recent mechanistic developments in the area of geometric isomerization of olefins. These two chapters combined provide over 300 references that should

be valuable to those seeking current knowledge of the excited-state geometric isomerization of olefins. It is unnecessary to remind the readers that one of the classic reviews on geometric isomerization, by Saltiel and coworkers, appeared in an earlier version of this series (Org. Photochem., **1973**, *3*, 1).

One of the important activities of chemists is to seek similarity among apparent dissimilarity. Fleming and Pincock have successfully done this in their chapter on photochemical cleavage reactions. Cleavage of the C—X bond prompted by light has been investigated by a number of workers (X being different in each case) and mechanisms for the cleavage process have been proposed. Further progress in the field depends on one's ability to connect all that is known on the photocleavage process. Fleming and Pincock have efficiently achieved this in Chapter 5. This chapter, along with one by Cristol and Bindel that appeared in the Organic Photochemistry series (**1983**, *6*, 327), is indispensable to those interested in basic mechanistic studies of cleavage process, as well as phototriggers, photocleavages, photoaffinity labels, and photoacid generation.

Despite intense activity in discovering new reactions and establishing mechanisms of photoreactions, control of the chirality of photoproducts is still unknown. While strategies for achieving high (e.e., >95%) asymmetric induction in a number of thermal reactions have been developed, such is not the case for reactions initiated by light. Activity in this area can certainly be expected in the coming years. The chapter by Everitt and Inoue (Chap. 2) provides a thorough critical summary of the literature on asymmetric photoreactions in solution. This chapter, along with a previous review by Inoue (*Chem. Rev.*, **1992**, *92*, 741), should be a valuable information package in the hands of photochemists wishing knowledge of asymmetric photochemistry.

Although the field of photochemistry has reached its maturity, certain critical gaps in our understanding of the photobehavior of molecules in organized assemblies exist. Two chapters are devoted to presenting the current status of activities in this area. Ito (Chap. 1) provides a summary of the literature on solid-state photoreactions of two component crystals. The literature in this area is quite spread out and Ito has done a wonderful job of distilling it into a single chapter. Molecular photochemistry has been a valuable tool in characterizing the interior of organized assemblies in terms of the parameters that we use to understand isotropic solvents. Bhattacharyya (Chap. 6) provides a critical evaluation of the various probes and their photoproperties that can be used to understand the reaction cavities of organized assemblies such as zeolites, cyclodextrins, and micelles.

It is our hope that the chapters presented in this volume will serve not only as a valuable resource for experts and active workers, but also as supplementary reading material for graduate students. As editors we have enjoyed reading the

work of the authors, who have done a wonderful job of presenting interesting and current material in a critical and consolidated manner. We hope that you will benefit from this book and support this series.

V. Ramamurthy
Kirk S. Schanze

Contributors

Tatsuo Arai, Ph.D. Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki, Japan

Kankan Bhattacharyya, Ph.D. Physical Chemistry Department, Indian Association for the Cultivation of Science, Calcutta, India

Simon R. L. Everitt, Ph.D. Inoue Photochirogenesis Project, ERATO, Japan Science and Technology Corporation and Osaka University, Toyonaka, Japan

Steven A. Fleming, Ph.D. Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah

Yoshihisa Inoue, Ph.D. Inoue Photochirogenesis Project, ERATO, Japan Science and Technology Corporation and Osaka University, Toyonaka, Japan

Yoshikatsu Ito, Ph.D. Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan

James A. Pincock, Ph.D. Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada

V. Jayathirtha Rao, Ph.D. Organic Chemistry Division II, Indian Institute of Chemical Technology, Hyderabad, India

Contents

vii

1

Solid-State Organic Photochemistry of Mixed Molecular Crystals

Yoshikatsu Ito
Kyoto University, Kyoto, Japan

I. INTRODUCTION

Organic photoreactions in the solid state are strictly controlled by the crystal structure, which in turn is the result of an interplay of a range of noncovalent, intermolecular interactions, e.g., van der Waals forces, hydrogen bonding, and donor–acceptor interactions. Thus, in principle, the solid-state photoreactivities and selectivities must be freely controllable by the high-level design of the crystal structure by exploiting these intermolecular forces. However, the balances between these forces are so subtle that one cannot predict, at present, the crystal structure from the molecular structure. In this connection, our efforts to devise various methods that can "forcibly" change chemo-, regio-, stereo-, and enantio-selectivities of particular solid-state photoreactions to desired directions through "crystalline supermolecule" formation is important [1].

This chapter surveys unimolecular and bimolecular photochemical reactions in mixed molecular crystals and solid mixtures. Various photoreactions occurring in mixed crystals (solid solution), hydrogen-bonded cocrystals, donor–acceptor crystals, crystalline organic salts, and solid mixtures are described. In contrast to one-component crystals [2], the organic photochemistry of such multi-

component crystals is still very young and hence has an abundant serendipity and possibility. In a recent review article [1], the author overviewed solid-state photoreactions in two-component crystals. It covered mixed crystals, hydrogen-bonded cocrystals, donor–acceptor crystals, inclusion crystals, asymmetric syntheses by using chiral hosts, crystalline organic salts, solid mixtures, solid-state sensitization and quenching, and solid-state asymmetric syntheses. Therefore, a substantial part of this chapter is based on this previous publication. However, photoreactions in inclusion crystals and of Lewis acid complexes and photophysical investigations of mixed crystals were not mentioned. For these subjects, the reader might be referred to Ref. 1. Finally, in order to save space, drawings of the X-ray crystal structure were not reproduced here. Those who want to know these details should consult the original papers.

II. WHAT IS THE MIXED MOLECULAR CRYSTAL?

The two-component crystal may be divided into three categories: 1.) mixed crystal (solid solution), 2.) crystalline molecular compounds, 3.) a simple mechanical mixture of component crystals. I propose the term "mixed molecular crystal" to represent both mixed crystal and crystalline molecular compounds and have used it as such in the title of this chapter.

Mixed crystal is a homogeneous crystal of two or more substances. Solid solution is a homogeneous solid mixture of substances. Both are virtually equal, although the latter can be amorphous. In general, mixed crystals are obtained from molecules of similar shapes and sizes. The forces between molecules are usually weak. Compositions can vary throughout a certain range and crystal structures are disordered.

When the intermolecular forces are relatively strong and directional, crystalline molecular compounds (crystalline molecular complexes) are formed. They have fixed stoichiometries and ordered structures. These two-component molecular crystals are also called *cocrystals* or maybe *adduct crystals*. Hydrogen-bonded cocrystals, donor–acceptor crystals (charge transfer crystals), and inclusion crystals (host–guest crystals) are examples of crystalline molecular complexes. Crystalline organic salt is a special case of hydrogen-bonded cocrystal or donor–acceptor crystal, i.e., proton (or electron) transfer from the acid (or donor) to base (or acceptor) occurred.

A solid mixture is any mixture of crystals of different substances, regardless of its solid-state structure. It may be a simple mechanical mixture of component crystals, a mixed crystal, a molecular complex, or an ionic salt. In this chapter, a simple mechanical mixture as well as all uncharacterized two-component crystals are grouped under solid mixtures.

Figure 1 describes three representative phase diagrams for a two-component system [3]. Diagram a has a eutectic point E and the region l is a homoge-
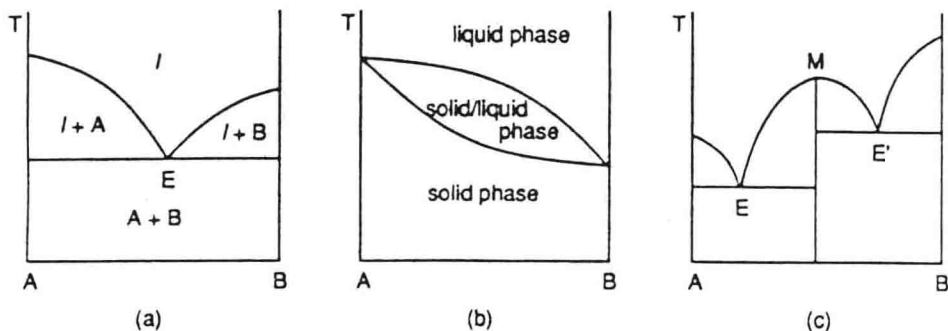
Figure 1 Three typical temperature versus composition diagrams for a binary system (A and B): (a) diagram with a eutectic point E; (b) diagram for the case of unlimited solubility; (c) diagram showing formation of a molecular complex M. Diagrams a–c represent the simplest case, respectively, where a simple mixture of component crystals, a solid solution (mixed crystal), or a crystalline molecular complex is brought about.

neous liquid phase. Below the eutectic temperature, there is a two-phase region (A + B) of a solid, which consists of crystals of component A and crystals of component B. This two-phase region conforms with a simple mechanical mixture of component crystals mentioned above.

When molecules of the two components have unlimited solubility both in the liquid and in the solid state, diagram b is obtained. The solid phase corresponds to a solid solution or a mixed crystal. Diagram c represents a case whereby a crystalline molecular complex M of the composition $A_m B_n$ ($m = n = 1$) is formed and, besides, the complex M does not form solid solutions with its components A and B. This diagram is the sum of two diagrams similar to example a.

III. PREPARATION AND CHARACTERIZATION OF TWO-COMPONENT CRYSTALS

Two-component crystals are usually prepared either 1.) by traditional cocrystallization or slow evaporation of solvent from a solution containing the components, 2.) by grinding the components together in a mortar and pestle [4] or in a ball grinder [5], or 3.) by melting together the components and subsequent solidification of the melt by cooling [6]. Recently, the second method has commonly been used. It has now been proved that molecular complexes prepared either by grinding (method 2) or by cocrystallization (method 1) exhibit not only similar chemical and photochemical reactivities but also similar spectroscopic and physical properties [4,5,7–12].

Solid materials thus prepared may exist as a mixed crystal (= a solid solu-

tion), a molecular compound (e.g., a hydrogen-bonded complex, a donor–acceptor complex, and an inclusion complex), an ionic salt, or a simple mechanical mixture of homocrystals of each component. Structural information of these solid samples is obtained by various physical means such as single-crystal X-ray diffraction, powder X-ray diffraction (PXD), solid-state ^{13}C nuclear magnetic resonance (NMR), IR and UV, electron microscopy, thermal analysis [differential scanning calorimetry (DSC) and thermogravimetric analysis], phase diagram determination, etc.

For example, each batch of crystals from cocrystallization can be examined under a polarizing microscope to determine whether the crystals have homogeneous morphologies or whether mixtures of crystals are present. Solution NMR results and elemental analyses can give the stoichiometry of components. Melting points of complexes are usually sharper than those of mixtures of components. A clearer distinction can be made from measurements of PXD, solid-state ^{13}C NMR, IR and UV, and DSC spectra. Because the spectral patterns for a simple mechanical mixture are composites of those for each component, observation of new peaks in these spectra indicates the formation of a molecular complex. When a molecular complex is available as a single crystal of sufficient size and quality, its crystal structure and molecular conformation can be unequivocally determined by single-crystal X-ray diffraction [4–11,13].

The PXD pattern of a solid solution is very similar to that of the host component. Differentiation of a solid solution from a simple mechanical mixture and a molecular complex may be best made on the basis of phase diagrams (Fig. 1), which are constructed from DSC measurements [3]. Probably, however, interpretations of these data are not always straightforward [14–16]. For weak complexes, X-ray quality single crystals are not available in many cases. Hence, the characterization of certain two-component crystals may potentially lead to dispute. Furthermore, a few institutions for organic chemistry are well equipped with the facilities mentioned above.

Irradiations of solid samples are carried out in various manners, depending on the researcher [1]. For example, in the author's group, solid samples are usually ground into powders and are irradiated externally in a specially designed apparatus (Fig. 2) [1].

IV. DESIGN OF CRYSTALLINE MOLECULAR COMPOUNDS

Hydrogen bonding is the most important directional interaction responsible for supramolecular construction [17]. Appendix 1 illustrates several typical hydrogen bond patterns which are present in two-component molecular crystals. Appendix 2 exemplifies a variety of reported cocrystals selected mainly from the recent papers [18]. Not only strong hydrogen bonds (i.e., O—H$\cdots$O, O—H$\cdots$N,
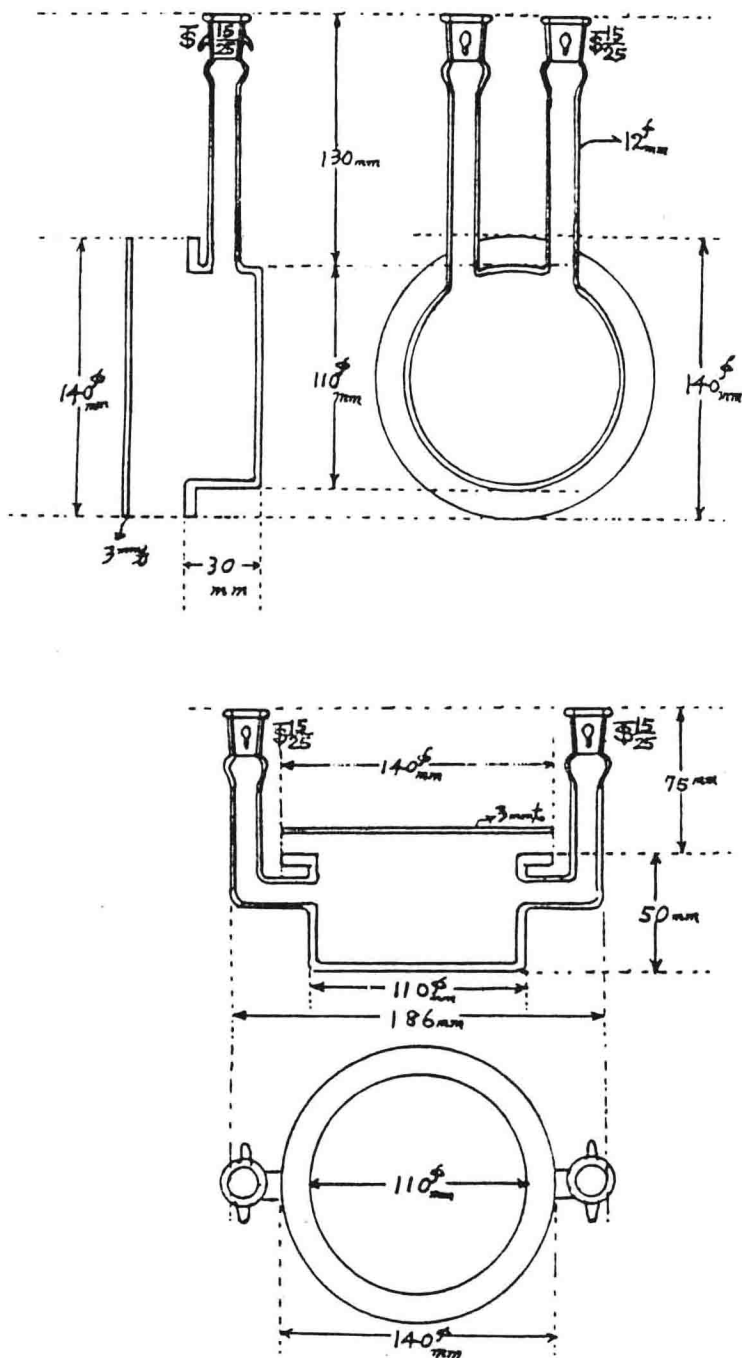
Figure 2 Two types of vessels for solid-state photolysis.

N—H···O, and N—H···N) but also weaker hydrogen bonds and other weak forces [i.e., C—H···O, C—H···N, O—H···π, N—H···π, and C—H···π interactions], halogen atom interactions (Cl,Br,I)···(Cl,Br,I), (Cl,Br,I)···(N,O,S), and C—H···Cl; chalcogen atom interactions (S,Se)···(S,Se), S···N, S···Cl, and S—H···S) are utilized for cocrystal formation.

Appendix 1 also describes aryl···aryl and hydrophobic interactions. Aliphatic side chains longer than around five carbon atoms may lead to preferential close packing of the side chains. Aromatic rings may associate via either a herringbone (edge-on) mode or a stacking mode. The herringbone geometry may be considered to be one manifestation of the C—H···π interaction. In the stacking mode, either face-to-face stacking or offset stacking is possible. A favorable geometry for the aryl···aryl interaction is determined by the electrostatic interaction, i.e., by the balance between π-σ attractions and π-π repulsions, although the magnitude of the overall interaction energy is controlled by the van der Waals interaction and probably by the charge-transfer interaction [19]. Planar π donors and π acceptors tend to form offset overlapped structures, e.g., cocrystals a–e in Appendix 2. Note, however, that the interaction between benzene and hexafluorobenzene in cocrystal a is electrostatic in nature, not a charge transfer type. Solid-state complex f is an example of O···C donor–acceptor interactions.

According to Kitaigorodskii's close-packing principle, molecules will pack in a manner that minimizes void space or, in other words, in a way to maximize van der Waals interactions [20]. Hence, effects of both molecular shape and size are important in crystal engineering. For example, since racemic crystals tend to pack into centrosymmetric space groups, this statistical preference was utilized to prepare cocrystal g in Appendix 2, which is a rare molecular compound called a quasiracemate. The formation of cocrystal g was made possible due to the isosteric nature of the isopropenyl and dimethylamino substituents, indicating that shapes rather than dipoles can be in fact the dominant factor (cf. Ref. 31).

Recently, many studies on the design of metal-containing crystalline supramolecular assemblies have been carried out [17f,17l,21]. A variety of coordination numbers and geometries associated with transition metals as well as various metal–ligand bonding reactions, including M—H···O, O—H···M, C—H···O≡C—M, and other hydrogen bond–like interactions, should be useful for construction of new functional materials.

As described below, investigations on the design and synthesis of photoreactive mixed molecular crystals are still very limited in number and scope. However, by very ingenious manipulation of the above-mentioned intermolecular interactions, construction of new crystals bearing desired reactivities should be possible for many types of bimolecular photoreaction. More investigations in this direction should be carried out.