CHAPTER 13

Supramolecular Organic Photochemistry: The Control of Organic Photochemistry and Photophysics through Intermolecular Interactions

13.1 The Current and Emerging Paradigm of Supramolecular Organic Chemistry

Supramolecular chemistry has evolved from molecular chemistry over the last half century as the science of "chemistry beyond the molecule." Supramolecular organic chemistry can be described in a number of ways, such as: (1) chemistry of molecular complexes; (2) chemistry of noncovalent bonds; (3) chemistry of the intermolecular bond; and (4) chemistry of molecular recognition. These are appealing, but somewhat fuzzy, descriptions of "chemistry beyond the molecule."[1–3] Nevertheless, they allow the chemist latitude in a wide range of concepts that are useful for deciding what is supramolecular and what is not. Rather than trying to pin down a precise definition of supramolecular organic chemistry, let us try to describe its fundamental intellectual foundation: Supramolecular organic chemistry is based on the concept that whereas organic chemistry is generally interpreted in terms of individual molecular structures and/or dynamics for which covalent bonding is the dominant feature determining molecular structure, there are situations where introduction of more than one interacting molecular structure is required to understand the chemistry under consideration. To a photochemist, the comparative ideas of molecular and supramolecular structures are analogous to the ideas of ground-state and excited-state potential energy surfaces. In this analogy, organic photochemistry is chemistry beyond the ground-state surface: A ground-state potential energy surface determines the ground-state chemistry and properties of a ground-state organic molecule (R), but an electronically excited-state surface determines the photochemical and photophysical properties of the electronically excited state (*R). Knowledge of the ground-state surface is *insufficient* to understand the photochemistry of organic molecules. When a single molecular structure is insufficient to describe the ground-state or excited-state chemistry of a molecule under investigation, *this is a signature that the transition from molecular organic photochemistry to supramolecular organic photochemistry has occurred*. In

Section 4.38, examples of supramolecular systems, exciplexes and excimers, were described. These are simple, yet definitive examples of electronically excited "supermolecules" for which a complex of two molecules is required to understand the photochemistry and photophysics of a system.

All of the features of modern molecular organic photochemistry may be readily transferred and incorporated into the developing paradigm of *supramolecular organic photochemistry*.[4,5] One must merge the "molecular" aspects of the organic photochemistry paradigm with those of *supramolecular* organic chemistry.

First, let us consider the essential and critical features of a supramolecular organic chemical system. We start by viewing a supramolecular system as "self-similar" to a molecular system in terms of structure and dynamics, and then add features that might be required to develop the paradigm of supramolecular organic photochemistry. The key intellectual unit of the molecular system is the *strong and directional covalent chemical bond* that holds the atoms of a molecule together. The paradigm of the covalent bond ties together the critical features of structure and reactivity of organic molecules. In this paradigm, intermolecular and noncovalent interactions are generally considered to be so weak, nondirectional, and nonspecific that they play only a secondary role in determining structure and reactivity in systems under study. As the intermolecular interactions or noncovalent interactions between molecules become increasingly selective and stronger, the system begins to transform from one that can be well described as molecular to one that *must* be described as supramolecular. In a truly supramolecular system, the basic features become difficult to understand simply on the basis of molecular chemistry. The contrast between monomer (molecular) and excimer (supramolecular) emissions (Section 4.38) is such an example. Indeed, for many supramolecular systems, the basic intuition derived from molecular chemistry will fail even at the qualitative level!

In summary, the term "supramolecular chemistry" invokes a chemistry beyond the molecule and emphasizes noncovalent intermolecular bonds between two or more molecules rather than emphasizing a single molecule and the covalent bonds that hold it together. In the same way that a molecule can be defined as an assembly of atoms that is held together by *strong molecular covalent bonds*, a "supermolecule" or "supramolecular assembly" can be defined as a complex of two or more molecules that are held together by *weak intermolecular noncovalent bonds*.[6,7] We are immediately confronted by the meaning of "weak" bonds. A useful benchmark for the "relative weakness" of a bond is a comparison of the strength of a bond to the average energy of collisional impacts between molecules. Around room temperature ($\sim$ 300 K, 27° C) this energy is on the order of 1 kcal mol^{-1} ($\sim kT$). Thermal energy, kT is the energy available from the thermal motion of colliding particles at a particular temperature (k = Boltzmann constant and T = temperature in Kelvin). With this benchmark in mind, bonds with an energy on the order of 5 kcal mol^{-1} will be rapidly broken with molecular collisions on the order of kT. For example (Section 8.4), if we take 5 kcal mol^{-1} as the activation energy for a bimolecular reaction (typical A factor in an Arrhenius equation, of 10^8 s^{-1}), the rate of bond breaking will be on the order of 10^5–10^6 s^{-1}. In other words, by the criterion of kT, "weak" bonds, will only last to the order of 10^{-5}–10^{-6} s or less! Individual noncovalent bonds are always weak and will

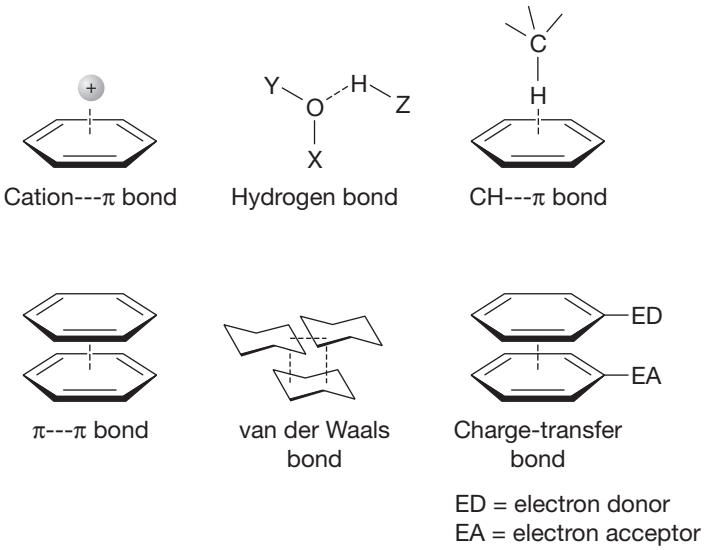


Figure 13.1 Examples of noncovalent bonds between molecules. The symbol --- indicates a weak intermolecular bond.

generally possess strengths < 5 kcal mol^{-1}. Examples of commonly encountered noncovalent bonds are shown in Fig. 13.1: cation---π bond, hydrogen bonds, C—H---π bonds, π---π bonds, van der Waals interactions (also termed dispersion interactions), and charge-transfer (CT) interactions.[8–12] We can compare noncovalent dynamics to the time required to break a "very weak" *covalent* bond of 30 kcal mol^{-1}, whose rate would be $\sim 10^{-8}$ s^{-1} (a lifetime of $\sim 50{,}000$ h, or ~ 6 years)! However, as we will emphasize throughout this chapter, although most individual noncovalent bonds may be weak relative to kT, when a significant number of noncovalent bonds operate together for a supermolecule, the overall net bonding, and therefore the lifetime of the supramolecular complex, can be significant.

Now, we consider a general strategy for translating the very successful paradigm of molecular structures and dynamics into a successful paradigm for supramolecular structures and dynamics. In describing the structure of molecules, chemists start with *molecular composition* (numbers and kinds of atoms), then move to the level of *molecular constitution* (how the atoms are connected by covalent bonds), then to *molecular configuration* (how the atoms around a given atom are arranged in space), and finally to *molecular conformation* (the possible shapes of a molecule resulting from plausible orientations of groups of atoms). Molecular dynamics is the study of the change of one or more of these molecular structural features with time. Similarly, in describing the structure of supramolecular systems, chemists consider *supramolecular composition* (numbers and kinds of molecules that make up the supermolecule), *supramolecular constitution* (how the molecules of the supermolecule are connected by noncovalent bonds), *supramolecular configuration* (how the molecules that make up the supermolecule are arranged with respect to each other around a given molecule in space), and *supramolecular conformation* (a specific set of plausible orientations for all of the molecules of the supermolecule in space). Supramolecular dynamics is

the study of the change of one or more of these supramolecular structural features with time.

Most of the intermolecular noncovalent bonds in Fig. 13.1 can be conveniently classified in general terms as resulting from classical polarization forces or quantum mechanically induced dispersion forces. *Polarization* forces arise from dipole moments that are induced in molecules by nearby permanent electrically charged poles (cation---π interaction in Fig. 13.1) or by nearby permanent dipoles (e.g., hydrogen bond in Fig. 13.1).[9,10] Dispersion forces are universal and are due to instantaneous variations in the electron clouds (a quantum mechanical idea) that cause fluctuating dipoles in a molecule. These fluctuating dipoles in turn induce dipoles in surrounding molecules (e.g., CH---π, π---π, van der Waals interactions in Fig. 13.1). Both polarization and dispersion forces contribute *additively* to weak noncovalent intermolecular bonds. Dispersion forces common to both polar and nonpolar molecules are general and among the most important types of forces contributing to the formation of noncovalent bonds. Finally, quantum mechanical interactions for which charge is transferred from a HO to a LU can be significant only when the HO is a good electron donor and the LU is a good electron acceptor (Section 6.21). We note that interactions can be either attractive (bonding) or repulsive (antibonding) for noncovalent interactions, just as they are for covalent and ionic interactions. Thus, an interaction per se does not guarantee net bonding.

This chapter deals with supramolecular organic photochemistry, the science in which intermolecular noncovalent bonding between two or more molecules is responsible for the failure of a single molecular structure to provide an understanding of experimental characteristics of photochemical processes along the pathway from an electronically excited state *R to a reactive intermediate I, and finally to an isolated product P. In particular, we are concerned with the supramolecular photochemistry of a special class of supermolecules: *guest@host complexes* where the @ symbol indicates a noncovalent complex between a guest and a host. Therefore, first we consider the paradigm of guest@host complexes and then develop a paradigm for the photochemistry of these supermolecules.

13.2 A Paradigm of Supramolecular Organic Chemistry: guest@host Complexes

Molecular biology has been at the center of some of the great intellectual revolutions of the twentieth and twenty first centuries. Chemistry has been an important contributor to this revolution and supramolecular organic chemistry provides the promise of reducing the enormous complexity of biological systems to manageable levels from knowledge of individual molecular structure and interactions between these molecular structures; the latter knowledge is at the heart of supramolecular chemistry. Many important biological processes operate on the basis of a common chemical event that can be termed *molecular recognition*, the highly selective binding of a molecule or molecular fragment by another molecule to form a *complex* through one or more weak noncovalent bonds between the molecules in guest@host complex.[13–16] It might be said that molecular recognition is an expression of *molecular sociology* that describes

the causes (attractions and repulsions) of how and why molecules behave and organize themselves into certain structures and exhibit certain structural dynamics in the presence of one or more molecules. Understanding the basis of molecular recognition is a major concern of supramolecular chemistry. While molecular chemistry was successful in achieving selectivity with aggregates of atoms possessing a relatively small number of strong covalent bonds, the supramolecular chemistry of biological systems achieves selectivity by large numbers of relatively weak noncovalent interactions between organic molecules *in aqueous media* (Section 13.6). The very unusual properties of water come into play in determining noncovalent interactions, such as hydrophobic bonding, and will be of special importance for the understanding of supramolecular organic chemistry in aqueous media.[17–20]

Although there is currently no available paradigm for supramolecular chemistry that is as powerful as the one for molecular chemistry, we will describe some general features of the developing paradigm of supramolecular chemistry that will be sufficient for us to understand the qualitative aspects of supramolecular photochemistry. Again, it is important to stress that an important feature of supramolecular systems is that in general a supermolecule is held together as an assembly by a number of *weak noncovalent* intermolecular bonds. Although individual noncovalent bonds may be weak, the *summation* of a large number of weak bonds in a guest@host complex can lead to a strong overall bonding of the components of the supermolecule. The reason for the strong bonding is that at any instant a certain number of these weak bonds will be in place and contribute to the overall stability of the supermolecule. However, because of the weak nature of the bonds, supermolecules may be constantly in flux of bond making and breaking processes that allows for the rich diversity and complexity of supramolecular systems, and especially of biological systems.

Let us consider in more detail the meaning of the symbol guest@host used to define the supermolecule. The distinction between guest and host is clearest when the guest is a relatively small molecule that is partially or completely surrounded by a relatively large molecular host. However, in this chapter we will see that the guest and host molecules also could be of a similar size. The formation of a guest@host supermolecule is called "*complexation*," a term that preserves (1) the concept of relatively labile and weak noncovalent bonds and (2) the concept that individual molecular components of the supermolecule substantially retain their individual molecular properties to a considerable extent. Every noncovalent bond that can be formed by a host to a guest can be considered as a *bonding valence.* In this sense, a host is polyvalent or multivalent and capable of making a multitude of weak bonds to a guest at any instant (e.g., see Fig. 13.2). Complexation is a form of noncovalent intermolecular bonding between the guest and host (i.e., a reciprocal and complementary molecular recognition of the noncovalent valences of the guest by the host and vice versa). Thus, "bond strength" of a guest@host complex refers to the average summation of all instantaneously weak noncovalent bonds between the guest and host. We recognize that, contrary to the situation for covalently bonded molecules, the instantaneous bond strength and number of noncovalent bonds of a guest@host complex may vary considerably with time. The latter characteristic is responsible for the flexibility and selective reaction chemistry of many guest@host complexes.

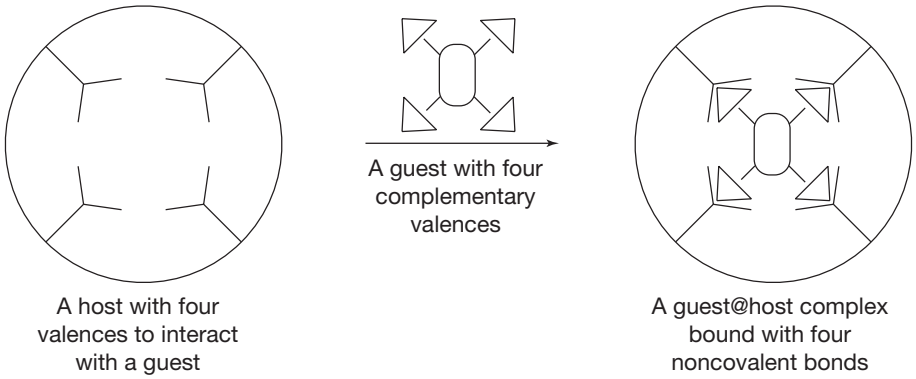
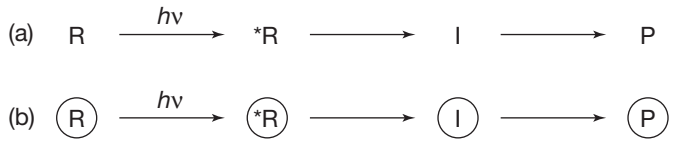


Figure 13.2 Schematic representation of the polyvalent noncovalent bonding of a guest to a host. The "Y" shape represents a valence of the host and the triangle shape represents a complementary valence of the guest.

13.3 Toward a Paradigm for Supramolecular Organic Photochemistry

A comparison of the paradigms of molecular organic photochemistry and supramolecular organic photochemistry is shown in Scheme 13.1. We saw throughout the text how the sequence of structures, such as those shown in Scheme 13.1a, works very well as a starting point for analyzing the mechanisms of molecular organic photochemical reactions that follow the pathway, $R + h\nu \rightarrow {}^*R \rightarrow I \rightarrow P$. An analogous elementary paradigm for *supramolecular* organic photochemistry is shown in Scheme 13.1b. The essential chemical difference between Scheme 13.1a and b is the inclusion of a "schematic circle" around each of the structures of Scheme 13.1b. *The circle represents any hypothetical host that forms a guest@host complex for each of the species R, *R, I, and P.* Thus, an overall supramolecular photochemical reaction may be represented by the sequence: R@host + $h\nu \rightarrow$ *R@host $\rightarrow$ I@host $\rightarrow$ P@host where the circle of Scheme 13.1b represents the host. The *molecular photochemistry* of Scheme 13.1a can be understood as an extension of a "solvent cage" model (Section 7.37);[21,22] the implication of the circle of Scheme 13.1b is that the understanding of supramolecular photochemistry requires a guest@host complex model for which the circle represents a specific host that binds the guest through noncovalent bonds and that these weak bonds control the pathways followed in a supramolecular photochemical reaction. Note that in general the supramolecular structure of *R is the same as that of R as the result of the Franck–Condon principle, which demands that the geometries of R@host and *R@host are identical at the instant of creation of *R@host.

This chapter describes examples of the guest@host complexation influence on both the primary *supramolecular photochemical* process, *R@host $\rightarrow$ I@host, and the secondary thermal processes, I@host $\rightarrow$ P@host. In addition, *supramolecular photophysical* processes, *R@host $\rightarrow$ R@host (+ heat or light), will be described. We will see that the ability to manipulate the course of photochemical reactions by photolyzing R@host complexes rather than R in a solvent cage expands considerably

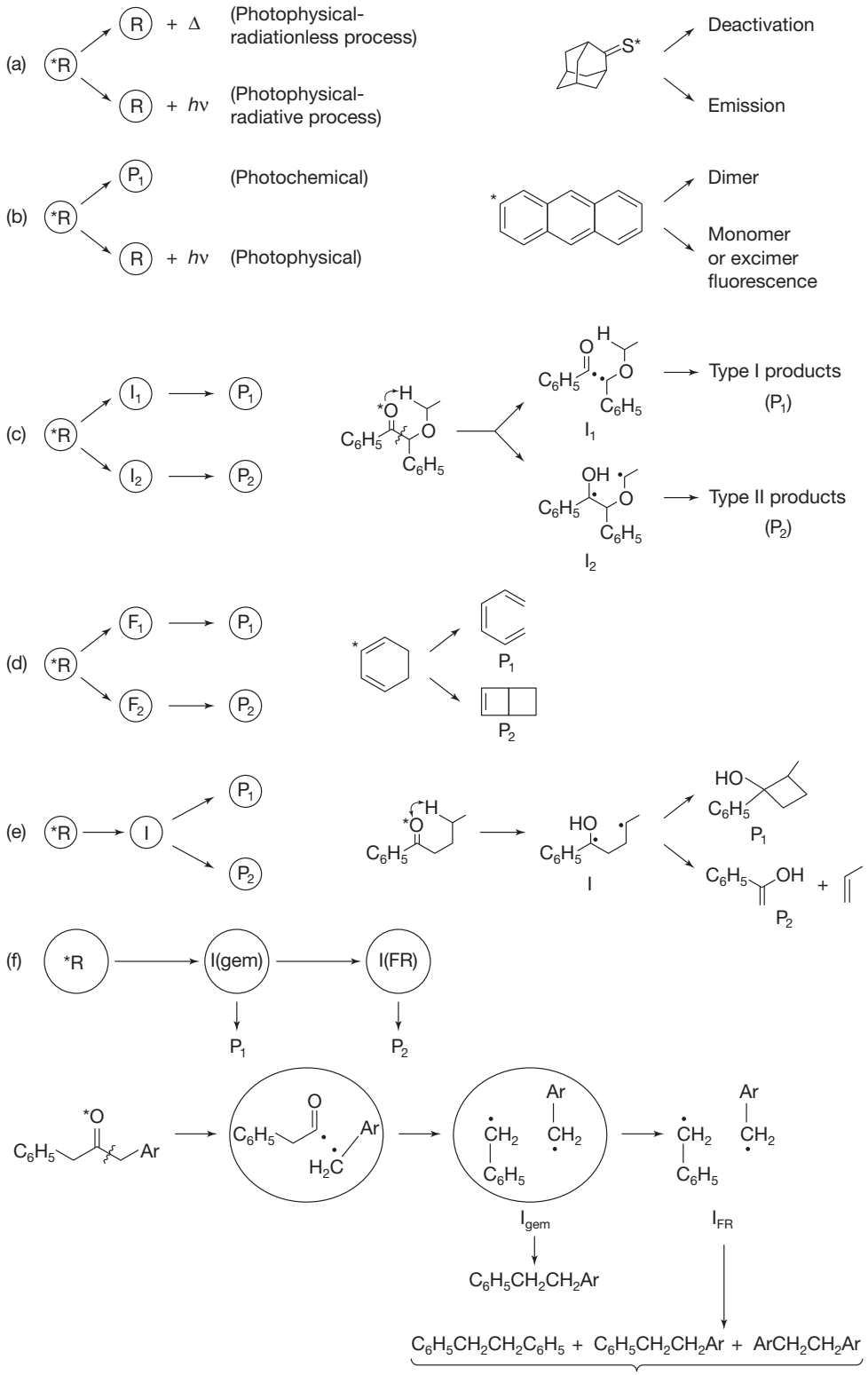


Scheme 13.1 (a) Paradigm of molecular organic photochemistry in ordinary organic solvents. (b) Paradigm of supramolecular organic photochemistry of guest@host complexes. The circle around R, *R, I, and P represents a supercage of a host that causes the overall photochemistry to occur differently than it does in an ordinary solvent cage.

the possible selective control of products from photochemistry of organic molecules and also the selective control of available mechanisms for investigation.

In Scheme 13.1a, a solvent cage made up of small molecules is understood to exist about R, *R, I, and P along the photochemical reaction pathway. Indeed, this solvent cage may be considered as the simplest supramolecular host. The chemical behavior of R, *R, I, and P in a solvent cage (e.g., guest@[solvent cage]) is a useful benchmark for comparison with the chemical behavior of supramolecular guest@host complexes. In this case, [solvent cage] represents the host in solution. It is important to note that interactions between guest and solvent molecules are very weak, random, and not directional. When the chemistry of a guest complexed to a host differs significantly from that expected from a *solvent cage*, we can term the host as a "*supercage*" that is responsible for the supramolecular behavior.

In general, there is more than one product (P) produced in a photochemical reaction as the result of competing primary ($^*R \rightarrow I_1 + I_2 + \cdots$) and secondary ($I \rightarrow P_1 + P_2 + \cdots$) processes. Let us say, for simplicity, that only two products (P_1 and P_2) are formed for the same $^*R$ and we would like to form one product selectively, either P_1 or P_2. Our goal is to employ supramolecular effects by simply putting a circle of Scheme 13.1 around $^*R$ to direct the $^*R$ to either P_1 or P_2, not both. Now, we develop a strategy to produce P_1 or P_2 selectively through supramolecular control as follows. Scheme 13.2a shows an example of the possible influence of supramolecular interactions on the partitioning of two photophysical processes. Scheme 13.2b shows an example of the possible influence of supramolecular interactions on the partitioning of a photophyscial and photochemical process. Conceptually and conveniently we can divide the competition between two photochemical reactions into three categories (Scheme 13.2): (1) $^*R$ yielding P_1 and P_2 via independent intermediates (I_1 and I_2, Scheme 13.2c); (2) $^*R$ giving P_1 and P_2 via funnels F_1 and F_2 (Scheme 13.2d), and (3) $^*R$ yielding P_1 and P_2 via a single primary intermediate (I, Scheme 13.2e). In addition, in the $I \rightarrow P$ secondary thermal processes for which I is a radical pair (RP), it is important to consider how supercages can influence competition between the $I_{gem} \rightarrow P_{gem}$ step and the $I_{gem} \rightarrow I_{FR} \rightarrow P_{FR}$ (free radical = FR) steps (Scheme 13.2f), since the geminate products (P_{gem}) and free radical products (P_{FR}) will generally be different. Next to each general example in Scheme 13.2 is a specific chemical example.



Scheme 13.2 Common competing primary photophysical and photochemical processes from *R and I with a specific example. Each arrow shown branching from *R or I has an associated first- or second-order rate constant. Supramolecular effects can control the relative magnitudes of the branching rates.

In the following sections, we will show how the molecular photochemistry and photophysics of guest@[solvent cage] systems, described in the earlier chapters, can be transformed into a description of the supramolecular photochemistry and photophysics of guest@host systems. Examples are discussed in the following sections. For the sake of easy conceptualization, the influence of the supramolecular effect on photoreactions is discussed under four sections, the influence of complexation to a host on R, *R, I, and P, respectively. As a concrete exemplar of a guest@host system of very wide scope, we will discuss guest@enzymes, which serve as an inspiration for the synthetic supramolecular guest@host complexes. Since enzymes operate in aqueous environments, first we will describe the photochemistry of guest@host complexes in aqueous media. In addition, we will consider examples in crystals and porous solids where a remarkable influence of the host has been observed. These selected systems serve as exemplars for a large number of supramolecular complexes.

13.4 An Enzyme as an Exemplar Supramolecular Host for guest@host Complexes. Control of Activation Parameters and Competitive Reaction Rates through Supramolecular Effects

Perhaps, the quintessential exemplar for the schematic host circle in Scheme 13.1b is the active site of an enzyme. Let us analyze the general and familiar mechanism of how a host enzyme transforms a small guest molecule (called a substrate by biologists) selectively into a targeted product molecule. We can then employ these mechanistic features to generate a general paradigm based on intuition gained from the enzyme model for all synthetic supramolecular guest@host complexes.

The first step in enzyme action is the *molecular recognition* of the guest substrate by the host enzyme (or the reciprocal molecular recognition of the host by the substrate).[6,13] Molecular recognition may be defined as the *selective* noncovalent binding of the substrate to the host to form a guest@host complex. After binding to the enzyme, the guest is transported to the active site of the enzyme (a reaction cavity built within the enzyme host structure). While bound to the active site, the guest is chemically transformed with extraordinary selectivity and at a remarkable rate to a desired, biologically functional product. The chemistry of the guest is determined entirely by the structure and dynamics of the guest@enzyme complex. By analogy, the chemistry of the guest in any guest@host complex is determined by the structure of the supramolecular complex and cannot be understood in terms of the guest molecular structure alone or the chemistry of the guest molecule in ordinary solvents. The chemistry performed on the substrate in a guest@enzyme complex is exquisite in terms of rate, chemioselectivity, regioselectivity, and stereoselectivity, all accomplished on (hydrophobic) organic molecules in an aqueous (hydrophilic) environment! One of the holy grails of supramolecular chemistry is the emulation of the extraordinary chemical selectivity of small guest molecule reactions in a guest@host complex in the chemist's laboratory. In developing a supermolecular organic photochemistry paradigm, we will be replacing large enzymes with small molecular hosts. A strategy to finding the holy grail is to mimic some of the structural and dynamic features

of guest@enzyme complexes in simpler organic guest@host complexes. This strategy is termed biomimetic chemistry. Molecular recognition in supramolecular organic chemistry means binding with the *purpose of product control.* Describing and understanding supramolecular control of organic photochemistry is a goal of this chapter.

Now, let us review some of the key supramolecular features of the substrate@enzyme complex that can be mimicked in simpler synthetic organic molecular guest@host complex: (1) *preorganization* of the guest in a host cavity whose size is on the order of a small organic molecule in dimension ($\sim$ 5–20 Å diameter); (2) *constraint and control* of the translational and rotational motions of the guest; (3) *control* of the extent, shape, and location of "free space" available to the guest; (4) *preorganization* of host chemical functionality so that it can operate on the guest and achieve the desired chemical selectivity on the reactions of the guest. Preorganization by complexation of the guest and host inhibits the freedom of motion of the guest molecule and correspondingly decreases the entropy (ΔS) of the guest. In the term $\Delta G = \Delta H - \mathrm{T}\Delta S$, a negative value of ΔS increases the free energy (i.e., makes the complexation thermodynamically less favorable, Section 13.8). Thus, the decrease in ΔS associated with preorganization (complexation) must be compensated by a decrease in ΔH, if the guest@host complex is to have an overall negative free energy and be stable. This opposing interplay between entropy and enthalpy, known as enthalpy–entropy compensation, is achieved through a number of weak interactions between the guest and the host. Nature has skillfully managed to balance opposing tendencies between ΔH and ΔS through the billions of years of supramolecular evolution of biological systems. When dealing with guest@host complexes in aqueous solutions it is also important to consider the entropic changes in solvent water in addition to those of individual host and guest molecules. Indeed, the so-called hydrophobic effect appears to be dominated by entropic changes in the water structure upon formation of certain guest@host complexes in aqueous solution.

Now we return to the issue of using supramolecular effects in selectively controlling the formation of either P_1 or P_2 (Scheme 13.2; Fig. 13.3).[23–25] In a completely general way, a high chemical selectivity for P_1 or P_2 can be interpreted in terms of a simple free energy diagram for which, hypothetically, a reactant (R) possesses a lower free energy of activation ($\Delta G^{\ddagger}$) to a *desired* product (say, P_1) than to a second undesired product (say, P_2). For simplicity, let us consider the energy diagram in Fig. 13.3 showing three different scenarios: (a) a molecular system for which the free energy barriers to P_1 and to P_2 are of comparable heights ($\Delta G_1^{\ddagger} = \Delta G_2^{\ddagger}$), resulting in comparable rates of reaction from R to P_1 and P_2 and in no selectivity in formation of P_1 or P_2 from R; (b) a supramolecular system for which the barrier leading to P_1 is more or less the same as the molecular system, but with a significantly reduced barrier leading to P_2($\Delta G_1^{\ddagger} > \Delta G_2^{\ddagger}$), resulting in a faster relative rate and high selectivity for P_2 formation; (c) a supramolecular system for which the barrier leading to P_1 is more or less the same as the molecular system, but the barrier leading to P_2 significantly increased $\Delta G_1^{\ddagger} < \Delta G_2^{\ddagger}$. This increase results in a faster relative rate and high selectivity for formation of P_1. Scenario (b) represents a case of selectivity based on supramolecular catalysis (selective reaction acceleration) of formation of P_1 and scenario (c) represents a case of selectivity based on supramolecular inhibition (selective

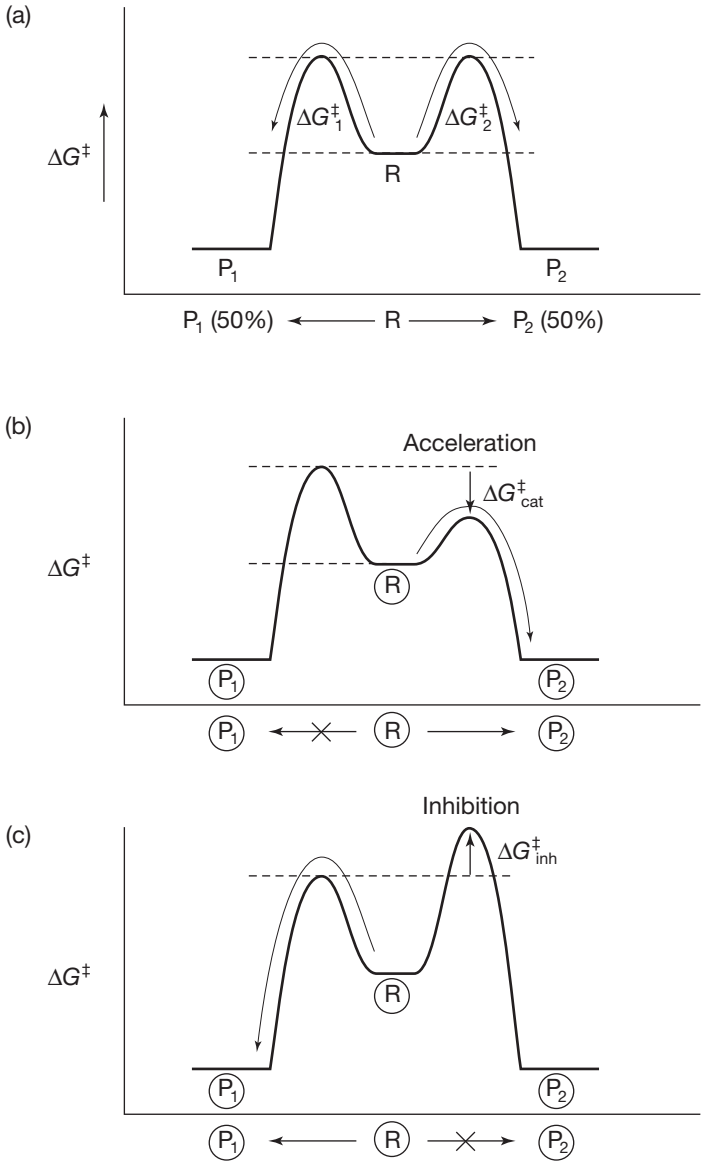
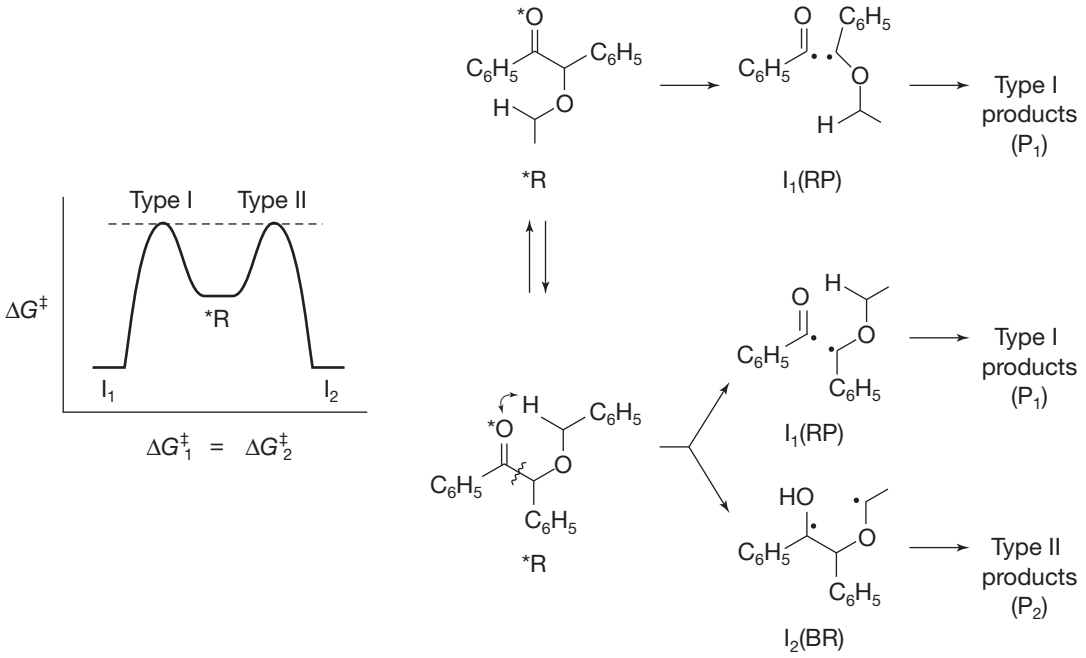


Figure 13.3 Schematic representation of (a) a nonselective chemical reaction $R \rightarrow P_1 + P_2$ for which $\Delta G_1^{\ddagger} = \Delta G_2^{\ddagger}$; (b) a selective reaction $R \rightarrow P_2$ for which $\Delta G_1^{\ddagger} > \Delta G_2^{\ddagger}$ through catalysis; (c) a selective reaction $R \rightarrow P_1$ for which $\Delta G_1^{\ddagger} < \Delta G_2^{\ddagger}$. (Catalysis = cat and inhibition = inh.)

reaction deceleration) of formation of P_2. The energy barriers shown in Fig. 13.3a can be manipulated by supramolecular control of rate controlling features, such as precomplexation, collision frequency, orientations, distance of separation, and conformational preferences. In each case, the *relative* free energy of activation for the



Scheme 13.3 A hypothetical situation for which the Type I and Type II molecular reactions possess comparable energies of activation ($\Delta G_1^{\ddagger} = \Delta G_2^{\ddagger}$).

formation of the desired product is lowered *relative* to the free energy for formation of the undesired product by either catalysis (Fig 13.3b) or inhibition (Fig 13.3c).[23]

As specific photochemical exemplars of the situations in Fig. 13.3, let us consider a competition between Type I α-cleavage and Type II intramolecular hydrogen atom abstraction (Scheme 13.3) from an excited state (*R). Both are unimolecular processes. However, the Type II reaction produces an I(BR) and has a stringent requirement that the γ-hydrogen required for abstraction be available through a conformation that places the C—H bond at the proper orientation relative to the half-filled n-orbital of the n,π^* state of *R. On the other hand, the Type I reaction produces an I(RP) and only requires the overlap of the bond connecting the carbonyl carbon to the α-carbon with the half-filled n-orbital of the n,π^* state of *R. The latter primary photochemical process does not depend significantly on the conformation of the *R side chain. Since the conformational equilibrium is rapid in solution one can assume both processes would occur with comparable efficiency. The situation shown in Scheme 13.3 can be considered in terms of the modified energy diagram shown in Fig. 13.4. Here P_1 and P_2 of the primary photochemical step are in fact intermediates I_1 and I_2. Consider the energy diagram in Scheme 13.3 and compare it with that in Fig. 13.3a, where the situation shown is such that the energy of activation for both Type I, *R $\rightarrow$ I(RP), and Type II, *R $\rightarrow$ I(BR), processes are essentially the same, so that the rate of formation of Type I and Type II products are comparable, (i.e., $\Delta G_1^{\ddagger} = \Delta G_2^{\ddagger}$ and $k_{\mathrm{I}} \sim k_{\mathrm{II}}$).

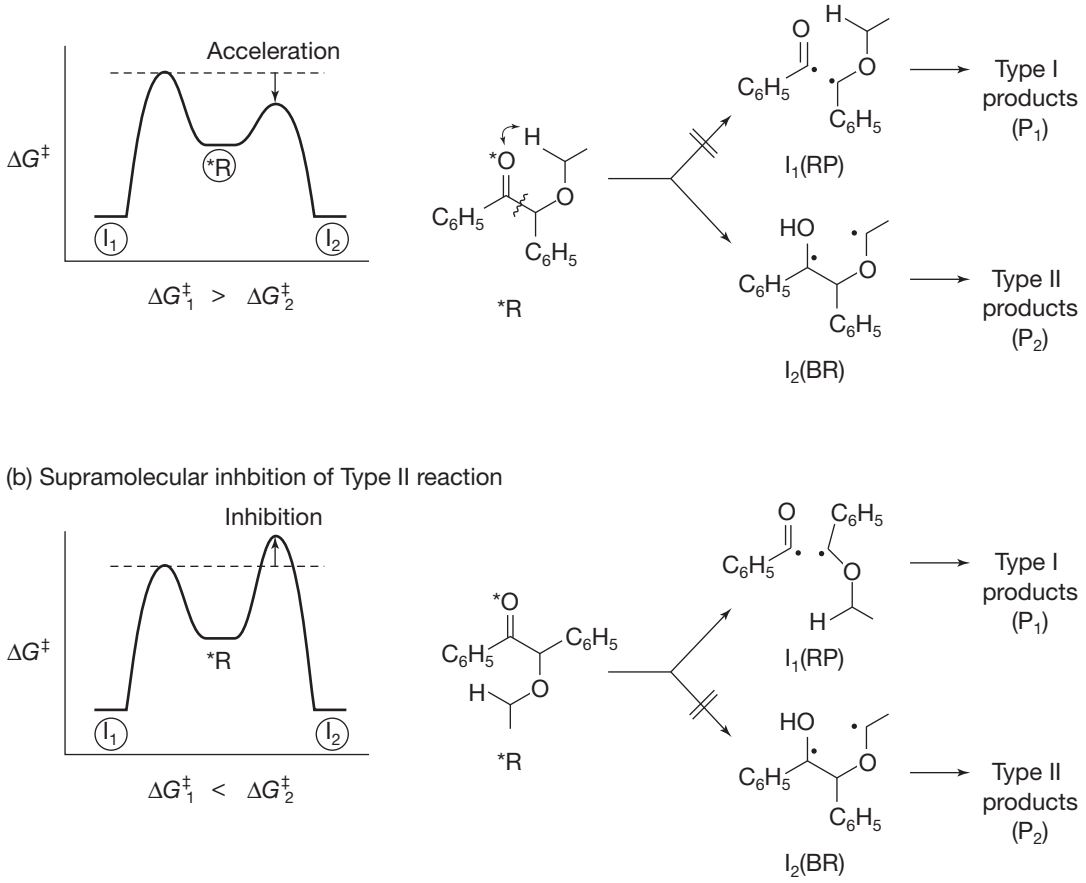


Figure 13.4 Effect of supramolecular conformational on Type I and Type II reactions. (a) The Type II reaction is catalyzed so that $\Delta G_1^{\ddagger} > \Delta G_2^{\ddagger}$; (b) The Type II reaction is inhibited so that $\Delta G_1^{\ddagger} < \Delta G_2^{\ddagger}$.

Thus, a strategy for favoring Type I over Type II products is to design *R@host complexes for which the conformation of the side chain places the γ-hydrogen at a distance far removed from the carbonyl oxygen in the n,π^* state of *R. In Fig. 13.4a (cf. Fig. 13.3), the supramolecular guest@host complex is imagined to favor, through preorganization, a conformation that brings the γ-H into the proximity of the n-orbital and "catalyzes supramolecularly" the rate of the *R $\rightarrow$ I(BR) process without significantly affecting the rate of the *R $\rightarrow$ I(RP) process. This favors the formation of the I(BR) and Type II products (P_2) over the formation of I(RP) and the Type I products (P_1). In Fig. 13.4b (cf. Fig. 13.3), the supramolecular host is imagined to favor, through preorganization, a conformation that places γ-hydrogen at a distant location from the n-orbital and "inhibits supramolecularly" the rate of the *R $\rightarrow$ I(BR) process. Such an inhibition favors the formation of the RP and Type I products (P_1) over the formation of the BR and the Type II products (P_2).

13.5 Extending Some of the Key Structural and Dynamic Features of guest@enzyme Complex to Organic guest@host Complexes. The Host Reaction Cavity Concept

A guest@host chemical reaction is viewed in the same mechanistic terms as reactions of the guest in ordinary molecular solvents. However, in the mechanism of guest@host reactions, the reactions of the guest can be controlled to a certain extent by the host, as we have seen in the examples in the previous section. The host control of the guest chemistry depends critically on the chemical structure of the host "cavity" that binds the guest, the dynamics of the guest in the cavity, and the dynamics of guest complexation (the rates of entry and exit of the guest from the guest@host complex). The cavity structure of the host is represented in a general and nonspecific manner by the circle around the guest in Scheme 13.1. The critical features of the cavity are related to its ability to preorganize the guest in a manner that either catalyzes or inhibits certain reaction pathways (Figs. 13.3 and 13.4). These structural features can be geometric, chemical, or physical. For example, size and shape are geometric features of a cavity. Another equally important geometric feature is the size and shape of portals that allow access to the host cavity. The fluidity and flexibility that a guest experiences in a cavity are physical features of the cavity. The critical chemical features of the cavity are the existence of chemically active groups that can operate on the chemistry of the guest in the guest@host complex.

We can compare the cavity of a supramolecular host to the cage around a solute in an isotropic solution of a small molecular solvent (e.g., benzene, acetonitrile, water). The solvent cage is very fluid and flexible. Consequently, its dimensions, size, and shape change with time and are therefore not well defined. Solvent molecules can be easily displaced, so that size matching of the reactant, products, and the reaction cavity generally requires very small activation energy on the order of kT. For example, larger molecules can use their thermal energy to just "push solvent" around so that the fluid solvent cage easily adjusts to "fit" around the molecule in the solvent cage. On the other hand, when the reaction cavity of a host possesses a well-defined molecularly rigid boundary, size and shape matching with the guest will become important and may even become the main factor controlling the feasibility of a reaction. A micelle resembles a solvent cage in that a hydrophobic guest can be considered to be "imbibed" in an oil droplet that is surrounded by water.

For example, consider the effect of size and shape dimensions on product formation for a molecularly inflexible (rigid) host cavity. In considering the space available in the host's cavity, the notion of "free space" is a useful concept (Fig. 13.5).[26] Whether a particular reaction is catalyzed or inhibited in such a cavity will depend on how the possible intermediates (I_1 and I_2) and products (P_1 and P_2) fit within the available space (including free space) provided by the host's cavity for occupancy by the guest reactant. It is important to note that geometrical features of free space are measured in terms of free volume. Free space, which describes size and shape, has more meaning than a free volume; for example, the free space could be chiral or achiral. There is free space between two molecules when the distance between them is greater than the

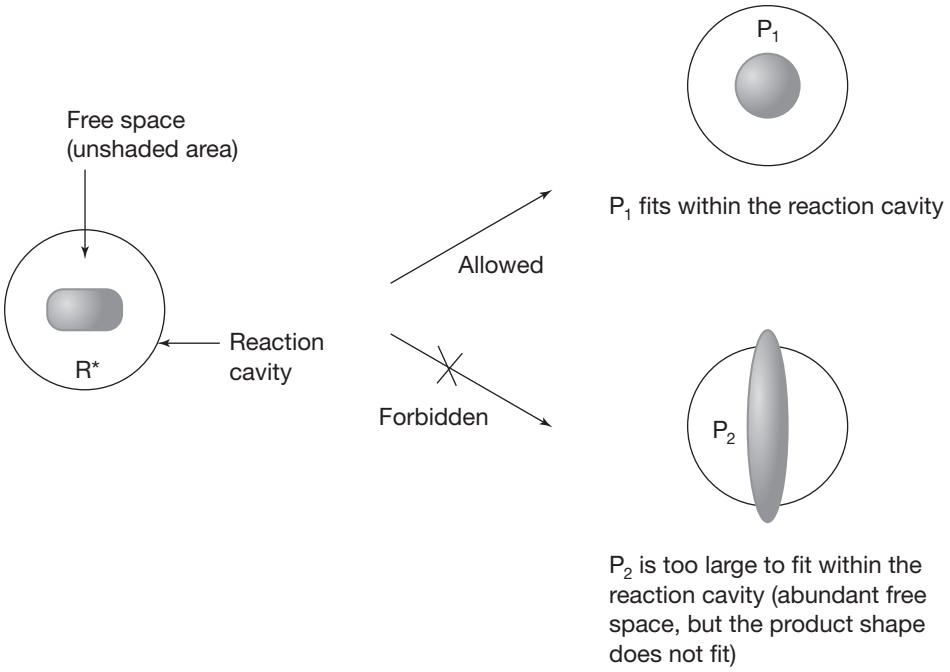


Figure 13.5 Schematic representation of the free space available in a guest@host complex and its effect on product formation. The shape of P_1 "allows" the reaction to proceed without supramolecular steric hindrance. The shape of P_2 "forbids" the reaction to proceed due to steric hindrance.

sum of their van der Waals diameters. Thus, the reaction cavity of a host is defined as the sum of space occupied by the guest in terms of its van der Waals size plus any available free space surrounding it within a host. A certain amount of free space is always present around a molecule in a guest@host assembly. The extent of available free space in a guest@host complex depends on the size and shapes of the host and guest.

The host reaction cavity concept emphasizes the size and shape changes that occur as the reactant guest is transformed into the product and how this phenomenon is commensurate or not with the available space of the reaction cavity.[27–31] For example, the reaction cavity, particularly as applied to guest@host complexes in water, possesses the following features:

1. A reaction cavity is a space in the host with noncovalent valences that can bind to a guest (Fig. 13.2).
2. The binding of the guest to the reaction cavity reduces the diffusional and rotational mobility of the guest molecules and provides a boundary (e.g., a hydrophilic–hydrophobic boundary in an aqueous solvent) across which the guest molecules (R, *R, I, and P) may not cross without overcoming an energy barrier.

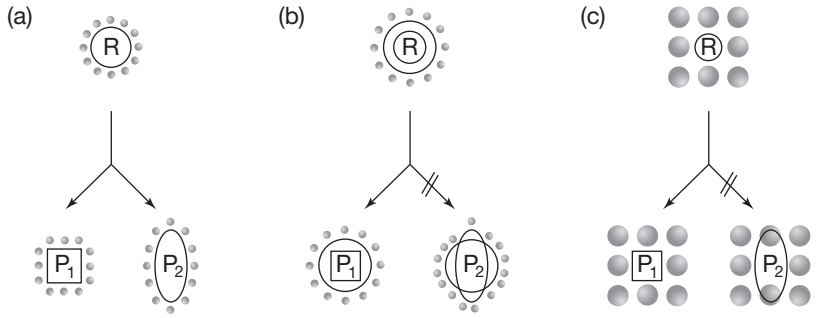


Figure 13.6 Examples of the effects of reaction cavity of a guest@host complex on product formation. (a) A fluid host reaction space that can easily adjust to surround a guest (e.g., solvent cage, micelles). (b) A relatively rigid cavity of a solution guest@host complex surrounded by solvent (e.g., cyclodextrins, zeolites). (c) A rigid cavity of a crystal guest@host cavity. In (b) and (c) P_2 is disfavored because of strong supramolecular steric hindrance.

3. The free space within a reaction cavity relative to the size and shape of the guest is an important parameter: The complementary guest and host shape, size, location, directionality, and dynamics control in large part the extent to which the host can influence a photoreaction (Fig. 13.5).
4. The size, shape, fluidity, flexibility, and rigidity of reaction cavities vary among various supramolecular assemblies (Fig. 13.6).
5. When the atoms–molecules constituting the walls of the reaction cavity are stationary and relatively rigid (possess time-independent positions on the time scale of the guest reaction, e.g., solids or crystals), the space necessary to allow the conversion of a guest molecule to its photoproducts must be built into the reaction cavity (e.g., zeolites). On the other hand, in systems where the walls of the host are relatively flexible (e.g., micelles), the space may adjust during the course of a reaction. For such media, the space of a reaction cavity is modified by structural fluctuations of the medium and cannot be readily represented by static molecular models (Fig. 13.6).
6. The reaction cavity may contain or be associated with specific functional groups or atoms that may interact strongly (attractively or repulsively) with guest molecules, the transition state or the intermediates as the guest proceeds to products (Fig. 13.2). Such specific interactions may lead to unique product selectivity and enhance or decrease the relative rates of primary and secondary processes and the quantum yields for reactions (Fig. 13.7).
7. The functional groups may exist as a coguest (CG) in the reaction cavity or within the exterior boundary of the cavity, but bound to the boundary by noncovalent bonds. In Fig. 13.8, CG could represent a molecule or an ion. Weak and directional bonds between CG and the guest (R, R*, and I) can significantly impact the course of photoreactions (Fig. 13.8).

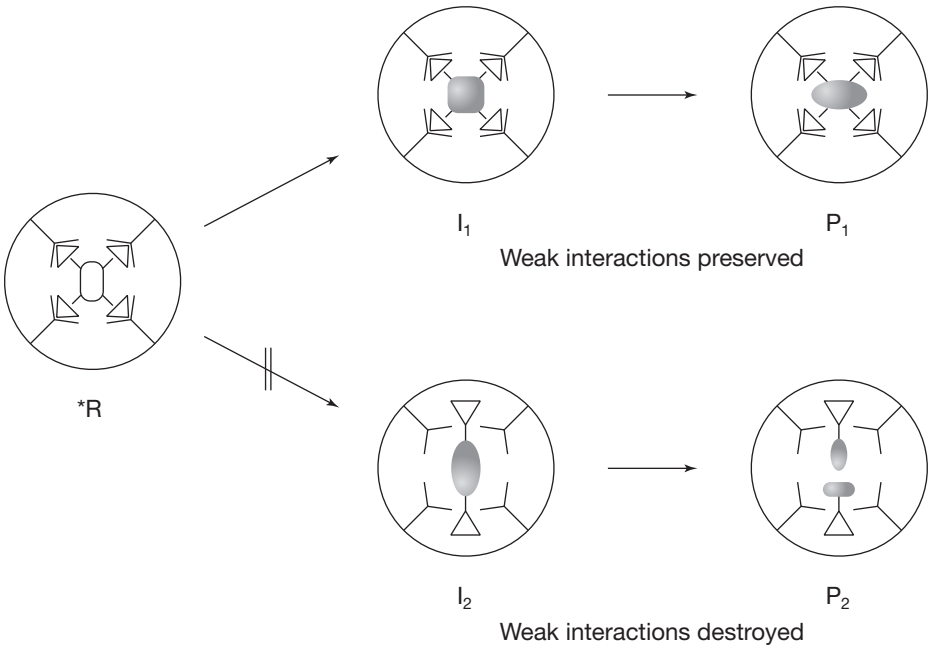


Figure 13.7 Schematic representation of favorable bonding interactions preserved during the formation of P_1, but destroyed during the formation of P_2.

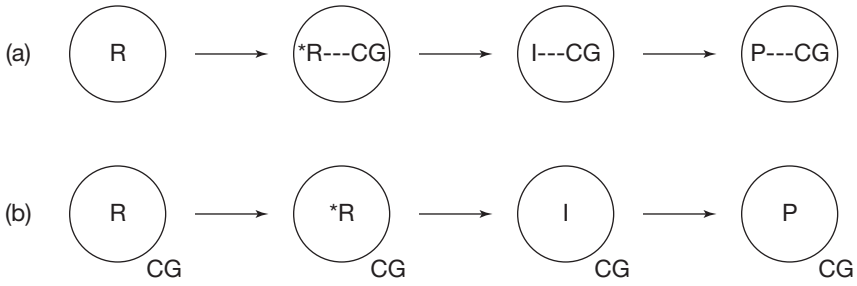
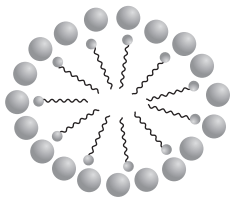
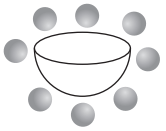
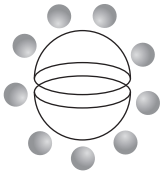
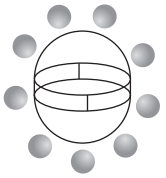


Figure 13.8 Schematic representation of two supramolecular preorganizations that can control the course of a photoreaction. (a) A coguest (CG) resides in the same cavity as *R. (b) A coguest resides outside the cavity, but is bound to it by noncovalent attractions.

13.6 Some Exemplar Organic Hosts for Aqueous Solution Supramolecular Photochemistry: Supercages, Cavitands, and Capsules

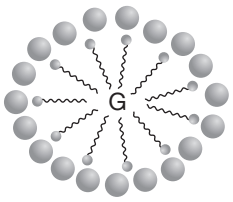
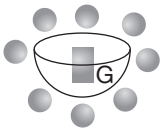
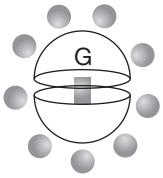
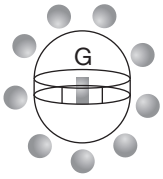
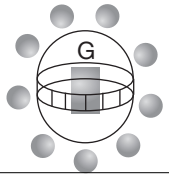
From the descriptions of supramolecular reactions presented in Sections 13.4 and 13.5, one may conclude that selectivity in photochemical reactions could be achieved if a "reaction cavity" of a host resembling that of an enzyme could be synthesized in

Table 13.1 Nomenclature, Characteristics, and Cartoon Representations of Various Hosts in Solution

Name of Host	Definition (Refers to the Host)	Schematic Structure (Large Spheres Represent Solvent)
Micelle	An assembly of small molecules, held together by noncovalent bonding that can completely surround a small guest molecule. Examples: sodium dodecyl sulfate (SDS), hexadecyl trimethyl ammonium chloride (HDTCl) (Sections 13.16 and 13.21)	
Cavitand	A molecule possessing a structurally intrinsic permanent cavity that can contain a small guest molecule by partially surrounding it. Examples: cyclodextrins (CDs) and cucurbiturils (CBs) (Sections 13.10 and 13.16)	
Capsule	An assembly of two cavitands that can structurally organize noncovalently to completely surround a small molecule. Examples: CD and octa acid (OA) (Sections 13.10, 13.11, 13.14, and 13.16)	
Carcerand and Hemicarcerand	A molecule possessing a structurally intrinsic permanent cavity that can completely surround, and thereby incarcerate, a small guest molecule. The cavity may possess portals through which guests may enter or exit the cavity. If the guest is unable to exit or enter through the portals during the relevant photochemical process the host is considered a *carcerand*. If the guest is able to exit or enter through the portals during the relevant photochemical process the host is considered a *hemicarcerand*. Examples: Cram's carcerand, supercages in faujasite (FAU) and pentasil (MFI) zeolites (Sections 13.10–13.12, 13.14, 13.20, and 13.22)	

the laboratory. Although the reaction cavity provided by an enzyme has not been duplicated in the laboratory, the reaction cavities more confined, ordered, and organized than the one offered by an isotropic solution of a small solvent molecules have nevertheless been exploited to achieve selectivity in photochemical reactions mimicking the thermal reactions of enzymes.[32–45] Hosts and guest@host complexes in aqueous solution that we discuss in this chapter are summarized in Tables 13.1 and 13.2. The

Table 13.2 Nomenclature, Characteristics and Cartoon Representations of Various guest@host Complexes in Solution

Name of guest@host Complex	Definition (Refers to Solution)	Schematic Structure (Large Spheres Represent Solvent)
Micelleplex	Guest@micelle complex. Examples: DBK@SDS (DBK = dibenzyl ketone), cylopentenone@deconate	
Cavitandplex	Guest@cavitand complex. Examples: cinnamic acid@CB	
Capsuleplex (Hemicapsulplex)	Guest@capsule complex. Examples: DBK@OA_2, anthracene$_2$@OA_2	
Hemicarceplex	Guest@carcerand complex (portals are large enough for guests to exit (ex) or enter the host cavity). $k_{ex} > k_{photo}$ Examples: biacetyl@Cram's carcerand	
Carceplex	Guest@carcerand complex (portals are too small for guest to exit or enter the host cavity). $k_{ex} < k_{photo}$ Examples: cyclobutadiene@Cram's carcerand	

names in the tables are arbitrary and intended only to be useful by suggesting certain supramolecular features of the host or the guest@host complexes without getting entangled in nomenclature. Many more hosts have been exploited, but the examples presented here amply illustrate the phenomena. For simplicity and convenience, the guest@host complexes can be classified into two groups: (1) complexes that exist as stable species in homogeneous solvents, of which water is the most important, and (2) complexes that exist as stable species in the solid state. In this section, we consider guest@host complexes in aqueous solution and will focus on a few selected systems. First, we describe the properties of several exemplar hosts that have been employed widely and have shown considerable scope in supramolecular photochemistry. Then

we go on to show how the molecular photochemistry and photophysics of organic molecules are controlled by the structure and dynamics of the guest@host complex.

Furthermore, we consider two families of supramolecular host supercages in solution: (1) supramolecular assemblies of small molecules that aggregate in solution to form a host for one or more guest molecules and (2) a large single molecule (or an assembly of two or several large molecules) with a cavity capable of binding to one or more guest molecules. Schematic representations of these two families are shown in Tables 13.1 and 13.2. For aqueous solvents, it is important to always keep in mind that water as a solvent has some very special properties because of its cohesive nature due to hydrogen bonds and to the strength and organization of these hydrogen bonds. In the same way that simply looking at a molecular structure is insufficient to understand supramolecular effects, considering the supramolecular guest@host structure alone may also be insufficient to understand chemistry in water. In Tables 13.1 and 13.2, the spheres represent solvent molecules and G represents a guest molecule in a guest@host complex. We use the term "supercage" to distinguish the characteristics of the space that surrounds a guest in guest@host complex with respect to that in a small molecule solvent. The cage surrounding the guest in an organic solvent is fluid (solvent cage). In micelles, though flexible, the supercage is more restrictive than in organic solvents. In solids, such as crystals and zeolites, the supercage is rigid and more restrictive than in micelles. Table 13.2 shows schematically a variety of guest@host complexes in which photoreactions have been conducted in solution; these complexes provide the potential for different extents of selectivity for the photochemistry or photophysics of *R. Names are provided to characterize structures in a manner that suggests the dominant features of the host as a molecular container and of the guest@host complexes that are formed.

As an illustration of polymolecular assembly of small molecules that form a supramolecular host, we will consider as an exemplar the micelles (Table 13.1) formed in water with SDS molecules shown in Fig. 13.9. The molecular structure of SDS (Fig. 13.9) consists of a hydrophobic hydrocarbon "tail," $-(CH_2)_{11}CH_3$, and a hydrophilic negatively charged "head" group, (SO_4^-) typical of compounds called surfactants.[46,47] In aqueous solution, near a critical concentration [8×10^{-3} M; critical micelle concentration (CMC)], spontaneous SDS molecules abruptly and spontaneously aggregate to form micelles. The roughly spherical structure of the micelle is composed of $\sim$ 60 SDS molecules with a diameter of $\sim$ 2–3 nm (20–30 Å). The "core" of the micelle is a hydrophobic supercage that can absorb hydrophobic organic molecules that are not soluble in bulk aqueous solution.

A micelle can be conceptualized as a special type of solvent cage, consisting of a self-assembly of molecules that behave as a fluid "supercage" and can serve as a host to hydrophobic organic molecules. In this case, the host "cavity" is considered to be a liquid hydrophobic space in water created by the micelle and is represented as a circle (Scheme 13.1) with several surfactant structures included to signify that the circle represents the supercage of a micelle (Fig. 13.9). An important feature of an SDS micelle is that it is fluid-like. As a fluid, its shape and size are not fixed, but can expand by adding more SDS molecules as the supercage absorbs and solubilizes hydrophobic organic molecules. In a truly supramolecular fashion, the hydrophobic organic guest

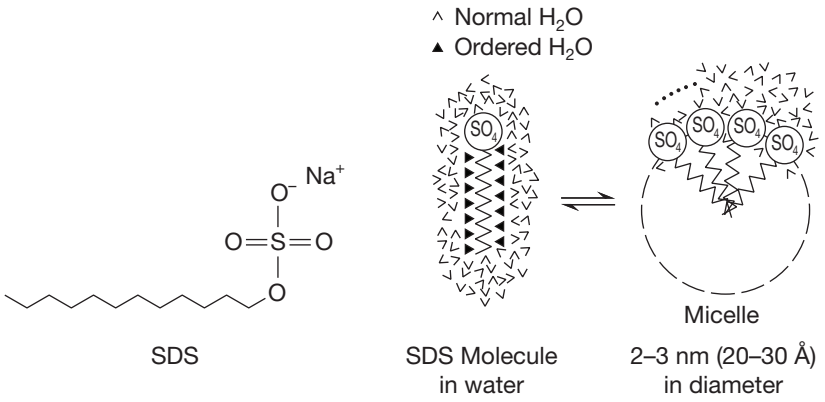


Figure 13.9 Schematic representation of an SDS molecule surrounded by water (left) and an SDS micelle surrounded by water (middle) and SDS molecules forming a spherical micelle.

molecule in the guest@SDS micelle complex can contribute to the stability of the hydrophobic supercage of the SDS micelle through noncovalent interactions with the surfactant molecules of the micelle. The guest@SDS complex behaves as an independent supramolecular unit for which the properties of the guest and host operate together and cooperatively. Micelles of structure, as described above (Fig. 13.9), are formed by a number of surfactant molecules, (cetyltrimethyl ammonium halide, sodium dodecanoate, sodium cholate, etc.).

An included hydrophobic organic molecule in a guest@SDS micelle complex, although in a bulk aqueous medium, is solubilized as a guest in a hydrophobic cavity provided by the micelle. However, significant quantitative and qualitative differences between a cage of nonviscous solvent and the supercage of an SDS micelle exist. For example, a guest diffuses out of a solvent cage of a nonviscous solvent in a few picoseconds; in a bulk solvent, the guest's translational motion is unlimited and its rotational motion is relatively unhindered. The time that an organic molecule in a guest@SDS complex spends in an SDS micelle depends on the hydrophobicity of the guest molecule. The more hydrophobic the molecule, the longer it stays in the micellar cavity. Alternatively, a hydrophobic organic molecule prefers to stay in the hydrophobic core of the micelle and is slow to exit to the aqueous phase. Rather than the few picoseconds dwelling time, an organic molecule, depending on its hydrophobic character, can reside in a micelle supercage for many thousands or millions of picoseconds! This greater residence time, as seen in Section 13.21, can have significant effects on the photochemistry of geminate radical pairs (Scheme 13.2f), produced by the Type I photoreaction in SDS and other related micellar structures.

Now, let us consider a different kind of host that is termed a "cavitand" (Table 13.1). A cavitand is defined as a *single* molecule with an intrinsic concave cavity that persists in solution. The concave cavity of a cavitand possesses polyvalences suitable for noncovalent binding of one or more guests. Thus, a cavitand may be viewed as a molecular container with a *preorganized*, structurally enforced, and permanent

concave internal surface that serves as a molecular free space for binding one or more guest molecules whose convex size and shape complement the concave shape of the cavitand. We will use the term cavitand in a very general sense to apply to molecules possessing a *bowl-shaped* concave cavity (with one or two openings) whose size and shape allow it to be a host to small organic molecules (Table 13.1). Cavitands are held together by strong, directional covalent bonds. As a result, they can only undergo minor conformational changes upon binding to guests. Thus, cavitands are flexible to a minor extent and possess relatively "hard" and solid-like reaction cavities. As a result, the size and shape of the reaction cavity of a cavitand does not change significantly during the binding of a guest or during the course of a reaction, in contrast to the soft and liquid-like cavities of micelles. A cavitand may be represented schematically as a bowl-shaped cavity or a cylinder with two openings, as shown in Table 13.1. A complex of a guest with a cavitand is known as *cavitandplex,* where the guest is partially exposed to solvent water and partially in the bowl of the cavitand host.

There are several water-soluble cavitands that are commonly used as reaction hosts for controlling supramolecular photoreactions.[48,49] Of these, we use CDs, CBs, and OA that bear very similar geometric structural features and we use them as exemplars for bowl-shaped water-soluble hosts (Figs. 13.10 and 13.11). There are several commonly available cyclodextrins (CDs) (known as α, β, and γ) whose major cavity opening termed portal (Fig. 13.11) varies from ~ 5 Å (α-CD) to ~ 6.4 Å (β-CD) to ~ 8.3 Å (γ-CD).[50,51] The size of the portal determines the size of molecules

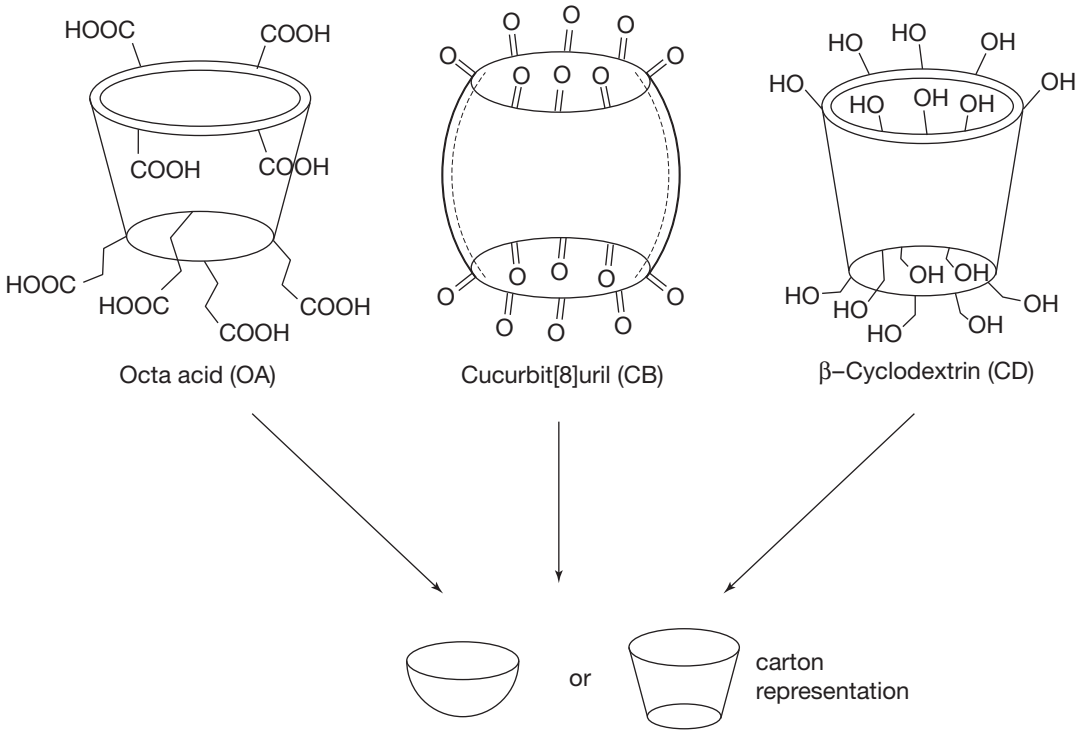


Figure 13.10 Schematic bowl-shaped representations of CD, CB, and OA (n = number). Note the polar groups at the portals of the hydrophobic cavities of the cavitands.

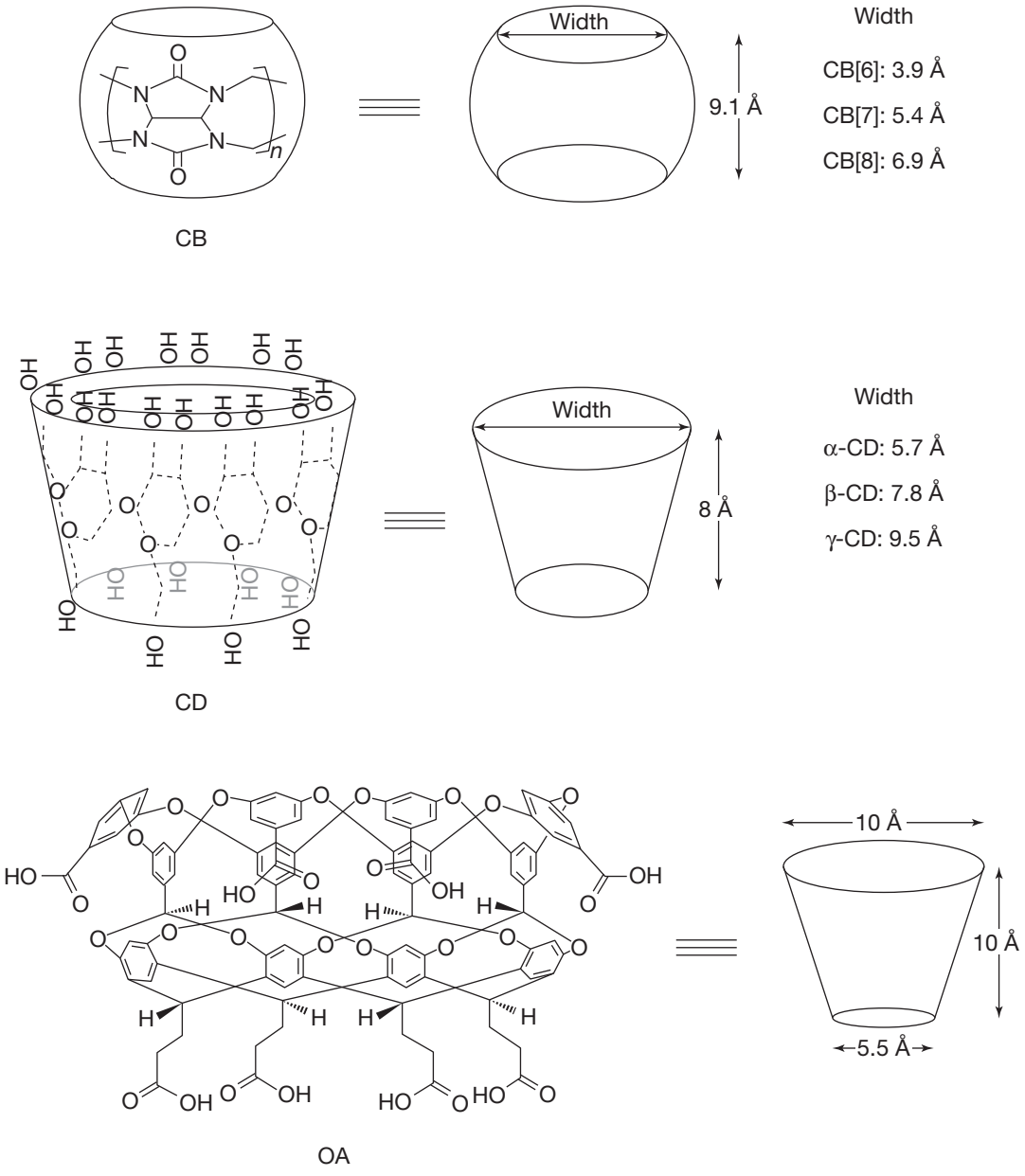


Figure 13.11 Structures and dimensions of CB, CD, and OA. Dimensions include van der Walls radius.

that can enter and be adsorbed in the cavity. Cucurbiturils (CBs) with different sizes are easily synthesized.[52,53] Cucurbituril portals (Fig. 13.10) are lined with polar carbonyl groups, whereas those of CDs are lined with polar hydroxyl groups. Similar to CDs, CBs, e.g., CB[6], CB[7], and CB[8], respectively, also exist in various sizes of the cavity. Octa acid, which has a structure similar to CD and CB, has four COOH groups at each of the top and bottom portals of $\sim$ 10 Å and 5.5 Å, respectively.[54] All three hosts are water soluble and capable of solubilizing in their hydrophobic cavities, hydrophobic organic molecules that are insoluble in water. Because the water only

"sees" the hydrophilic exterior of these cavitands, hydrophobic molecules may be solubilized as guest@cavitand complexes in aqueous solution.

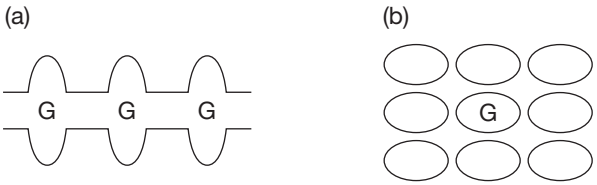
In aqueous solutions, the guests in the 1:1 guest@CD, guest@CB, or guest@OA complexes are surrounded partially by the cavity of the host and partially by the solvent water; such complexes are termed cavitandplexes (Table 13.2). In some cases, a 1:2 guest@$(CD)_2$ or 2:2 $[guest]_2$@$(CD)_2$ complex may form where the guest is encapsulated by the two bowl-shaped molecules of CD aligned one above the other by their wider portals and the complex itself is completely surrounded by water. Under such circumstances, the two cavitands are said to form a "capsule" that surrounds the guest(s). The entire 1:2 guest@$(CD)_2$ or 2:2 $[guest]_2$@$(CD)_2$ complexes is termed a capsuleplex. In general, OA with COOH at the portals prefers to form a closed capsuleplex rather than a cavitandplex. Dipolar repulsion between the carbonyl groups at the portals strongly inhibits capsule formation in CBs. Depending on the dynamics of the capsule, the capsuleplex could have the properties of either hemicarceplex or carceplex. If the guest is able to escape during the time scale of photoreaction, it would be termed a hemicarceplex; if not, it would be termed a carceplex (Section 13.8). These terms are intended to be a qualitative descriptive, and therefore useful to categorize and characterize the qualitative features of a wide range of supramolecular host and guest@host complexes.

Enzymes operate in an aqueous environment where hydrophobic bonding (driven mostly by entropic factors, e.g., such as release of cavity-held water molecules and gain of freedom for water molecules surrounding the guest) plays an important role in encouraging the water insoluble substrate to bind to the hydrophobic pockets of an enzyme. A similar effect operates during complexation of organic guests with micellar, capsule, and cavitand hosts in water (Fig. 13.9). Upon entry of the guest into the host cavity, weak intermolecular forces, such as van der Waals, hydrogen bonding, C—H---π and π---π interactions (Fig. 13.1) in addition to the hydrophobic bonding hold the guest in.

As with all supramolecular systems, the above guest@host complexes are held together only by weak noncovalent intermolecular forces; hence, at equilibrium they are labile in nature and within a certain time scale undergo reversible dissociation. When dissociation occurs, the guest is very weakly bound and can rapidly escape into the bulk aqueous media. However, if the two halves of the host cavitands are covalently linked, a carcerand Table 13.1 composed of a single molecule is created. In such a carcerand, there is internal free space available for occupancy by guests that can pass through the portals provided by the covalent linkages. Such examples are discussed in Section 13.22.

13.7 Some Exemplar Hosts of Supramolecular Photochemistry in the Solid State: Crystals and Porous Solids

The concept of a molecular host for small organic molecules in solution can be extended to solid hosts. On first consideration, it may seem that solids would not be particularly suitable as supramolecular hosts, as one might envision very little free



Scheme 13.4 Schematic representation of guest@host complexes in solids: (a) guest@zeolite and (b) guest@crystal. In the latter, each molecule can be viewed as a guest, surrounded completely by other molecules of the same structure that serve as a rigid "supercage."

space, causing crystals to be too rigid for the molecular motion required to make and break bonds, especially in bimolecular reactions. However, many organic crystals and porous inorganic solids have been shown to be particularly useful hosts for controlling a range of supramolecular photochemical and photophysical processes.[55–59] Scheme 13.4 shows schematically the structure guest@host complexes in crystalline porous solids (a) and in organic crystals (b). We will consider zeolites as an exemplar of inorganic supramolecular porous hosts. Several exemplars of organic crystal hosts will also be described.

Silica (SiO_2) is a well-known porous inorganic solid capable of adsorbing and noncovalently bonding to organic molecules (as in chromatography). Although silica is a macroscopic solid, it possesses a huge internal porous void space capable of adsorbing organic molecules. The walls of the pores are made of very strong and rigid O—Si—O bonds; the oxygen atoms are tetrahedrally arranged around each Si atom. Zeolites are *crystalline* materials that are related to silica where an aluminum atom is substituted for a fraction of the tetrahedral sites of pure silica.[55] The frameworks of these porous solids thus obtained contain well-defined and uniform empty pores, channels, and cages that can serve as cavities or supercages for organic molecules of the appropriate size and shape. Substitution of trivalent aluminum ions for a fraction of the tetravalent silicon ions at lattice positions results in a network of void space that bears a net negative charge for each aluminum atom. Each of these negative charges in turn must be compensated by a positive counterion (Li^+, Na^+, K^+, etc.). The latter counterions are mobile and may occupy various exchange sites depending on their radius, charge, and degree of hydration. They can be replaced, to varying degrees, by exchange with other cations. Many organic molecules whose sizes are on the order $\sim$ 5–10 Å can be accommodated in the intracrystalline cavities of zeolites.

We describe examples of the supramolecular effects of two families of crystalline zeolites, the so-called FAU and MFI families (Fig. 13.12), on the photochemistry of organic molecules. The topological structure of the FAU family of zeolite consists of an interconnected three-dimensional (3D) network of relatively large spherical cavities termed supercages (diameter of $\sim$ 13 Å; Fig. 13.12a). Each supercage is connected to four other supercages through 8 Å portals that are tetrahedrally arranged about the center of the supercage. The MFI family of zeolites also has a 3D porous

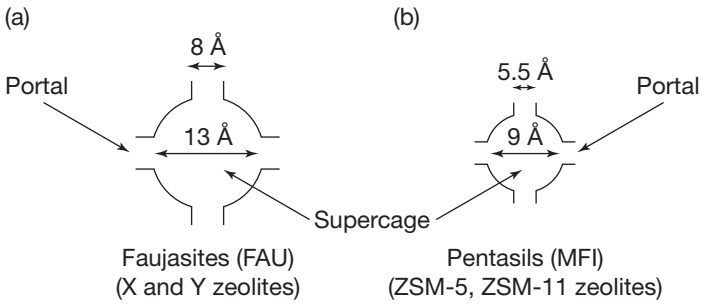


Figure 13.12 Schematic structures of the internal portals of (a) FAU and (b) MFI zeolites.

structure (Fig. 13.12b). The supercages of FAU are essentially directly connected to one another; in the case of the MFI, channels ~ 5.5 Å long exist between the supercages. The intersection of these channels form supercages whose diameter is ~ 9 Å. In summary, both the FAU and MFI zeolites possess portals leading to supercages, with the FAU portals and supercages being somewhat larger than those of MFI. An important feature of zeolites as host is that guest molecules can only access the supercages of the void space by squeezing through the portals leading to the internal surface. Thus, although the supercage of a FAU zeolite possesses a diameter of ~ 13 Å, the portal leading to the supercage is only ~ 8 Å in diameter. A similar situation is found in MFI zeolites as well, where the diameter of the cage and the portals are 9 and 5.5 Å, respectively.

Since zeolites are crystalline materials, the supercages are organized in a regular repeating pattern of supercages in a macroscopically solid material (Scheme 13.4). An important difference between the two families of zeolites is that in contrast to the FAU family, the MFI family possess very little aluminum in their framework, and consequently have very few charge compensating cations in their void space. Thus, the FAU can be considered to have very polar and hydrophilic supercages filled with cations whereas the pentasils have nonpolar and hydrophobic supercages with very few cations.

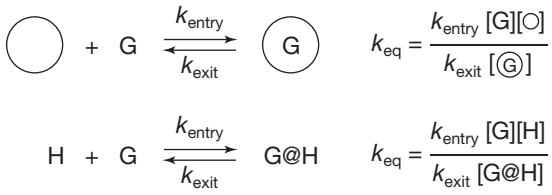
The cations occupying the internal supercages of the FAU zeolite take up some of the free space of the supercage, and therefore provide steric hindrance to guests and species undergoing reaction in the supercage. We will see examples of how the steric effects of cations in a FAU zeolite provide outstanding examples of supramolecular steric effects on the course of photochemical reactions of guest@faujasite complexes.

It is easy to understand that zeolites, porous solids with internal empty supercages, can bind a guest molecule to form guest@zeolite complexes (Scheme 13.4a). But not all solids are porous. For example, most organic crystals are nonporous solids that form by a regular repeated pattern of molecules adjacent to one another and bonded by noncovalent interactions. In organic crystals, however, a collection of molecules called the unit cell is repeated periodically in exactly the same arrangement over and over throughout the entire crystal. In organic crystals, molecules are arranged in an

orderly, geometric, 3D structure (Scheme 13.4b). Unlike other guest@host systems discussed above, the guest and host molecules are the same molecule in a pure crystal. The most important characteristic of crystals is their molecular periodicity and rigidity. In organic crystals, each molecule may be considered as a guest that is surrounded by a host (made up of the same molecule) consisting of a cage of regularly spaced molecules surrounding it. This rigid, solid guest@crystal complex is structurally analogous to, but at the opposite extreme of, the flexible, liquid solvent cage. We will discuss the roles of these features in controlling photoreactions in a crystal.

13.8 The Role of Time Scale and Dynamics in Supramolecular Organic Photochemistry. The Transient and Persistent Supramolecular Complex Concept. Hemicarceplexes and Carceplexes

Supramolecular complexes are formed through association of host (represented by a circle in Scheme 13.5) and guest (represented as G in Scheme 13.5) molecules that are held by weak intermolecular forces. In an overall photochemical reaction G can be a reactant (R), an electronically excited state (*R), an intermediate (I), or a product (P). The strength of these guest@host complexes are measured in terms of an equilibrium constant (K_{eq}) defined in Scheme 13.5. This constant measures the binding strength of guest–host complex.[60] As the structures of R, R*, I, and P differ, their equilibrium constants of complexes with the host are not expected to be identical. To avoid complications from uncomplexed R, R*, I, and P, one needs to establish what fraction of the G molecules are complexed to the host and what fraction is dissolved in the bulk solvent. The value of K_{eq} for the complex depends on the kinetics of complex formation and dissociation (Scheme 13.5). The bimolecular formation rate of the complex is equal to k_{entry}[G][O] and the unimolecular rate of dissociation of the complex is k_{exit}[G@H]. Since formation of a guest@host complex is a bimolecular process the fraction in the guest@host complex can be controlled by the concentration of host molecules. For example, a large excess of the host will favor the formation of the complex. Once the R@host is excited, *R@host is formed and photochemical–photophysical processes are initiated. The extent of the supramolecular host influence



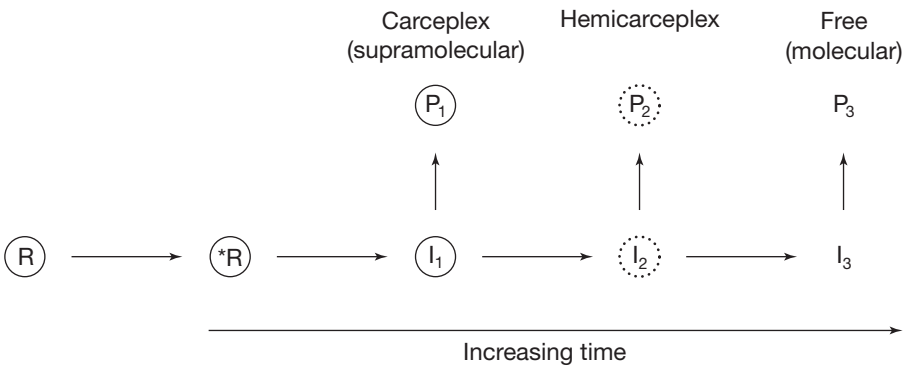
Scheme 13.5 Complexation and decomplexation of guest@host complexes. The circle represents a host.

on the photochemical–photophysical processes depends on the equilibrium constants of R*, I, and P with the host; for the supramolecular influence to be fully effective, the rates of each step in the photochemical reactions and photophysical processes must be faster than the exit rate of G from the complex. In this section, we discuss this phenomenon in terms of the time scale of photochemical–photophysical processes compared to the rate of exit of the guest from the host.[61]

The time scale for common photochemical and photophysical processes spans over 12 orders of magnitude, that is, from $\sim 10^{-12}$ s (vibrational, electronic relaxation, ultrafast photoreactions) to ~ 10 s (long-lived phosphorescence). The dynamics of the assembly and disassembly of a guest@host complex can also span over a wide temporal range of many orders of magnitude. Even the dynamics of host structures can span many orders of magnitude. For example, the supercages of zeolites are essentially infinitely long lived on any achievable time scale since the disruption of the supercage requires breaking strong covalent bonds. On the other extreme, the lifetime of an individual micelle may be a few milliseconds or shorter. We say that the supercage of a zeolite is persistent and the supercage of a micelle is transient on conventional time scales of laboratory measurements (minutes or longer). The terms persistent and transient are relative and we need to refer to a benchmark time scale of interest in a particular experiment.

In photochemistry, the benchmark time scales are the lifetimes of *R and I, species whose inherent dynamics will remove them from the system by chemical reaction or photophysics. Thus, the pertinent benchmark lifetime of an *R@host or I@host complex is the lifetime of either the host or the guest (in this case the guest is either *R or I). For simplicity of presentation of the photochemistry of the supramolecular complexes, we will assume that the host structure is persistent throughout the photochemical steps; that is, the host structure does not change during the lifetime of the reaction. However, we cannot in general assume that the time scale of dissociation of an *R@host or I@host complex will be long relative to the photochemical events of interest; the structure of an *R@host or I@host complex may not be constant during the lifetime of the reaction. For example, the exit rate of *R (or I) from an *R@micelle (or I@micelle) complex may be fast or slow relative to the photochemistry or photophysics of *R (or I) in the complex. Thus, *R@micelle (I@micelle) may be persistent or transient relative to the rates of photochemistry or photophysics.

From the above discussion, we can see that an *R@host complex has meaning as a supramolecular photochemical object during a certain time scale, namely, the lifetime of the *R@host complex itself relative to the time scale of the photochemistry or photophysics of *R in the complex. We will apply the term "carceplex" to *R@host or I@host complexes for which the guest is persistent; that is, it is completely "incarcerated" by the host during the lifetime of a photochemical or photophysical process under investigation (Table 13.2). We will apply the term "hemicarceplex" to *R@host or I@host complexes for which the guest is transient; that is, *R exits from the host during the lifetime of a photochemical or photophysical process under investigation (Table 13.2).



Scheme 13.6 Schematic of the time-dependent conversion of a supramolecular carceplex (full circle) to a supramolecular hemicarceplex (dotted circle) to a molecular system (no circle).

As carceplexes, *R@host and I@host see a single host environment during the photochemical events of interest. In hemicarceplexes, *R@host and I@host witness a range of environments during the photochemical events of interest. These differences in host environments between carceplexes and hemicarceplexes are illustrated below.

Since the lifetime of photochemical and photophysical processes vary over many orders of magnitude, the notions of a persistent carceplex and transient hemicarceplex (partially caged) are relative and not absolute. Accordingly, we modify the circle representation of the host (Scheme 13.1) to accommodate the time-dependent carceplex and hemicarceplex situation: A closed circle represents a persistent carceplex and a dotted circle represents a hemicarceplex (Scheme 13.6). The absence of any type of circle represents guests in the bulk solvent. For example, $^*R(S_1)$@micelle may be persistent (rate of fluorescence faster than the rate of exit from micelle), whereas $^*R(T_1)$@micelle may be transient ($^*R(T_1)$ may exit the micelle and react essentially only when present in solvent).

As an example of the carceplex and hemicarceplex paradigm Scheme 13.6 shows a hypothetical situation for a system that starts with a persistent *R@host carceplex to produce a persistent I_1@host complex that leads to two products: P_1 and a secondary transient I_2@host complex. The latter transient hemicarceplex is visualized to be able to produce a product P_2 or escape to the solvent and produce a third product in the solvent, $I_3 \rightarrow P_3$. A chemical exemplar of this possibility is discussed in Section 13.21.

Thus, we can see that the rate of exit of a guest from a guest@host complex is an important parameter in determining whether a photochemical or photophysical process is best described as molecular, supramolecular, or a combination of the two. An extreme example of how the definition of supramolecular depends on the lifetime of *R can be seen by considering a photochemical reactions that take place on the picosecond or shorter time scale. For such a reaction, an ordinary solvent cage behaves as a carcerand since *R does not leave the host during its lifetime.

13.9 Supramolecular Control of Photochemical and Photophysical Processes: General Principles

What do we mean by a "supramolecular control" of a photochemical reaction? To answer this question, we will integrate the fundamental and familiar paradigm of molecular organic photochemistry (e.g., the R + $h\nu$ → *R → I → P sequence) with the paradigm of supramolecular organic chemistry (guest@host chemistry).

It will be convenient to consider supramolecular control of unimolecular and bimolecular reactions separately. In both cases, the notion of preorganization of the guest(s) by the host will be a critical factor.

For unimolecular reactions:

1. Host (and coguest) *enforced proximity* of functionalities that actively inhibit or accelerate photophysical processes from *R or I. Examples: heavy atom effect in micelles, cyclodextrins, and zeolites. (See Sections 13.10 and 13.13.)
2. Preorganization of the guest molecular structure in a guest@host complex through host *enforced conformation* of the guest that either inhibits or accelerates one of the competing reaction pathways from *R or I (or both). Examples: Type I versus Type II from *R and fragmentation versus cyclization of I(BR). (See Sections 13.14.)
3. Host *enforced constraint* of the translational or rotational motions of *R or I(RP). Examples: control of reactions of geminate RP. (See Sections 13.20 and 13.21.)
4. Influence of the host (and coguest) on the *cavity-free space that is* accessible to *R and I. For example, creation of chiral space that can lead to supramolecular diasteriomeric relationships for I(RP). (See Sections 13.15 and 13.19.)
5. Host and coguest *enforced supramolecular steric effects* that control the free space available to *R and I(RP) in the host cavity. Examples: cage effect on I(RP) for DBK (see Section 13.21).

For bimolecular processes the most common supramolecular effect is host enforced spatial location and relative orientation in space of guest and coguest in the host's cavity that leads to one of the following:

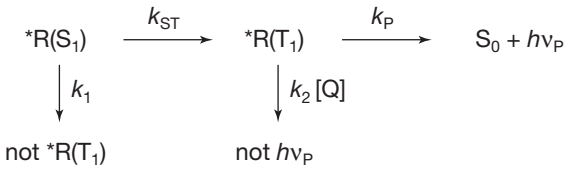
1. An enforced spatial proximity of guest and coguest that leads to a high "effective" local concentration of the coguest that is accessible to *R or to I. Example: excimer formation (see Section 13.11).
2. An enforced spatial separation of guest and coguest that causes protection of *R or I from reagents that are external to the host cavity. Examples: protection of *R from quenching by O_2 and other quenchers, energy transfer (ET), and by electron transfer (et) through walls of host cavity inhibition of I(RP) from radical–radical reactions, and making transient species persistent: radicals, cyclobutadiene (see Sections 13.10 and 13.12).
3. An enforced spatial proximity and selective orientation of *R or I with respect to coguest. Example: [2 + 2] cycloadditions (see Sections 13.16–13.18).

13.10 Supramolecular Control of Unimolecular Photophysical Processes by Preorganization of guest@host Complexes: Enhancement of Room Temperature Phosphorescence

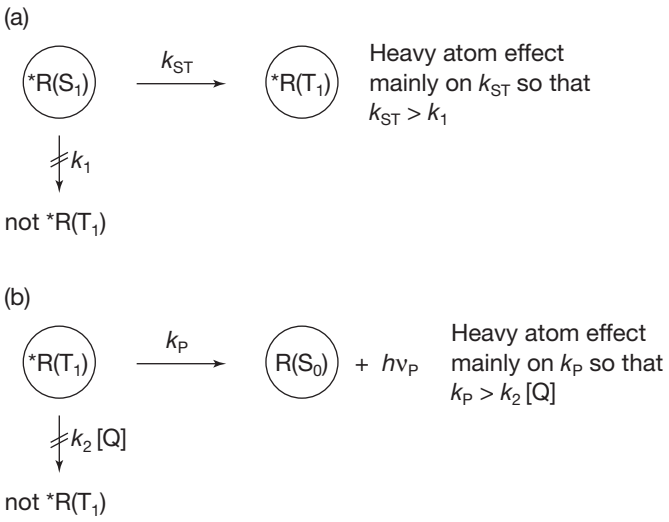
Phosphorescence from aromatic hydrocarbons AH (e.g., naphthalene, phenanthrene) is not observed in fluid solutions for several reasons: (1) The rate constant (k_P) for phosphorescence from $^*R(T_1)$ of aromatic hydrocarbons is extremely small, typically on the order of $1\ s^{-1}$ or less; (2) the $^*R(T_1)$ state of aromatic hydrocarbons is quenched by impurities (Q) at close to the rate of diffusion; (3) the quantum yield of formation of $^*R(T_1)$ from $^*R(S_1)$ for some aromatic hydrocarbons (AH) is low. Impurities (Q) represent any quencher present in the system that competes with phosphorescence, with molecular oxygen from air being the most common and ubiquitous quencher (Section 14.1). Now, we employ a supramolecular preorganization strategy to rationally design guest@host complexes that will exhibit strong phosphorescence from AH guests in solution at room temperature.

Scheme 13.7 shows a general situation for the steps leading to phosphorescence from $^*R(T_1)$. In order to observe a significant quantum yield of phosphorescence from an AH, the following conditions must hold: $k_{ST} > k_1$ and $k_P > k_2[Q]$. A supramolecular strategy for the observation of room temperature phosphorescence would involve designing a AH@host system that makes $k_{ST} > k_1$ and $k_P > k_2[Q]$ (Scheme 13.8).

In Chapter 4, we saw that for molecular systems heavy atoms can enhance the rate of both k_{ST} and k_P. In addition, incarceration of $^*R(T_1)$ in an $^*R(T_1)$@host will inhibit bimolecular quenching by species in the bulk solution. Thus, an $^*R(T_1)$@host complex that preorganizes heavy atoms into the proximity of $^*R(S_1)$ and $^*R(T_1)$ is a candidate for enhancing the observation of phosphorescence of AH at room temperature. Cyclodextrins, micelles, and zeolites are examples of potential hosts that can preorganize heavy atoms into proximity with the $^*R(S_1)$ and $^*R(T_1)$ of an AH. In the case of micelles, the Na^+ ions of SDS can be readily exchanged for heavy cations, such as Tl^+. Thus, a AH@TlDS (thalium dodecyl sulfate) micelle will bring the $^*R(S_1)$ and $^*R(T_1)$ of an AH into proximity of a heavy Tl^+ ion (atomic number $Z = 81$). This supramolecular feature will increase both k_{ST} and k_P. In addition, the incarceration of $^*R(S_1)$ and $^*R(T_1)$ in the micelle supercage will inhibit bimolecular quenching of $^*R(T_1)$ by any potential quenchers in the aqueous phase, especially oxygen. In CDs, the preorganization involves bringing a molecule posessing a heavy atom as a coguest into the same cavity as the AH guest.



Scheme 13.7 Schematic representation of the kinetics of competing pathways on the way to phosphorescence.



Scheme 13.8 Strategy for the supramolecular control of room temperature phosphorescence.

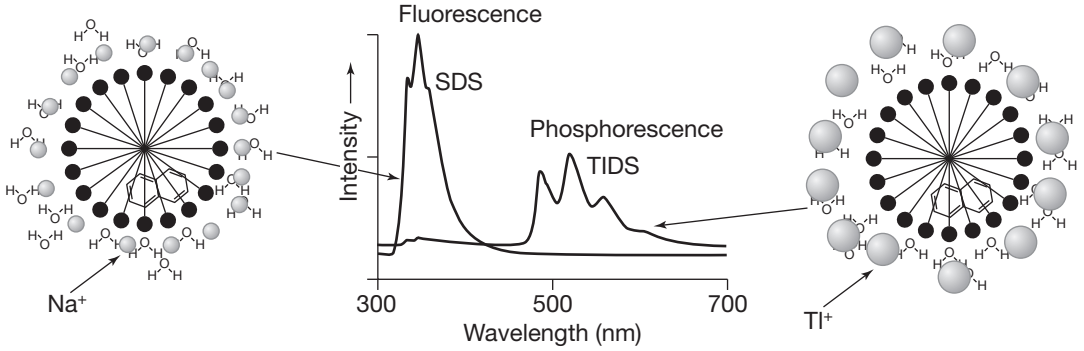


Figure 13.13 Luminescence of naphthalene@SDS and naphthalene@TlDS.

This preorganization strategy has proved successful in a number of cases. An example for naphthalene adsorbed in micelles is shown in Fig. 13.13.[62,63] Although no phosphorescence is observed with naphthalene in aqueous solution, when it is included within a TlDS micelle, a strong phosphorescence ensues.

Cyclodextrins have also proven to be excellent hosts to observe phosphorescence at room temperature when heavy atom containing coguests are absorbed together with an AH. For example, when CDs are used as hosts and brominated coguests (e.g., dibromomethane, 2-bromoethanol) are present, phosphorescence from aromatic molecules, such as phenanthrene, can be readily observed at room temperature in aqueous solutions (Fig. 13.14).[64]

The same strategy as described above for micelle and CD hosts of AH were also used with porous solid FAU zeolites. The supercages of FAU zeolites contain a large number of exchangeable cations. These cations can be considered as coguests that can

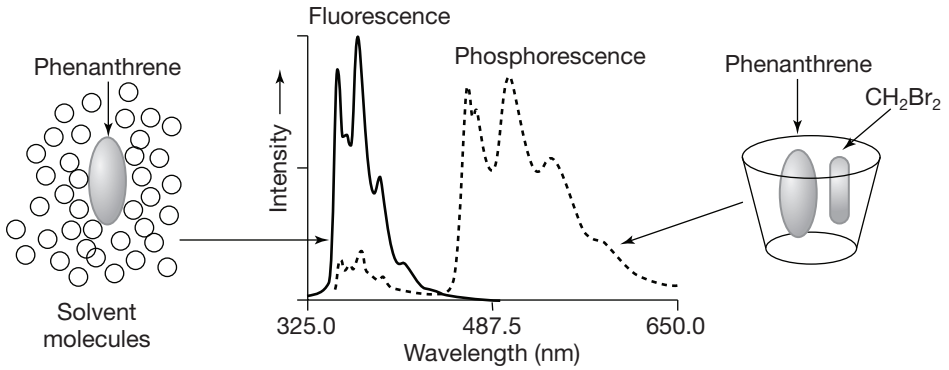


Figure 13.14 Luminescence of phenanthrene@CD in solution in the absence (solid line) and presence of CH_2Br_2 (dashed line). In the latter case, a phenanthrene/CH_2Br_2@CD complex is formed. Cartoon representations of phenanthrene in solution and as a CD complex are shown on the left and right, respectively.

interact with incarcerated guest molecules in the supercages. By careful choice of the cations, one can control the photochemistry of guest (*R and I) that takes place inside the supercage. For example, phosphorescence at room temperature has been observed from a number of AH in a series of heavy atom exchanged AH@zeolites.[65] One of the most important FAUs is the MX zeolite, where M refers to the exchangeable cations of the zeolite and X refers to high Al content in the framework of the zeolite. For example, FAU with M = Na^+ is commonly available. The Na^+ may be exchanged for monovalent heavy ions, such as Rb^+, Cs^+, or Tl^+, to produce RbX, CsX, or TlX. Naphthalene in fluid solution is strongly fluorescent, but nonphosphorescent. When naphthalene is incarcerated in the supercages of LiX, intense fluorescence and only weak phosphorescence are observed from naphthalene@LiX. However, naphthalene@CsX and naphthalene@TlX exhibit intense phosphorescence and very little fluorescence (Fig. 13.15). The correlation of phosphorescence intensity with cation mass (and more fundamentally with atomic number, Z) clearly suggests the

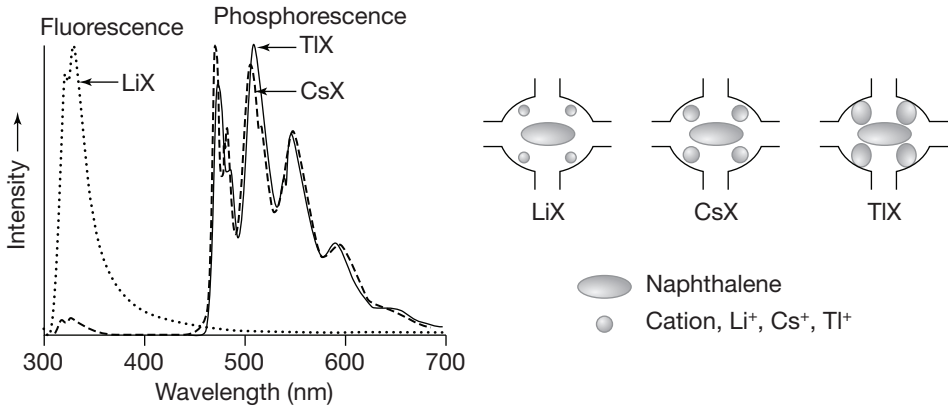


Figure 13.15 Luminescence of naphthalene in FAU zeolites MX as a function of M.

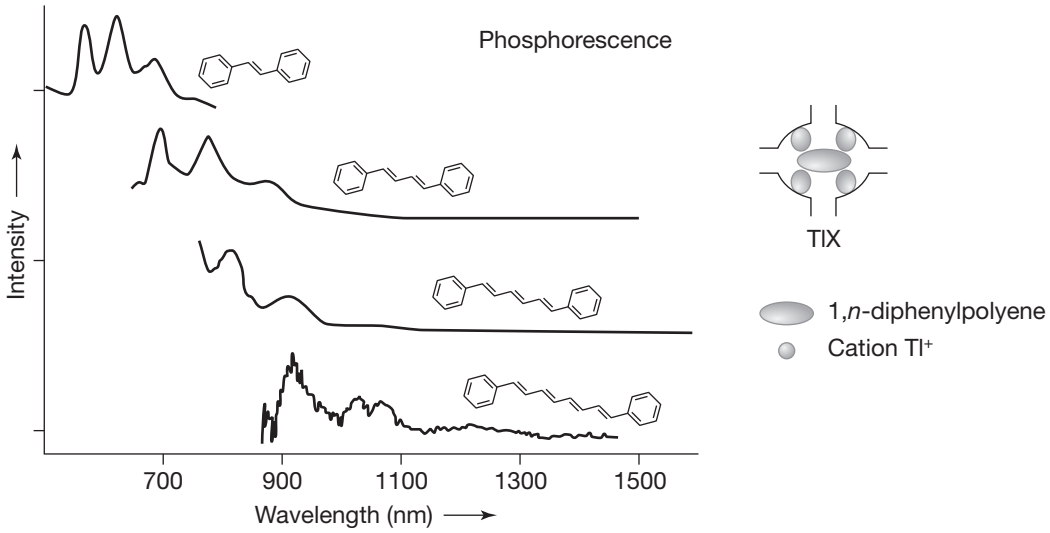


Figure 13.16 Phosphorescence of 1,*n*-diphenylpolyenes@TlX zeolites (n = number).

external heavy atom perturbation strongly increases as one goes from Li ($Z = 3$), Cs ($Z = 55$) through Tl ($Z = 81$).

Polyenes do not phosphoresce significantly, even at low temperature in rigid media, because even if $^*R(T_1)$ is produced, it undergoes rapid twisting motions about C═C bonds (Section 10.5). Hence, the observation of phosphorescence from polyenes (e.g., *trans*-stilbene and 1,6-all-*trans*-diphenylhexatriene) incarcerated within Tl^+ exchanged zeolites is remarkable (Fig. 13.16). The observed phosphorescence is the result of the enforced close proximity between the heavy atom cations and the olefin within a zeolite. In this case, a combination of the heavy atom effect on k_{ST} and k_P, and the constrained twisting motion (e.g., *cis–trans* isomerization) lead to rapid $^*R(T_1)$ deactivation. Intersystem crossing and phosphorescence rates have to compete with other processes, such as *cis–trans* isomerization that deplete the S_1 and T_1 states. Zeolites lower the normally efficient *cis–trans* isomerization process from both S_1 and T_1 states through supramolecular steric hindrance and the heavy cations enhance the k_{ST} and k_P (see Scheme 13.8).

The final example in this category of supramolecular enhancement of phosphorescence deals with phosphorescence of thioketones, molecules analogous to ketones except for the replacement of oxygen by sulfur (Chapter 15). Although these molecules have high values of k_{ST} and k_P, they do not phosphoresce in solution at room temperature, due to quenching by oxygen and by ground-state thioketone molecules (self-quenching) at diffusion controlled rates. No measurable phosphorescence could be observed at a concentration $> 10^{-6}$ M. Once again, the supramolecular approach helps solve this problem.[66] For example, although thiocamphor (Fig. 13.17) shows no phosphorescence in aqueous solution (10^{-4} M), it phosphoresces intensely when encapsulated as a 2:2 complex with OA in water. Though the effective concentration within the complex is 0.35 M, no self-quenching occurs. This phenomenon is

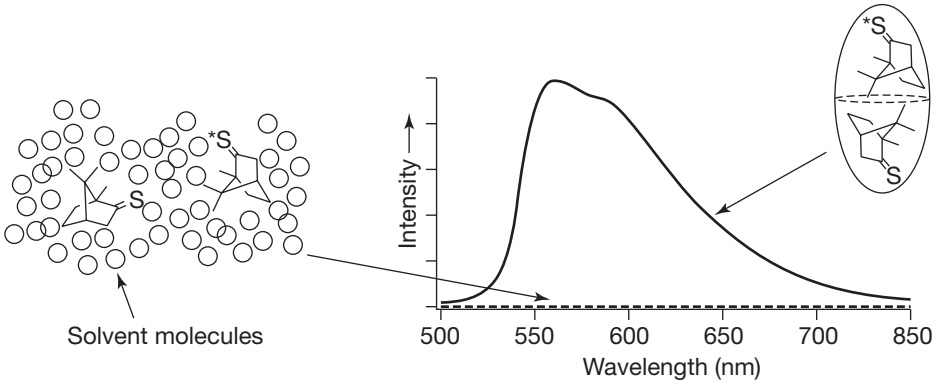


Figure 13.17 Phosphorescence of thiocamphor@OA in water (solid line) and perfluorodimethylcyclohexane solvent (dashed line) at room tempearture. Cartoon representation of thiocamphor in solution and in an OA capsule are shown on the left and right, respectively.

explained as the result of supramolecular preorganization of the two incarcerated thioketones into a relative orientation such that the two C═S groups are situated at a significant distance from one another (Fig. 13.17) and are unable to reorient to the quenching configuration required during the lifetime of *R. Thus self-quenching is eliminated by host enforced preorganization that occurs as a result of guest@host complexation. Furthermore, the thione is also protected by an OA capsule from quenching by oxygen.

13.11 Supramolecular Control of Bimolecular Photophysical Processes by Preorganization of guest@host Complexes: Enhancement of Excimer Formation of *R

In Section 4.38, we learned that excimer formation and emission are observed for certain AHs, such as pyrene. However, in homogeneous solvents other AHs, such as anthracene, do not exhibit significant EX emission even at very high concentration; in the specific case of anthracene, the reason is anthracene undergoes efficient [4 + 4] photocycloaddition that competes favorably with EX emission (Section 12.8). However, the supramolecular preorganization with a coguest strategy provides a means for designing systems that will allow the observation of EX formation for molecules, such as anthracene, that do not exhibit EX emission in homogeneous solvents.

Anthracene and the cavitand OA form a 2:2 capsule, $[\text{anthracene}]_2@[\text{OA}]_2$, soluble in aqueous solution.[67] Figure 13.18 shows a schematic of the structure for this complex. Supramolecular preorganization of two anthracenes in $[\text{anthracene}]_2@[\text{OA}]_2$ compel these anthracene molecules to be organized in an excellent geometry for excimer formation. Indeed, a strong excimer fluorescence is observed upon photoexcitation of $[\text{anthracene}]_2@[\text{OA}]_2$ (Fig. 13.18). But we may now ask, why does the [4 + 4] photocycloaddition reaction not occur in the complex? There are at least two possible supramolecular answers: (1) The orientation in the complex may place the

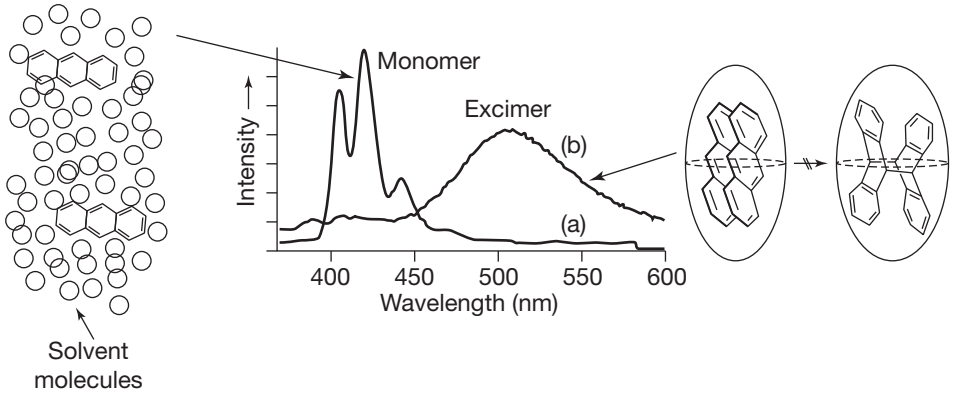


Figure 13.18 Left: (a) Monomer emission from anthracene in aqueous solution. (b) Excimer emission of anthracene in a $[\text{anthracene}]_2@[\text{OA}]_2$ complex. Cartoons on either side of the emission spectra represent possible arrangements of two anthracene molecules in solution (left) and in a 2:2 capsuleplex.

two anthracenes so that the 9,10-positions of the anthracenes are in close enough proximity for excimer formation, but are too far apart for bond formation, and (2) the final product formation is inhibited because it has a geometry that is larger than the space available in the host cavity (Fig. 13.6) causing a barrier to the [4 + 4] reaction. The latter would be an example of a supramolecular steric hindfance to product formation. Thus, application of supramolecular preorganization strategies provides a means for observing the excimer of anthracene, not observed in solutions in which anthracene is highly soluble, to be observed easily in aqueous solution!

The above preorganization strategy extends to solid-state hosts as well. For example, anthracene exhibits excimer emission when adsorbed onto dry NaY zeolite (FAU type zeolite), but monomer emission on coadsorption of water by the zeolite (Fig. 13.19).[68] The interpretation for these results is analogous to the one reported above in solution. In anthracene@(dry)NaY assemblies, cation---π interaction (Fig. 13.19) favors aggregation of two (or more) anthracene molecules in the ground state leading to excimer emission. The importance of cation---π interaction becomes obvious when the zeolites are hydrated and anthracene@(wet)NaY complexes are formed. When sodium ions are hydrated, as would be the case in zeolites impregnated with water, only monomer emission is observed. As indicated in Fig. 13.19, within dry NaY, cation---π interaction attracts two anthracene molecules closeby (favoring excimer formation). When the cation is hydrated with water, the cation---π interaction is replaced by a stonger H_2O---Na^+ noncovalent bond and the two anthracene molecules separate from one another inhibiting excimer formation and favoring monomer emission.

The final example in this category relates to pyrene excimer emission. In spite of pyrene's tendency to form an excimer, at very low concentration ($< 10^{-6}$ M), the rate of excimer formation does not compete with the other processes that deactivate

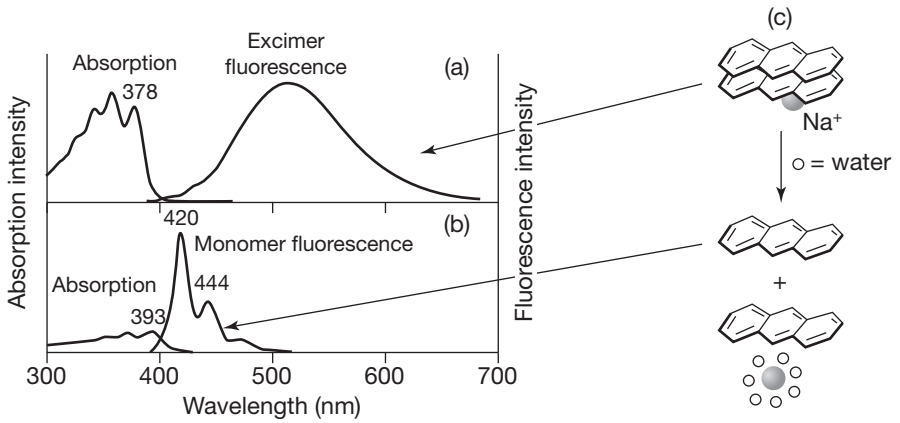


Figure 13.19 (a) Absorption and emission spectrum of anthracene@NaY in a dry sample. (b) Absorption and emission spectrum of anthracene@NaY in a sample to which water was added. (c) Schematic of the alignment of two anthracene molecules within dry and hydrated NaY zeolites; water = smaller open circles and cation = larger shaded circle.

S_1. However, even when the bulk concentation is $< 10^{-6}$ M, the effective "local concentration" can be increased to values $> 10^{-1}$ M with the help of supramolecular guest@host complexation. Such effective concentrations can be achieved with the cavitand CD (Fig. 13.20) and with micelles. Both β-CD (1:1 complex) and γ-CD (2:1 complex) solubilize hydrophobic pyrene in water. However, only the 2:1 complex with γ-CD brings two such molecules within van der Waals distance (Fig. 13.20) and enhances EX emission.[69] Thus, EX formation from pyrene even at a bulk concentration of 10^{-6} M could be observed provided γ-CD is present in solution. The local concentration within the reaction cavity of γ-CD is $> 10^{-1}$ M.

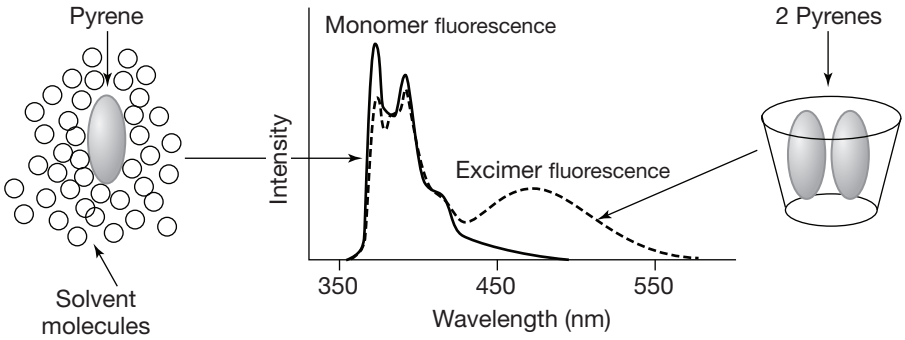


Figure 13.20 Luminescence spectrum of an aqueous solution of pyrene in the presence (dashed line) and absence (solid line) of γ-CD. Cartoon representations of pyrene in solution (left) and within a CD cavity (right).

13.12 Supramolecular Control of Triplet–Triplet Energy Transfer through the Walls of a Carcerand Host

In Sections 7.4–7.10, we learned that ET and et between molecules can occur over distances of 10 Å or greater through solvent molecules or through a molecular spacer separating the donor and acceptor molecules. We defined a carcerand as a host that completely surrounds its guest (Table 13.1). Biacetyl (**1**) has been incarcerated as a guest in "Cram's carcerand" (**2**) to form a **1@2** complex (Fig. 13.21). The et and ET transfer from electronically excited $\mathbf{1}(T_1)$@**2** to energy acceptors and electron donors in the solution surrounding the complex has been investigated.[70–72] The carcerand serves as a "molecular host spacer" that prevents the HO and LU orbitals of **1** from overlapping directly with the orbitals of an ET or et partner. Nevertheless, both ET and et from $\mathbf{1}(T_1)$@**2** to energy and electron partners have been observed in CH_2Cl_2 solution; the latter processes occur, however, with considerably smaller rate constants than those observed in nonviscous solvents in which direct collisions between the $\mathbf{1}(T_1)$ and the ET or et partners occur. For example (Table 13.3), both ET from $\mathbf{1}(T_1)$ to pyrene and et from diphenylaniline to $\mathbf{1}(T_1)$ occur with a rate close to that of diffusion ($\sim 5 \times 10^9\ M^{-1}\ s^{-1}$) in CH_2Cl_2 solution. However, for the $\mathbf{1}(T_1)$@**2** complex, the rate constant of the ET drops by more than three orders of magnitude to $\sim 1 \times 10^6\ M^{-1}\ s^{-1}$ and the rate constant of the et drops by more than five orders of magnitude to $\sim 3 \times 10^4\ M^{-1}\ s^{-1}$, respectively.

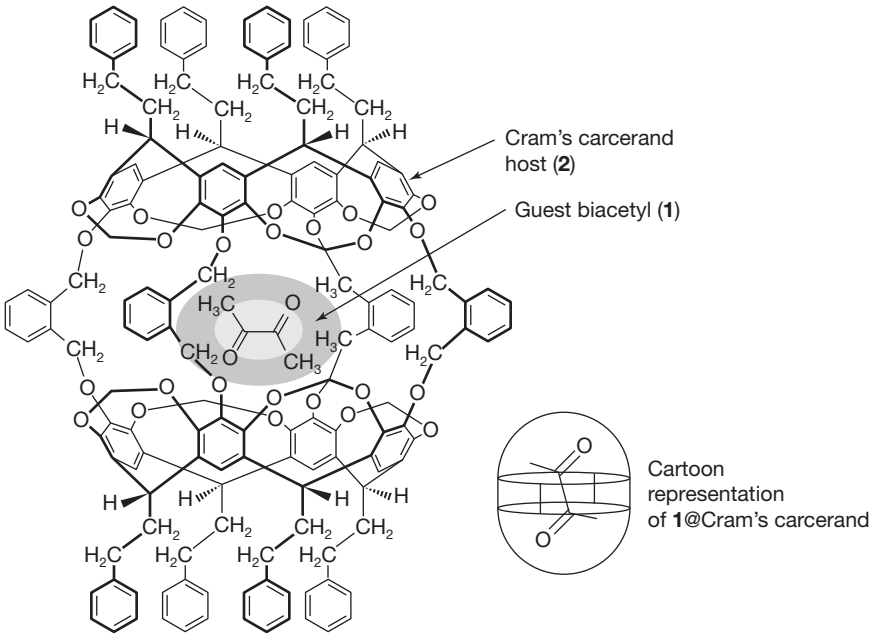


Figure 13.21 Biacetyl (**1**) incarcerated in Cram's carcerand (**2**). The insert to the right is a schematic of the **1**@Cram's carcerand (**2**).

Table 13.3 Comparison of the Rate Constants for ET and et Reactions of $\mathbf{1}(T_1)$ as a Free Molecule in Solution and as $\mathbf{1}(T_1)@\mathbf{2}$ in Solution

Energy Donor or Electron Acceptor	Energy Acceptor or Electron Donor[a]	Product from **1** Due to ET or et	Product from Py and Amine Due to ET or et	Rate ($M^{-1}\,s^{-1}$)
$\mathbf{1}(T_1)$ (ET)	$Py(S_0)$	$\mathbf{1}(S_0)$	$Py(T_1)$	$\sim 5 \times 10^9$
$\mathbf{1}(T_1)@\mathbf{2}$ (ET)	$Py(S_0)$	$\mathbf{1}(S_0)@\mathbf{2}$	$Py(T_1)$	$\sim 1 \times 10^6$
$\mathbf{1}(T_1)$ (et)	$(C_6H_5)_2NH(S_0)$	$(\mathbf{1}^{\bullet-})$	$[(C_6H_5)_2NH]^{\bullet+}(S_0)$	$\sim 5 \times 10^9$
$\mathbf{1}(T_1)@\mathbf{2}$ (et)	$(C_6H_5)_2NH(S_0)$	$(\mathbf{1}^{\bullet-})@\mathbf{2}$	$[(C_6H_5)_2NH]^{\bullet+}(S_0)$	$\sim 3 \times 10^4$

a. Py = pyrene.

These numbers suggest that, although the host molecular cage prevents direct van der Waal's overlap of the electron clouds of $\mathbf{1}(T_1)$ and the electron clouds of either pyrene or diphenylaniline, sufficient orbital overlap occurs. This result may be due to either a superexchange overlap mechanism or through the overlap of very weak portions of the wave functions that extend (tunnel) in space beyond the van der Waals' size of the guest and energy and electron partners. Although ET and et can quench $\mathbf{1}(T_1)$ through the walls of the host carcerand, chemical reactions, such as hydrogen atom abstraction, cannot quench $\mathbf{1}(T_1)$ at a measurable rate. For example, phenols, such as resorcinol, which can quench $\mathbf{1}(T_1)$ through hydrogen atom abstraction at close to the rate of diffusion, cannot quench $\mathbf{1}(T_1)@\mathbf{2}$ at a measurable rate.

Electron transfer across supramolecular walls is not unique to the above guest–host combination. For example, *trans*-4,4'-dimethyl stilbene (DMS), a neutral hydrophobic molecule, forms a $DMS@OA_2$ capsule.[73] On the other hand, OA (Fig. 13.11) does not encapsulate cationic methylviologen (MV), a good electron acceptor. However, the latter is attracted to the exterior of the OA through Coulombic cation–anion (COO^-) interaction. In spite of physical separation between the electron donor DMS and acceptor MV by the molecular walls of OA, the fluorescence of $DMS@OA_2$ is quenched by MV through et from the $^*R(S_1)$ state of DMS to MV (Fig. 13.22). The fact that et can occur through the walls of OA could be inferred by the use of a supramolecular technique. Methylviologen has an excellent affinity for the cavitand host CB[7] (Figs. 13.11 and 13.22). Thus, upon addition of CB[7], MV readily forms a MV@CB[7] complex (Fig. 13.22). In aqueous solution, the donor DMS remains as a $DMS@OA_2$ complex and the acceptor MV as an MV@CB[7] complex. Because of individual incarcerations, the donor and acceptor molecules are separated by double wall of the two capsules. Interestingly, once the MV is separated from the walls of OA via supramolecular complexation with CB[7], the fluorescence of DMS is recovered. This example illustrates the extent of possible manipulations with supramolecular assemblies.

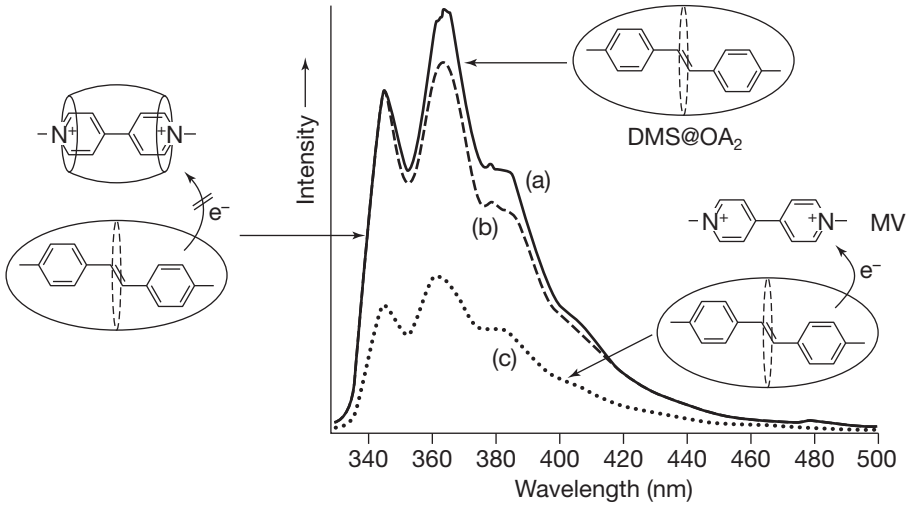
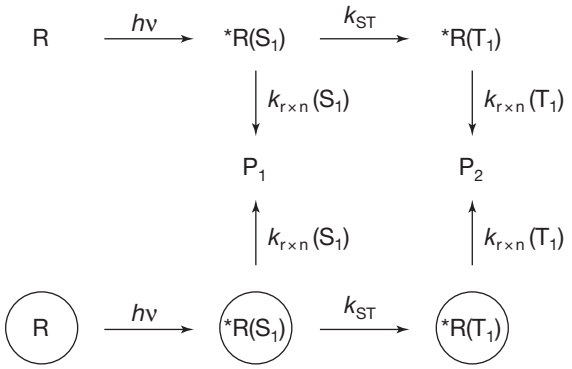


Figure 13.22 Quenching the fluorescence of DMS@OA_2 ([DMS]$= 6 \times 10^{-7}$ M, [OA] $= 1.2 \times 10^{-6}$ M, $\lambda_{ex} = 320$ nm) by MV (6×10^{-6} M) and recovery of fluorescence upon addition of CB[7]. (a) Emission from DMS@OA_2; (b) emission from DMS@OA_2 in the presence of MV; (c) emission from DMS@OA_2 in the presence of MV@CB[7].

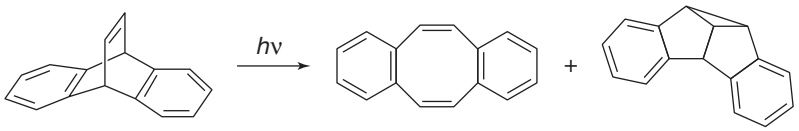
13.13 Supramolecular Control of Unimolecular Photochemical Processes by Preorganization in guest@host Complexes: Supramolecular Selectivity of the Reactive State

In some cases, different products, P_1 and P_2, originate from $^*R(S_1)$ and $^*R(T_1)$, respectively (Scheme 13.9). One such example is provided in Scheme 13.10. Dibenzobarrelene (**3**) upon direct excitation yields product **4**, while upon triplet sensitization (acetone) it yields product **5**. Product **4** originates from $^*R(S_1)$ and product **5** originates from $^*R(T_1)$. Now, let us consider how to use supramolecular preorganization to control which of two primary photochemical processes occurs. In Section 13.10, we saw that preorganization of heavy atoms as coguests in a guest@host complex will accelerate spin forbidden transitions of $^*R$. Thus, the heavy atom effect can also be used to enhance $^*R(S_1) \rightarrow {}^*R(T_1)$ intersystem crossing (ISC) and thus control product distributions in photochemical reactions when one reaction occurs from $^*R(S_1)$ and the other from $^*R(T_1)$. In the absence of the heavy atom effect, $^*R(S_1)$ leads to P_1 and in the presence of the heavy atom effect, $^*R(S_1)$ leads to P_2.

As an example of supramolecular control of selection of P_1 and P_2 by photolysis of **3** through the strategy of Scheme 13.9, the coguest heavy cation effect was used to fine-tune product distributions of **4** and **5** within a zeolite.[74] For example, irradiation of dibenzobarrelene included in zeolite KY (Z of K $= 19$) gives **4** as the major product, whereas photolysis in TlY (Z of Tl $= 81$) yields **5** as nearly the exclusive product (Scheme 13.10). The coguest cation Tl^+ accelerates the $S_1 \rightarrow T_1$ intersystem crossing



Scheme 13.9 Schematic representation of the path from $^*R$ to products P_1 and P_2 for a molecular (top) and a supramolecular (bottom) system.



3	**4**	**5**
Acetonitrile	77	23
Acetone	—	100
KY	75	25
TIY	1	99

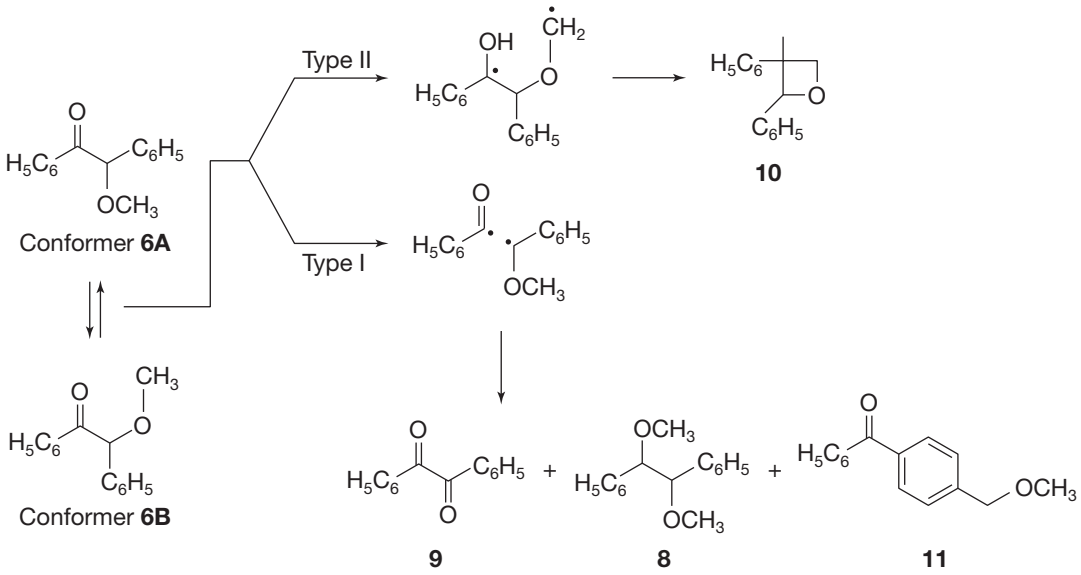
Scheme 13.10 Supramolecular heavy atom control of **4** and **5** formation during the photolysis of dibenzobarralene **3**.

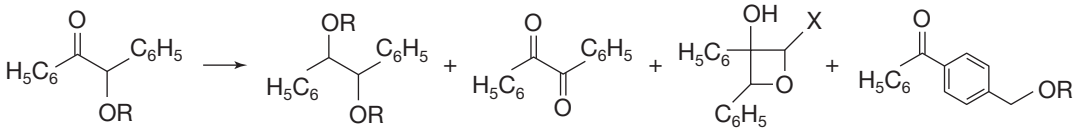
to a rate faster than reaction from S_1. Once T_l is formed it produces **5** selectively. The lighter cation K^+ has little effect on ISC and the product distribution is similar to that in acetonitrile proving the role of the heavy cation.

13.14 Supramolecular Control of Unimolecular Photochemical Processes by Preorganization of guest@host Complexes: Supramolecular Selectivity of the $^*R \rightarrow I$ Processes

On occasion, there may be two (or more) competing primary photochemical reactions proceeding from a single $^*R$. Scheme 13.2c shows schematically the situation where one primary photochemical reaction produces an intermediate (I_1) that leads to a product (P_1) and a second primary photochemical reaction produces a second intermediate

(I_2) that leads to a different second product (P_2). As an exemplar of such a possibility, we present the photochemistry of benzoin alkyl ethers that undergo competing Type I and Type II primary processes (Scheme 13.11). The Type I reaction from $^*R$ is expected to be essentially independent of the conformation of the ketone. On the other hand, the Type II reaction is strongly conformation dependent because the alkyl chain for the γ-H to be abstracted must be close to the cabonyl group during the lifetime of $^*R$.





R = CH_3 (**6**)			X = H	
Benzene	39%	23%	—	—
Cetyltrimethyl ammonium chloride micelle	8%	7%	52%	—
R = CH_2—$(CH_2)_6$—CH_3 (**7**)			X = CH_2—$(CH_2)_5$—CH_3	
Benzene	49%	—	—	—
Cetyltrimethyl ammonium chloride micelle	36%	—	—	45%

Scheme 13.11 Comparison of the products from the Type I versus Type II reactions of benzoin alkyl ethers in homogeneous solution and in micellar solution.

In homogeneous solutions, the Norrish Type I reaction is the only photoreaction that occurs for the benzoin alkyl ethers shown in (Scheme 13.11). The Norrish Type II reaction, although plausible, is not observed, due to the unfavorable conformation of $^*R$ for this reaction in solution. Incorporation of benzoin alkyl ethers in a micellar medium suppresses the Type I pathway via the cage effect (for details see Sections 13.21 and 8.42).[75] Under such circumstances, the normally less competitive Type II reaction becomes more competitive for certain benzoin alkyl ethers and is the major pathway for benzoin methyl ether (**6**) (Scheme 13.11) in cetyltrimethyl ammonium bromide and cetyltrimethyl ammonium chloride micelles. This result is explained as the consequence of conformational control of the guest by the interface of the host micelle (Fig. 13.23). Of the two conformations **6A** and **6B** shown in Fig. 13.23b and Scheme 13.11, the conformer **6B** at the micellar interface (probably due to the preference for the polar carbonyl and methoxy groups to be in the aqueous phase) leads to the Norrish Type II products. Benzoin octyl ether (**7**) failed to give the Norrish Type II products and afforded only the para-substituted benzophenone (rearrangement product **11**) via the Norrish Type I reaction followed by radical–radical coupling in the same micelle media (Scheme 13.11). For **7**, the long alkyl chain prefers to remain in the hydrocarbon interior leading to predominantly conformer **7A** at the micellar interface (Fig. 13.23c). Under such conditions, the alkyl chain is unfavorably placed relative to the oxygen atom of the n,π^* state for the excited ketone to abstract the γ-hydrogen.

Conformational control of the competition between Type I and Type II reactions can also be achieved by incarceration of $^*R$ in OA (shown schematically in Fig. 13.24).[76] α-Alkyl dibenzyl ketones, similar to α-alkyl benzoin ethers discussed above, can undergo both Type I and Type II primary photoreactions. Independent of the chain length, the two α-alkyl dibenzyl ketones (α-propyl and α-octyl) shown in Scheme 13.12 upon irradiation in hexane solution yield predominantly the Type I product; the length of the alkyl chain has no influence on the distribution of products in the homogeneous solvent hexane. On the other hand, upon irradiation these ketones incarcerated within the OA as a guest@$(OA)_2$ complex in water the product distribution is different. While **12**@$(OA)_2$ yields predominantly the Type I products, **13**@$(OA)_2$ yields predominately Type II products (Scheme 13.12). In the latter case, the minor Type II products in hexane are the major products within the confined reaction cavity of OA.

This change in reactivity pattern is attributable to the supramolecular control by the host cavity through conformational preorganization. Nuclear magnetic resonance (NMR) analysis confirms that for **13** the alkyl chain is preorganized favorably for facile γ-hydrogen abstraction, while for **12** the abstractable γ-hydrogen on the alkyl chain is spatially remote from the carbonyl chromophore.

It is interesting to note that the reactivity pattern for α-alkyl benzoin ethers@micelles (Scheme 13.11), is contrary to what is observed in the α-alkyl dibenzyl ketones@$(OA)_2$ complex. In micelles, the interface between the hydrophobic core and the aqueous phase plays a major role in controlling the conformation of guests in guest@micelle complexes. For example, ketones, such as α-octyl benzoin ether, in a

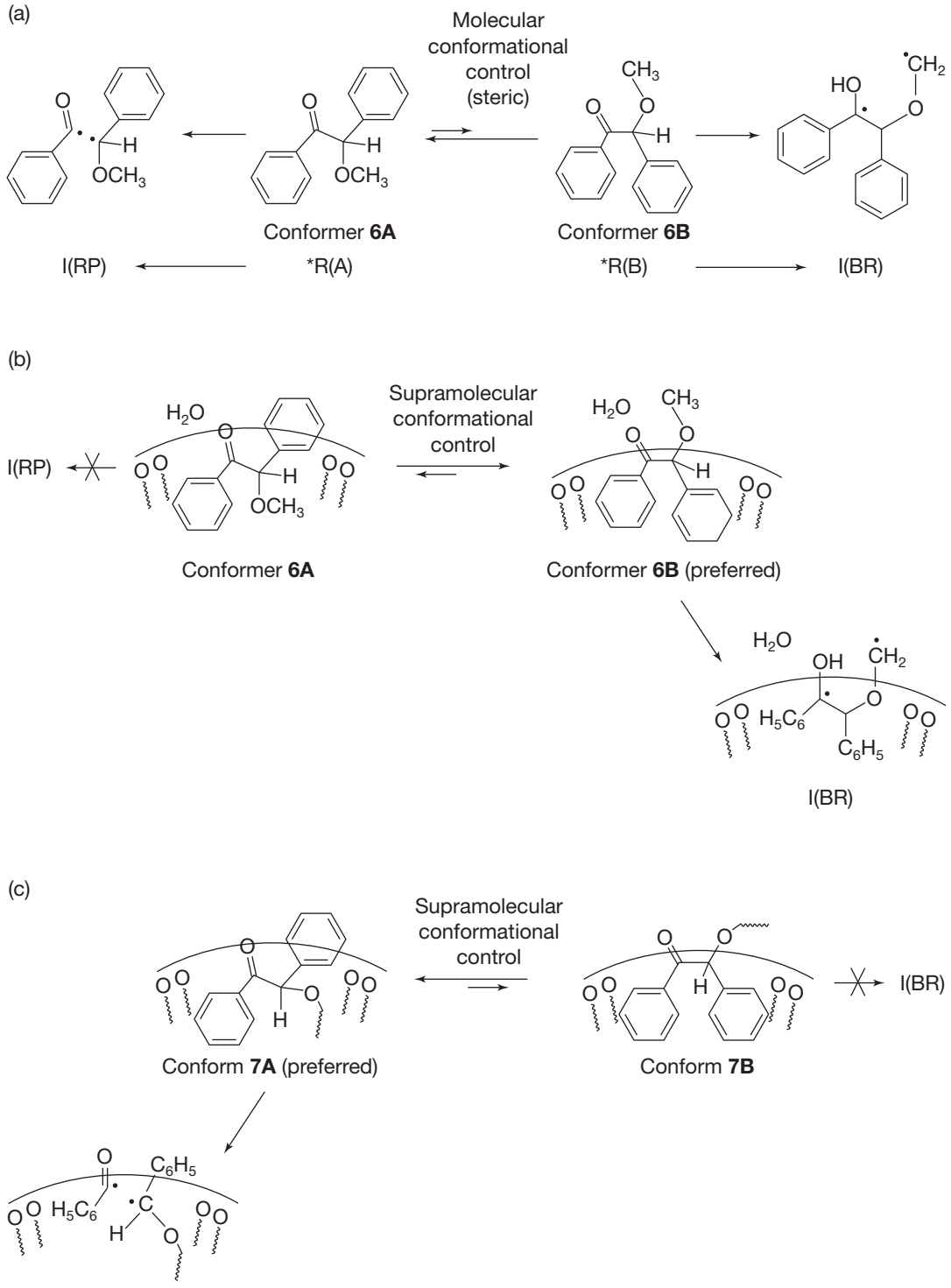


Figure 13.23 Schematic interpretation of the conformational control of the Type I versus Type II reactions of benzoin alkyl ethers. (a) In solution, conformational equilibrium controls the products distribution. (b) Within a micelle, benzoin methyl ether is favored to undergo Type II reaction. (c) Within a micelle, the Type II reaction of benzoin octyl ether is forbidden.

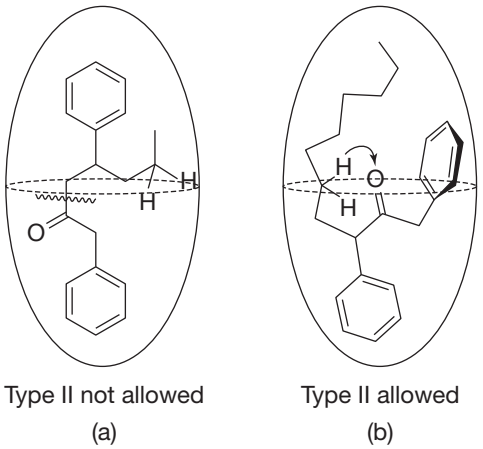
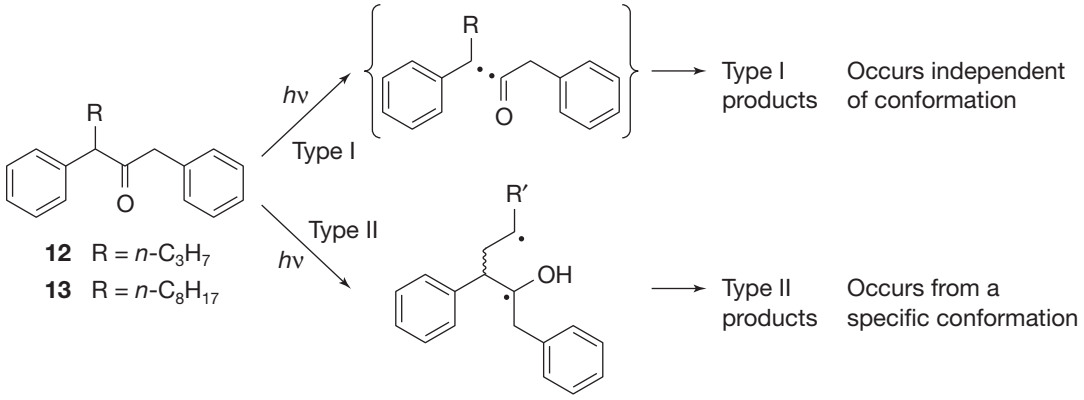


Figure 13.24 Schematic of the supramolecular conformational control of Type I versus Type II reactions from $^*R$. If the host preorganizes the conformation (a), the Type I reaction is favored. If the host preorganizes the conformation (b), Type II reaction is favored.



Substrate	Medium	Type 1/Type II Products Ratio
12	Hexane	80 : 20
	OA/H_2O	89 : 11
13	Hexane	85 : 15
	OA/H_2O	10 : 90

Scheme 13.12 Alkyl chain length dependent conformational control on product distributions in α-alkyl dibenzyl ketones.

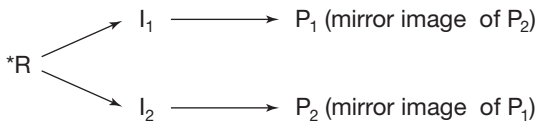
micellar medium adopt a conformation such that the polar carbonyl group is placed at the interface and the nonpolar octyl chain deep in the hydrophobic core (Fig. 13.23c). On the other hand, the preferred conformation of α-octyl dibenzyl ketone@OA is one in which the octyl chain is closer to the carbonyl, favoring the Type II reaction (Fig. 13.24). Such exquisite control on product selectivity could not be obtained without supramolecular control through preorganization of the conformation of the guest by the host.

13.15 Supramolecular Chiral Effects on Two Competing Primary Processes of *R Involving Biradical Intermediates: Preorganization in guest@host Assemblies

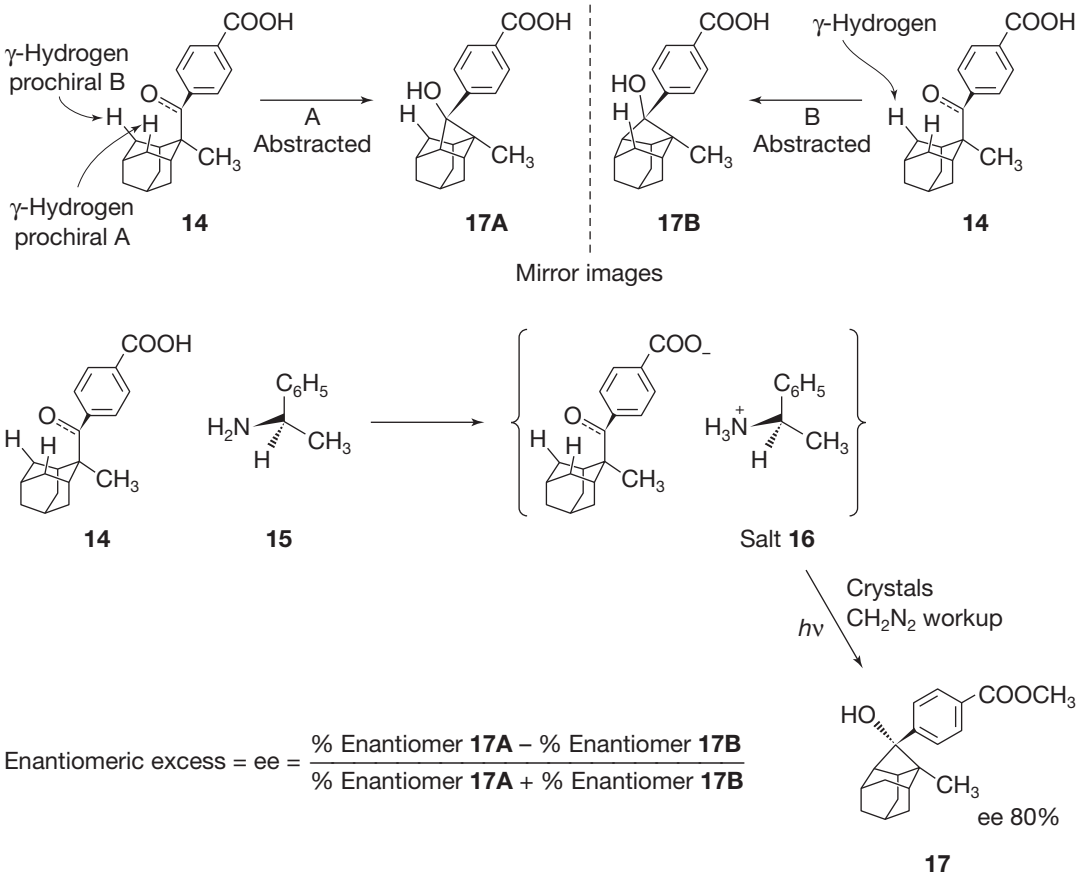
So far, we dealt with examples where a single *R gave two different intermediates through two different primary photoreactions or two *R (S_1 and T_1) underwent different primary photochemical processes. Now, we consider examples where the reaction products (P_1 and P_2) from *R are stereoisomers (Scheme 13.13). Thus, final products are either enantiomers (when the reactant is achiral) or diastereomers (when the reactant contains a chiral auxiliary; the products here are not mirror images). Stereocontrol of photochemical reactions that are difficult to achieve in homogeneous solution may be achievable with supramolecular effects.

For example, a remarkable feature of the photolysis of ketones in crystals is the possibility of selective formation of one enantiomer from achiral molecules. The basis for this enantiomeric selectivity requires an overall chirality of the crystal. Thus, the chirality of the crystal structure as a chiral "host" is propagated down to the level of the molecular "guest" during a photochemical process. As a specific example, we consider the formation of two enantiomeric biradicals from a γ-hydrogen abstraction reaction involving an achiral molecular guest in a chiral crystal host.

One example of such enatiomerically selective intramolecular γ-hydrogen abstraction reaction in the case of ketone **14** is shown in Scheme 13.14.[77,78] This achiral molecule possesses two prochiral γ-hydrogens (A and B). Prochiral hydrogens are those when replaced give chiral products that are enantiomers. In this particular example, the C—H bond would be replaced by a C—C bond. In an achiral environment of a homogeneous solution, each of these prochiral hydrogen is abstracted by the excited



Scheme 13.13 Possibility of formation of enantiomeric products from *R via the same primary photoreaction involving different intermediates.



Scheme 13.14 An example of chiral induction in the crystalline state. Chiral crystals yield enantiomerically enriched products.

carbonyl with exactly equal rates leading to a 1:1 racemic mixture of the two optical isomers for the chiral cyclobutanol product. Thus, in solution the two pathways have identical activation free energy barriers. However, when acid (**14**) and a chiral amine (**15**) are crystallized, a crystalline chiral salt (**16**) is formed. When salt **16** is irradiated, one of the two possible cyclobutanol products (**17**) is formed in high enantiomeric excess (ee; see Scheme 13.14). As expected, in solution both prochiral γ-hydrogen atoms are abstracted with equal efficiency. However, in the crystal there is a clear preference for only one of the prochiral γ-hydrogen atoms. The main effect of the host molecules surrounding *R is the preorganization of the reactants in a single chiral conformation that enhances abstraction of only one of the two possible prochiral hydrogens. The non-identical two prochiral hydrogens in the chiral crystal have different energy barriers for abstraction. Indeed, the X-ray crystal structure shown for the salt (**16**) in Fig. 13.25 clearly shows that one of the two prochiral hydrogens is closer.

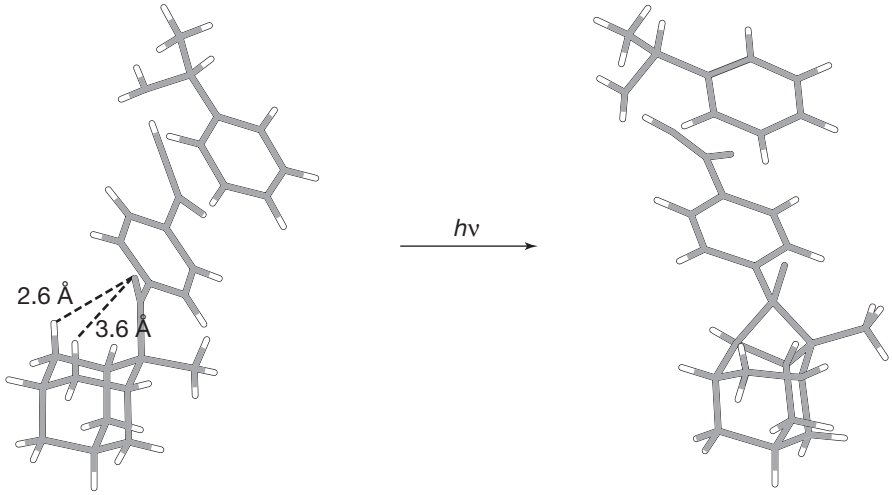


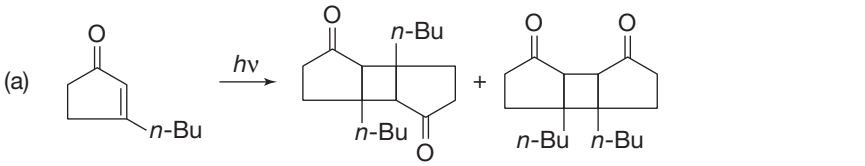
Figure 13.25 X-ray crystal structure of salt **16**. Note that the two prochiral hydrogens are at different distances from the carbonyl group. The excited carbonyl would prefer to abstract the closer hydrogen (2.6 vs. 3.6 Å).

13.16 Supramolecular Effects on Bimolecular Primary Processes: Preorganization through Orientational Effects in guest/coguest@host Supramolecular Assemblies

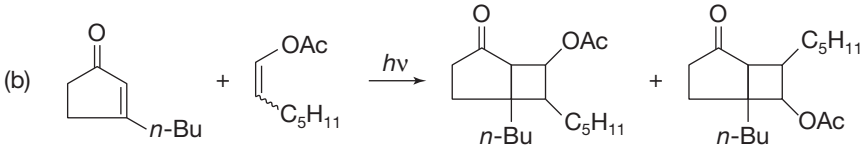
In Section 13.11, we saw how supramolecular preorganization of a guest and coguest in the cavity of a host can lead to enhancement of EX formation. Supramolecular preorganization can also be employed to control the products of bimolecular primary photochemical reactions from *R. As an example, we describe the control of reaction regioselectivity on [2 + 2] photocyloadditions.

The irradiation of 3-*n*-butylcyclopentenone (**18**) in homogeneous solution leads to a "head-to-tail" [2 + 2] photocyclodimer (**19**) as the major product (Scheme 13.15a). However, irradiation of this ketone incarcerated in a micelle leads to the "head-to-head" [2 + 2] cycloadduct (**20**) as the major product.[79] This disparity in product selectivity results from preorientation in the micelle of the ketone in a head-to-head fashion (Fig. 13.26). Upon absorption of a photon, 3-*n*-butylcyclopentenone molecule adds to an adjacent 3-*n*-butylcyclopentenone molecule before the relative orientation changes. In homogeneous solution, the head-to-tail orientation is preferred by the more favorable head-to-tail interactions of two dipoles of the molecule. In the micelle supercage, this favorable interaction is weakened by the strong dielectric constant at the micelle–water boundary. Head-to-head orientation is favored by the attraction of the negative end of the molecular dipole into the aqueous portion of the boundary and the hydrophobic attraction of the alkyl chain into the hydrophobic portion of the micelle supercage.

Upon irradiation, **18** adds to heptenyl acetate (**21**) in organic solvents to give a single adduct **23** (Scheme 13.15b) via a 1,4-BR intermediate (see Section 11.15).



	19	20
C_6H_6	91%	9%
C_6H_{12}	96%	4%
KDC Micelle	2%	98%



	22	23
CH_3OH	0%	100%
C_6H_{12}	0%	100%
KDC Micelle	70%	30%

Scheme 13.15 Products of (a) photodimerization and (b) cross-cycloaddition in organic solvents and micelles. Product distribution in micelles is controlled by molecular preorganization at the micellar–water interface (see Fig. 13.26). (Potassium dodecanoate = KDC; *n*-Bu = *n*-butyl).

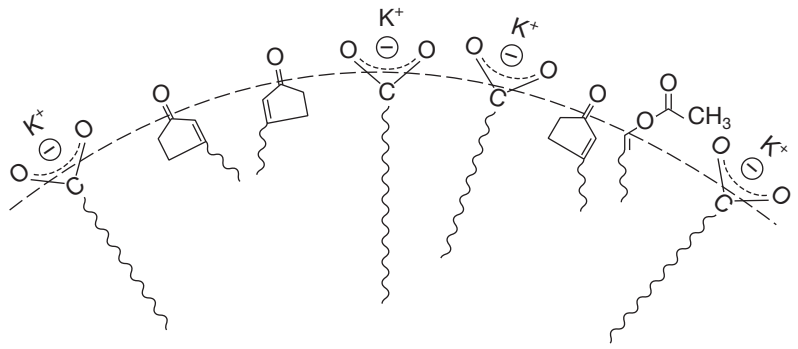


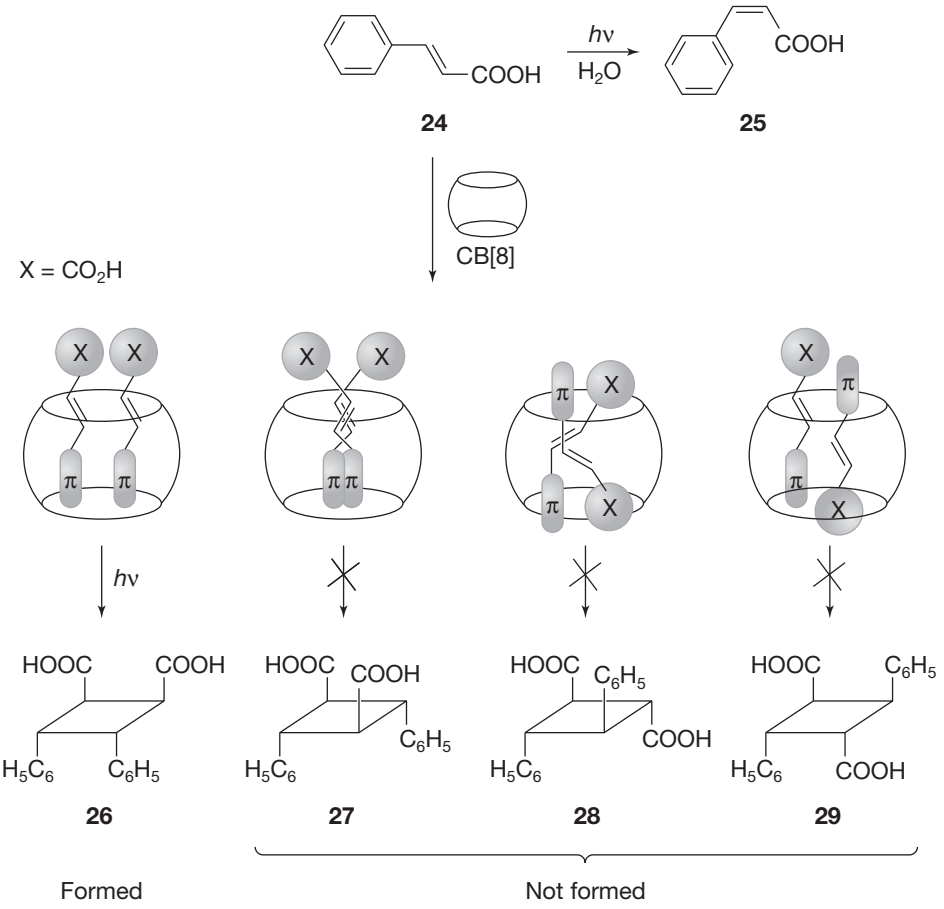
Figure 13.26 Preorganization of cyclopentenone and vinyl acetate molecules at the micellar–water interface.

However, irradiation of these two molecules incarcerated in a potassium decanoate micelle yields a mixture of two adducts (**22** and **23**), with **22** as the major product. This finding is consistent with the notion that a micellar interface helps to orient the reactant molecules (Fig. 13.26).[80] A higher yield of cross-adducts over dimers was achieved with 30 mol excess of the vinyl acetate. Similar to the example shown in

Scheme 13.11 and Fig. 13.23, the long alkyl chain of the olefin helps to anchor the olefin at the micelle–water interface in the geometry shown in Fig. 13.26.

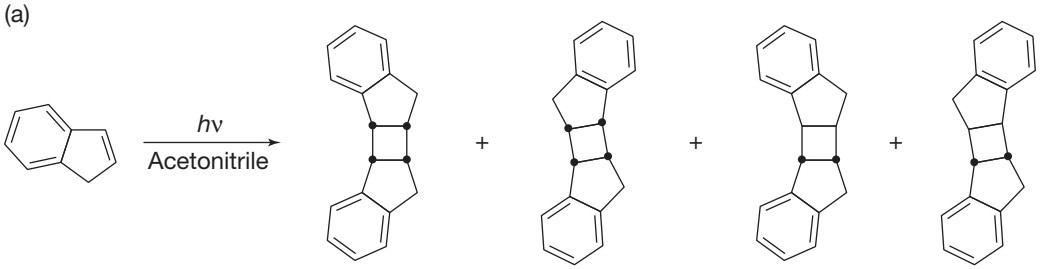
The above two examples illustrate how the interface of a micelle can preorient molecules and thus reverse the observed photobehavior of molecules in homogeneous solvents.

Photoselectivity based on preorganization of guest molecular orientation can also be achieved within water-soluble carceplexes composed of CB and OA hosts (Fig. 13.11). Two examples of [2 + 2] cyclodimerizations are provided in Schemes 13.16 and 13.17. The [2 + 2] photodimerization of *trans*-cinnamic acid (**24**) could result in the formation of four different stereoisomeric dimers (**26**–**29**), differing in the orientation of the carboxylic acid and phenyl groups. However, irradiation of **24** in water produces *cis*-cinnamic acid (**25**) exclusively. Irradiation of the supramolecular complex of cucurbituril **24**@CB[8] results in the mirror symmetric dimer (**26**) shown in Scheme 13.16.[81] This product is formed to the exclusion of the several other possible stereoisomeric [2 + 2] dimers. This result illustrates the remarkable ability of the host CB[8] to preorient two cinnamic acid molecules in a mirror symmetric



Scheme 13.16 Photodimerization of cinnamic acid included in CB[8].

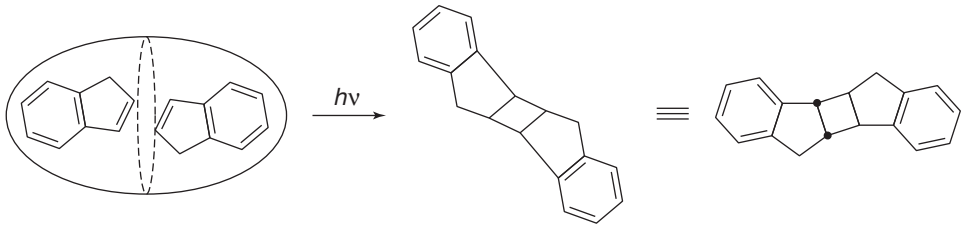
(a)



30 **31** **32** **33** **34**

	Syn HH	Syn HT	Anti HH	Anti HT
Direct	74	5	12	6
Triplet sensitized	3	5	84	8
Electron-transfer sensitized	—	—	96	4

(b)



34 **34**

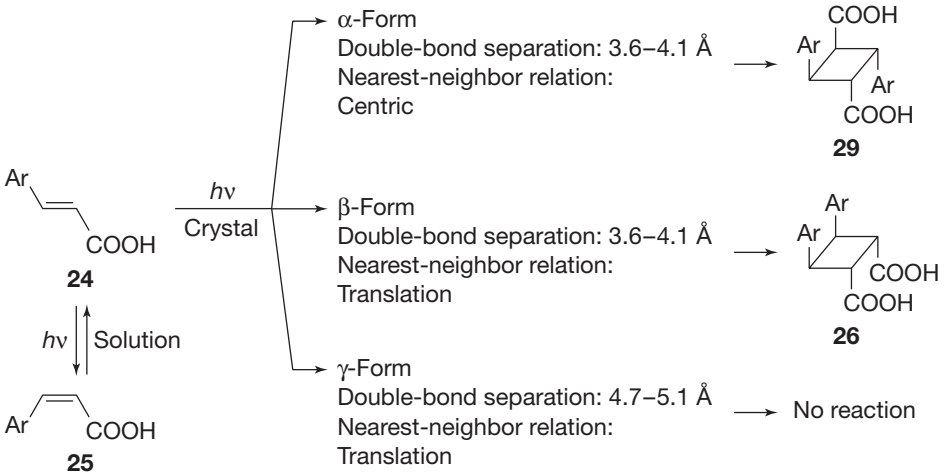
Scheme 13.17 (a) Photodimerization of indene under various conditions in solution. (b) Expected orientation of indene molecules wihin OA capsule.

fashion (Scheme 13.16). This selective preorganization is facilitated by weak forces, such as the hydrophobic effect (which drives the incarceration of two *trans*-cinnamic acid molecules in the host cavity) and π---π interactions between the phenyl groups, which facilitates the favored mirror symmetry of the two incarcerated guests. The tight fit within the organic host results in an enhanced barrier inhibiting geometric isomerization and preorganization of reactive molecules favors a single dimer.

The polar head group and nonpolar tail of the olefins in the above examples facilitated their orientation at the hydrophobic–hydrophilic interface. Control of photodimerization of olefins lacking these features could nevertheless be achieved within the OA capsule.[82] As shown in Scheme 13.17 upon direct excitation, triplet and et sensitizations the anti-head-tail dimer (anti HT; **34**) was formed in $< 10\%$ yield from indene (**30**). But when indene$_2$@OA$_2$ was irradiated in aqueous solution, **34** was produced as the sole product. The structure of the preferred dimer results from the preorganization of the two indene molecules in the host capsule. Lack of free space precludes reorientation of the indene to produce dimers with the structure found in solution photolysis.

13.17 Supramolecular Effects on $^*R$ in the Solid State: Preorganization through Conformational and Orientational Control in the Solid State

There are many examples of supramolecular preorganization for control of [2 + 2] photodimerizations in the crystalline solid state.[58,83,84] As mentioned in Section 13.16, irradiation of *trans*-cinnamic acid (**24**) in solution yields *cis*-cinnamic acid (**25**) and [2 + 2] photodimerization does not occur. On the other hand, irradiation of crystalline **24** leads exclusively to [2 + 2] photodimerization (Scheme 13.18). The crystalline state can be considered as a hard and rigid "host" for all of its constituent molecules. Thus, it "arrests" substantial molecular motion, such as the *cis–trans* isomerization, by increasing the barrier for this process in the excited state $^*R$. More importantly, preorganization in the crystal can favor the photodimerization to a single [2 + 2] photodimer. Let us see how the crystalline state favors a single photodimer. Cinnamic acids are observed to crystallize in three polymorphic forms, termed α, β, and γ forms, each showing a distinct photochemical behavior, as determined by the structural relationship of nearby cinnamic acid molecules in the polymorphic form. In the α-crystalline form, the double bond of a molecule in one stack overlaps with that of a centrosymmetrically related molecule in an adjacent stack that are within $\sim$ 4.2 Å (a plausible distance for bond formation in the solid state) (Fig. 13.27). Crystals of this type, upon irradiation, produce the centrosymmetric dimer (**29**). In the β-type packing, the molecules are separated by a short repeat distance of $\sim$ 4 Å (Fig. 13.27). In this form, neighboring molecules up the stack are translationally equivalent and show considerable face-to-face overlap of the C═C bonds that are involved in the [2 + 2] photodimerization. All cinnamic acids that crystallize in this structure react photochemically to give products of the same stereochemistry, namely, mirror symmetric dimer **26**. In the γ-type structure, adjacent molecules are offset so that the potentially reactive double bonds do not overlap, and furthermore the distance between them is large ($\sim$ 5 Å). Crystals of this type are photostable toward [2 + 2] dimerization.



Scheme 13.18 Photoreactivity of crystalline cinnamic acids in three polymorphic forms.

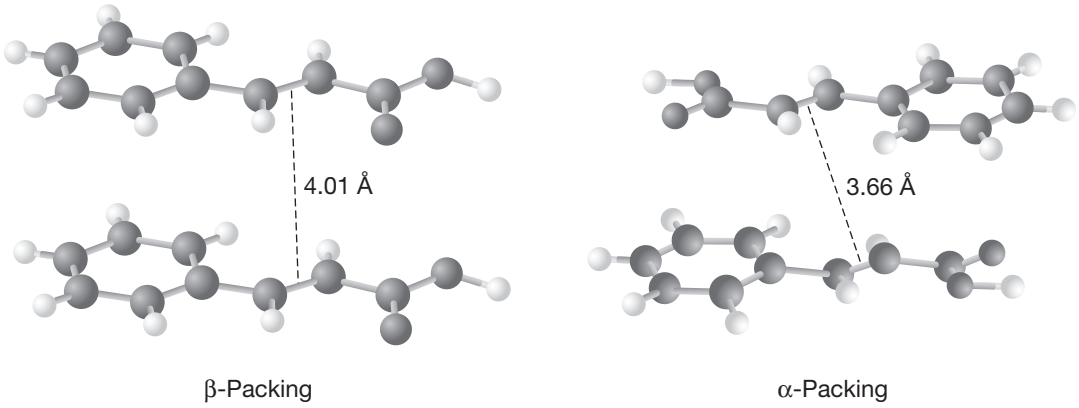
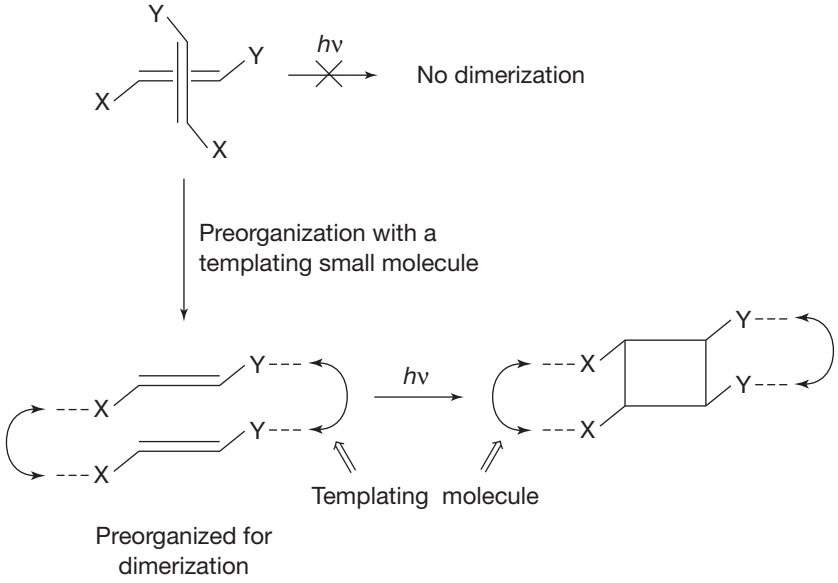


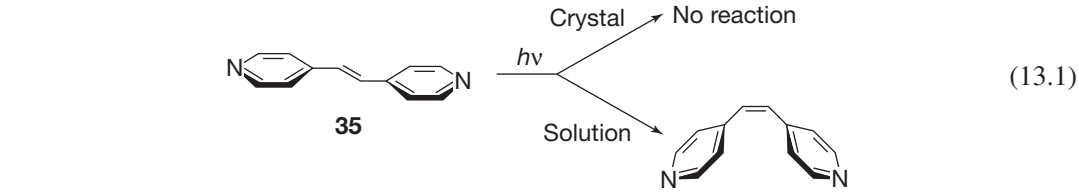
Figure 13.27 Packing arrangements of cinnamic acid in α- and β-forms. Olefins are within a reactive distance ($\sim$ 4 Å) in both crystalline forms and each one would give different isomers.

13.18 Supramolecular Effects on *R: Templated Photodimerization in the Solid State

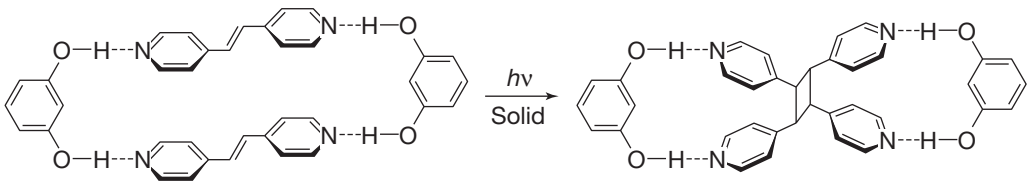
The analogy with the supramolecular complex in solution and the crystalline state is closer for certain two-component crystals (also known as mixed crystals) where one molecule in the crystal lattice serves as an orienting or "templating" host for a second molecule that is photoactive. The term templating has been coined for the action by which the host molecule enforces the orientation of the photoactive guest (Scheme 13.19) in a mixed guest@host crystal.[85] The strategy of the templation



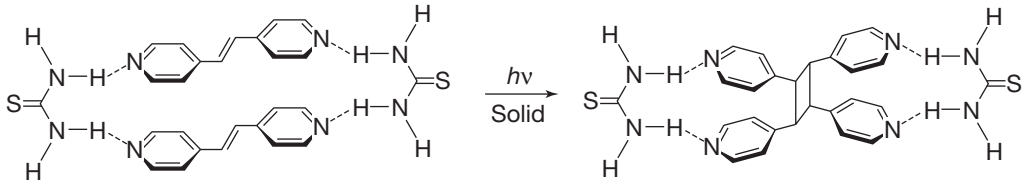
Scheme 13.19 Schematic representation of the principle of templation for dimerization of olefins. The template helps to preorganize olefins toward formation of a single dimer after photoexcitation.



(13.1)



(13.2)



(13.3)

Scheme 13.20 Templated photodimerization of olefins in the crystalline state. Hydrogen bonding between the template and the olefin directs the dimerization process.

approach to photochemistry of mixed crystals, while not of general scope, works out remarkably well in selected cases. In this strategy, a template molecule is chosen such that the predictable packing of the template–host molecules in the crystalline state will enable the potentially reactive guest molecules to pack in a manner that would facilitate selective [2 + 2] photodimerization.

As an example of the templating effect, consider the photochemistry of *trans*-1,2-bis(4-pyridyl) ethylene (**35**) upon irradiation in solution and in templated mixed crystals (Scheme 13.20, Eq. 13.1).[86] Olefin **35**, like cinnamic acid (**24**), undergoes only *cis–trans* isomerization in solution (Eq. 13.1). Furthermore, irradiation of crystals of **35** does not yield any dimeric products or *cis–trans* isomerization. Based on the crystal structure of **35**, absence of dimerization upon irradiation of crystals is not surprising. Olefin **35** crystallizes in a layered structure in which olefins of neighboring molecules are separated by > 6.5 Å. However, two adjacent C═C groups, **35**, can be engineered to pack within 4.2 Å with the help of templates, such as 1,3-dihydroxybenzene (**36**)[86] and thiourea (**37**).[87] Irradiation of mixed crystals of **36** and **35** (Eq. 13.2) or **37** and **35** (Eq. 13.3) results in the formation of a single photodimer in quantitative yield! In these cases, hydrogen bonding between the template hosts (**36** or **37**) and the guest (**35**) preorganizes C═C bonds of the reacting olefins parallel to each other and within ~ 4.2 Å, thus facilitating the dimerization process in the crystalline state, to yield a single [2 + 2] photodimer (Eqs. 13.2 and 13.3). The key feature that makes

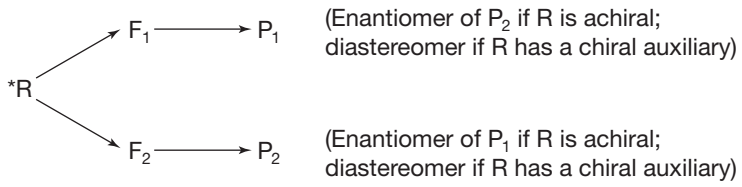
these templates work in the solid state is that they have the hydrogen-bonding centers separated by ~ 4 Å, which holds the olefin (**35**) at either end of the molecule. As expected, the same templates will not work for olefins that lack the hydrogen-bonding ability. Also, these templates are only effective in the solid state and do not have the ability to align **35** for dimerization in solution.

13.19 Supramolecular Chiral Effects on *R in Concerted Reactions and Reactions Involving Funnels: Preorganization in guest@host Assemblies

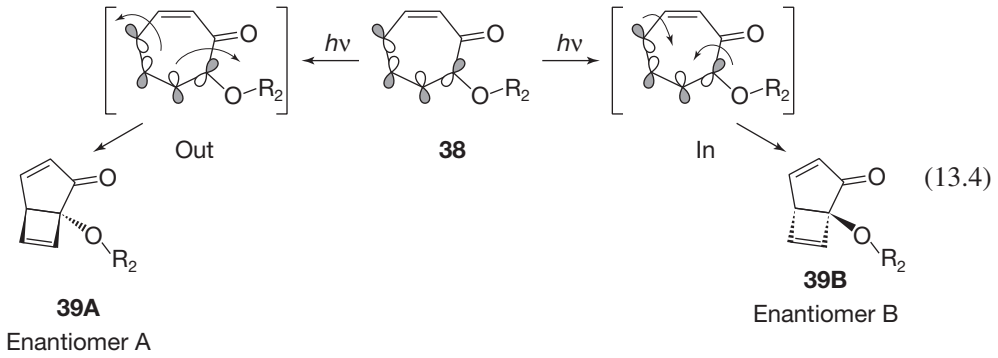
Note that in Sections 6.9 and 6.12 pericyclic photoreactions and *cis–trans* isomerization were predicted to be concerted or to proceed through funnels and that a distinction between the two mechanisms was generally not possible through experiments. As a result, we will not attempt to distinguish the supramolecular effects on concerted reactions versus funnels, but will consider both of them to respond in a similar fashion to supramolecular preorganization effects. For simplicity, we will use the funnel notation $^*R \rightarrow F \rightarrow P$ to describe the effects. In addition, we will consider only stereoselectivity in pericyclic reactions, which generally proceed via singlet states involving $^*R(S_1) \rightarrow F$ steps (Section 6.22). In particular, we will describe the use of supramolecular effects to control the enantiomeric or diastereomeric selectivity of selected photoreactions (Scheme 13.21), a subtle and challenging general problem in organic synthesis.[88]

As a specific exemplar of Scheme 13.21 for which the host forms the chiral environment, consider the electrocyclic ring closure of the tropolone (**38**, Scheme 13.22, Eq. 13.4).[89] There two "allowed" disrotatory motions are possible from *R, which are equally probable in a symmetric environment. Therefore, a racemic mixture of the ring-closed cyclobutenes (**39**) is expected (Eq. 13.4). Molecule **40** forms a complex with β-cyclodextrin (**40**@β-CD). Since β-CD is a chiral host, the complex **40**@β-CD is chiral. This result means that the two disrotatory motions, which are completely equivalent in an achiral environment (i.e., in the absence of CD), are different to some extent in the chiral environment of the host. Depending on the difference in the free energies of activation for the two disrotatory motions of ***40**@β-CD, one of the two enantiomers **41** will be formed in an ee. In this case, the value of ee is 33% (Scheme 13.22, Eq. 13.5).

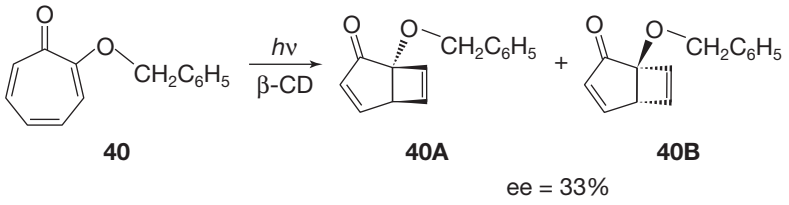
As a specific exemplar of Scheme 13.21 for which a chiral coguest forms a chiral environment in the cavity of a host, consider the exemplar of Eq. 13.6 for tropolone (**42**) in the zeolite NaY. An ee of 78% is found in product **43** upon photolysis of the tropolone ether (**42**) in the achiral FAU zeolite NaY when a chiral coguest, ephedrine, is incarcerated in the same supercage as **42** to form a **42**/ephedrine@NaY. In this case, the inclusion of ephedrine in the supercage causes the free space in the supercage to become a chiral space. Thus, the photochemistry of the **42**/ephedrine@NaY complex leads to the formation of a considerable excess of one of the enantiomeric products, **43**. As expected, chiral inductors do not give any ee in the photoproducts in methylene



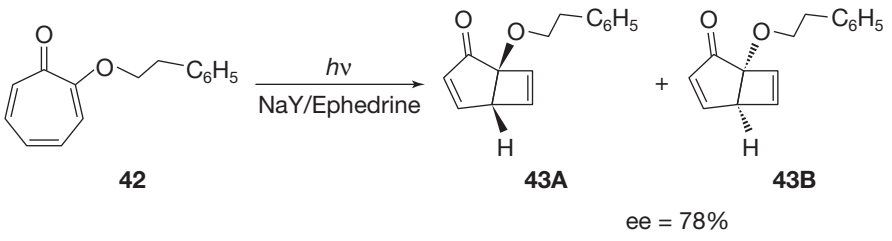
Scheme 13.21 Schematic representation of two pathways for photochemical reactions going through two funnels that lead to different products.



(13.4)



(13.5)

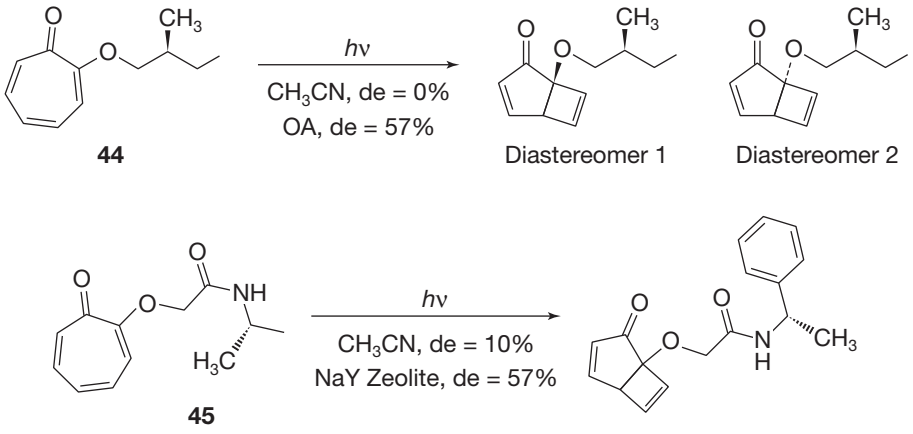


(13.6)

Scheme 13.22 Photocyclization of achiral tropolones gives chiral products. Chiral induction is observed in supramolecular assemblies, but not in solution.

chloride solution where supramolecular preorganization through guest@host complexes is absent.[42]

In the examples above, a chiral inductor or a chiral host was used to achieve chiral induction in the photoproduct. A common technique used in ground-state organic chemistry to achieve enantioselectivity or diastereoselectvity is to use a chiral



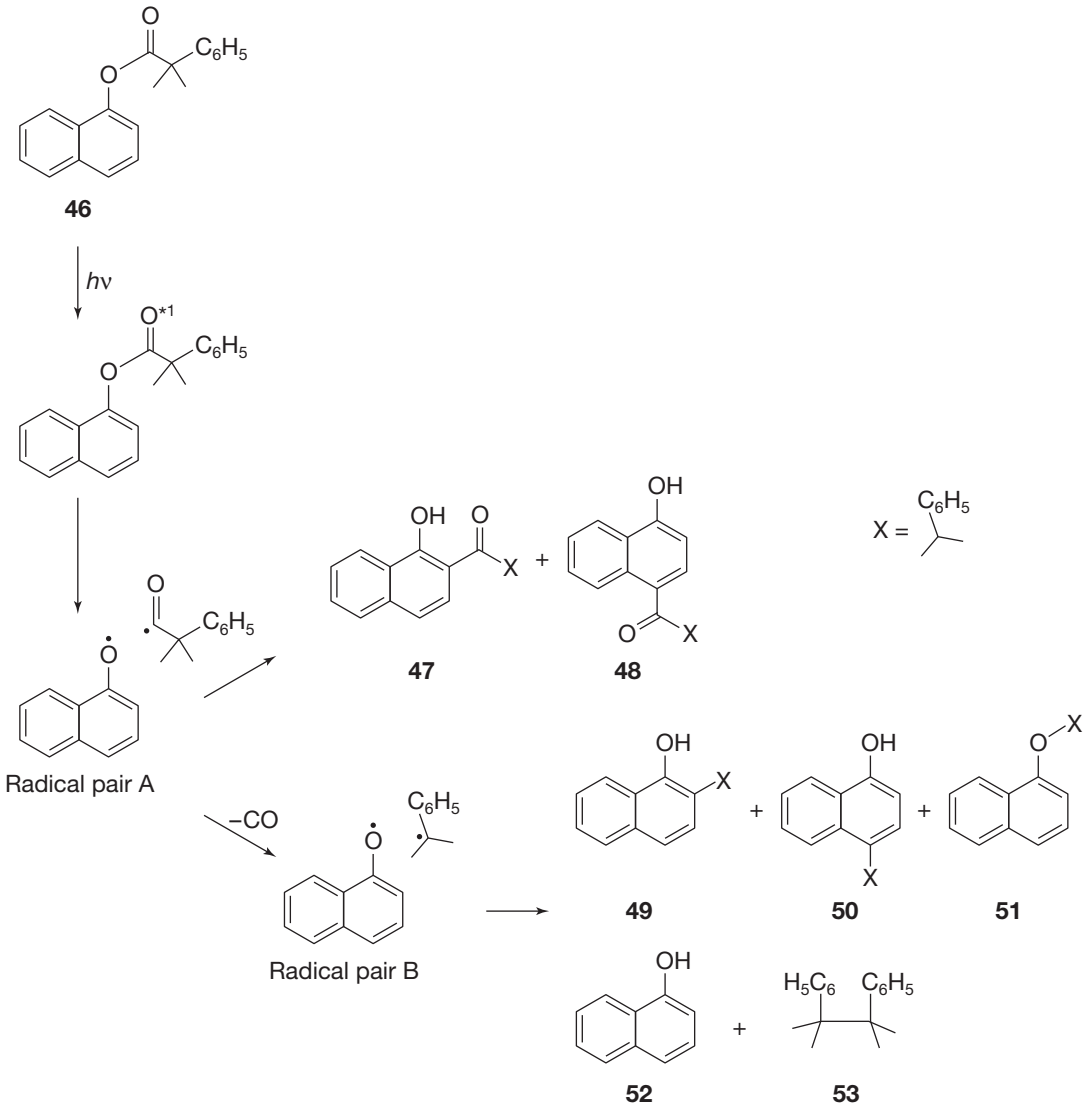
$$\text{Diastereomeric excess} = \text{de} = \frac{\%\ \text{Diastereomer 1} - \%\ \text{Diastereomer 2}}{\%\ \text{Diastereomer 1} + \%\ \text{Diastereomer 2}}$$

Scheme 13.23 Photocyclization of tropolones appended with chiral auxiliaries. A chiral auxiliary has a better influence within a supramolecular structure than in solution.

auxiliary, a covalently linked chiral inductor, to induce chiralilty in the products. Generally, this method does not work well for photochemical reactions in solution. However, by a host enforced preorganization technique that creates a close proximity between the reactive center and the chiral auxiliary, chiral induction in photoproducts has been achieved.[42] Two examples, **44** in which the host is an OA capsule and **45** in which the host is a NaY supercage, are presented in Scheme 13.23.[90,91] In these cases, the chiral auxiliary has no influence in solution and the diastereomeric excess (de) is small ($< 10\%$) while in a supramolecular environment it is able to bring about diastereoselectivity in the photoproducts to the extent of 88%. Cation---π interaction in zeolites and confined space in an OA capsule probably play an important role in this unusual phenomenon.

13.20 Supramolecular Effects on Reaction Intermediates I: Mobility Control on I@host Assemblies

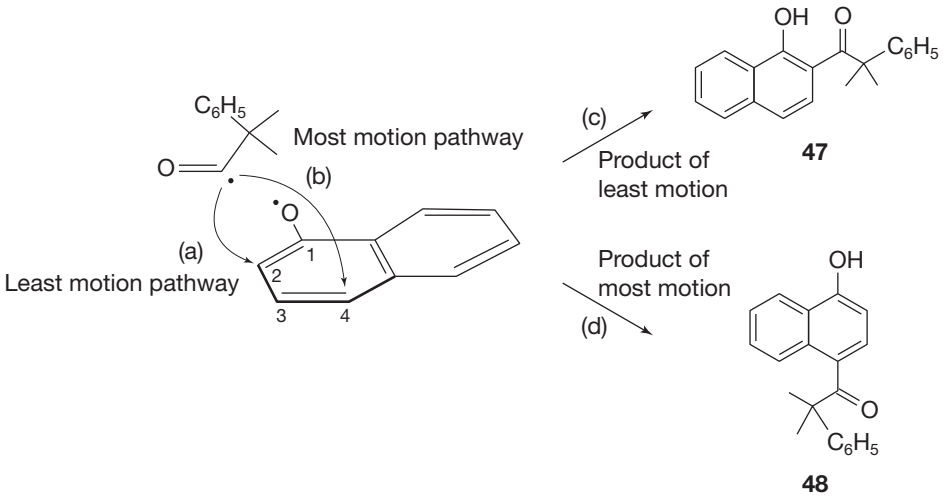
This section deals with examples where the supramolecular effect is used to control reactions for which a single primary photochemical process produces a single intermediate (I) that leads to multiple products (Scheme 13.2e). For example, photolysis of naphthyl ester (**46**) gives a geminate singlet radical pair A via β-cleavage (Scheme 13.24).[92] This radical pair, as shown in Scheme 13.24, results in at least seven products (**47**–**53**). Can this reaction be made selective to the extent that only products from the initial primary geminate singlet radical pair, **47** and **48**, are formed? To achieve this, first we need to restrict the translational mobility of the partners of the radical pair. We also need to keep the radical pairs close to each other to enable



Scheme 13.24 Photo-Fries reaction of a naphthyl ester.

faster radical–radical recombination than decarbonylation (to produce **49**–**53**) to favor formation of **47** and **48**. A supercage rather than a solvent cage is needed to keep the radical pair together for a longer time and meet the requirements for selectivity.

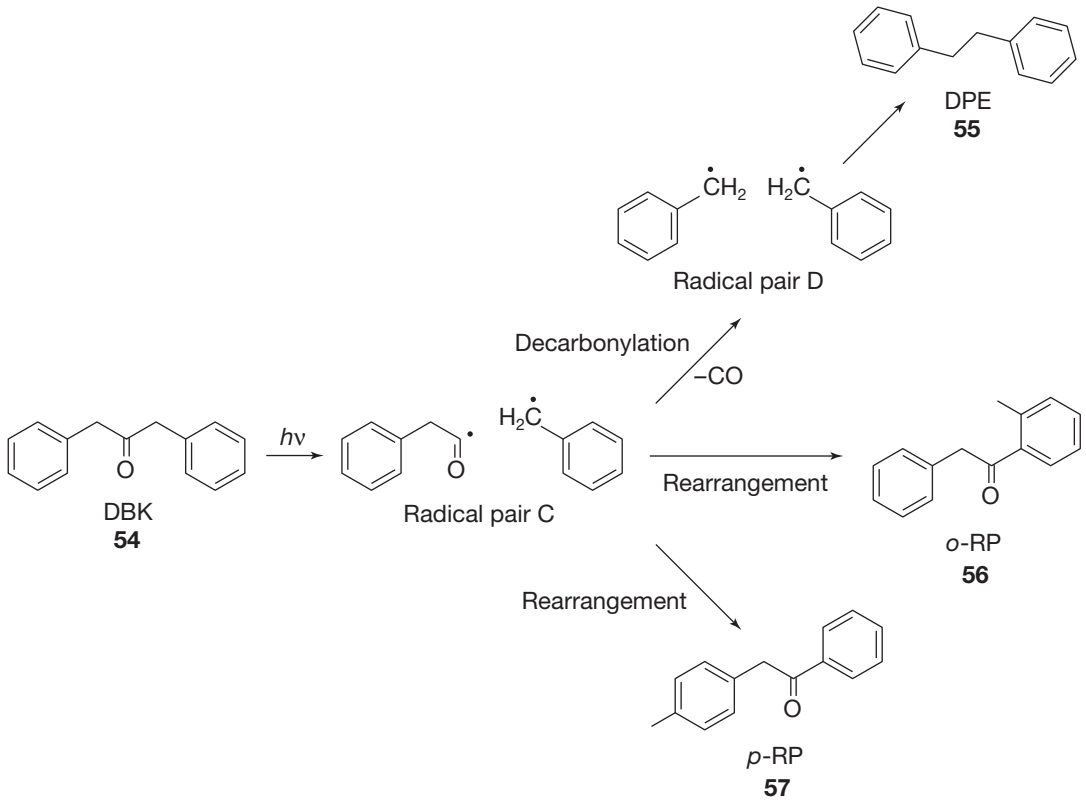
Thus, in principle, a micelle, a cavitand (CD), a hemicarcerand (OA), or solid host, such as zeolite, should reduce the observed products from nine to two. Photolysis of supramolecular complexes of guest **46** with any of the above hosts has proved this reasoning to be correct by only producing **47** and **48**.[92–97] Thus, the incarceration effectively restricts translational motion to favor formation of **47** and **48**. To further enhance the selectivity of the reaction, the system must reduce the rotational



Scheme 13.25 Two pathways requiring different extents of motion yield different products during photo-Fries reaction of a naphthyl ester.

mobilities of the radical pair A. Migration of the acyl radical to the 2-position of the naphthoxy radical requires much less relative rotational motion than migration to the 4-position (Scheme 13.25). Thus, if the rotational mobility of the acyl radical pair is severely restricted, a single product (**47**) is possible and was achieved with **46**@NaY supercages and **46**@$(OA)_2$ complexes. The rotational mobility is reduced in NaY by the cation Na^+---radical interaction and the acyl radical migration to the 4-position of the naphthoxy radical forbidden by the lack of free space in the OA capsule.

The above exemplar of the supramolecular control to favor products **47** and **48** during photo-Fries reaction results from a series of steps involves only singlet states: $^*R(S_1) \rightarrow {}^1I(RP) \rightarrow {}^1P$. The $^1I(RP) \rightarrow {}^1P$ step is spin allowed and occurs efficiently when the pair is constrained from diffusional separation. The situation is quite different when a $^3I(RP)$ is involved. As an exemplar of the latter (Scheme 13.26), we consider DBK (**54**), which upon photolysis in solution yields the only product, diphenyl ethane (DPE, **55**) via an α-cleavage process similar to the one described above. In this case, rearrangement similar to the one that occurred in naphthyl ester (**46**) to yield *o*-RP (**56**) and *p*-RP (**57**) could compete with the decarbonylation process; however, in homogeneous solution decarbonylation is essentially complete. This variation has its origin in the different spin characteristics of the reactive intermediates (I): Photoreaction of **54** occurs from the triplet state, while that of **46** occurs from the excited singlet state. In **54**, the radical pair $^3I(RP)$ is generated by the cleavage process in $^*R(T_1)$; therefore, ISC to singlet radical pair, $^1I(RP)$, must precede the coupling. In solution, the rate of ISC $^3I(RP) \rightarrow {}^1I(RP)$ is much slower than the rate of diffusion of $^3I(RP)$ out of the solvent cage. As a result, the rearrangement products **56** and **57** are formed as very minor products ($\sim 0.2\%$). Therefore, to control the reaction toward formation of the rearrangement products, first we must provide a supercage for the primary radical pair. This reasoning indeed works to a certain extent even in the



Scheme 13.26 Possible products during Norrish Type I reaction of DBK.

relatively fluid supercages of micelles: Irradiation of **54**@SDSmicelle yields 5.5% of the *p*-RP (**57**).[98] Since micelles are fluid and flexible structures and offer much less restriction than carcerands and zeolites, we would expect the yield of rearrangement products to increase with the more rigid carcerands and zeolites as hosts.

Indeed, a significant enhancement of the restriction of mobility of the I(RP) occurs in the more rigid supercages of zeolites. For example, photolysis of **54**@NaX gave **56** and **57** in 40% yield, a dramatic increase from that in solution (0.2%) and micelle (5.5%).[99–101] The reaction within a zeolite occurs in the small and rigid supercage (Fig. 13.12), where the complexation to cations reduces the translational and rotational mobility of the primary radical pair C. The data in Table 13.4 clearly show that with increasing size of the exchangeable cation the following changes in product distributions occur: (1) The extent of primary radical pair coupling products relative to decarbonylation product increases and (2) the ratio of the products from ortho-coupling to para-coupling increases. These results are consistent with a simple supramolecular steric effect in the reduction of the free space (Fig. 13.28) available to the primary, ($C_6H_5CH_2CO^{\bullet}$ $^{\bullet}CH_2C_6H_5$), and secondary, (decarbonylated) radical pairs ($C_6H_5CH_2^{\bullet}$ $^{\bullet}CH_2C_6H_5$), produced by photolysis of **54** (Scheme 13.26). Observed

Table 13.4 Product Distributions from the Photolysis of **54**@MX, **54**@OA_2, and **54**@micelle

Medium	DPE (**55**) (%)	*o*-RP (**56**) (%)	*p*-RP (**57**) (%)	[**56** + **57**]/**55**
LiX Zeolite	80	5	15	20/80
NaX Zeolite	60	15	25	40/60
KX Zeolite	40	40	20	60/40
NaX/C_6H_6 Zeolite	5	60	35	95/5
OA Capsule	51		49	49/51
SDS Micelle	95		5.5	5.5/94.5
Water	100		0.2	0.2/99.8

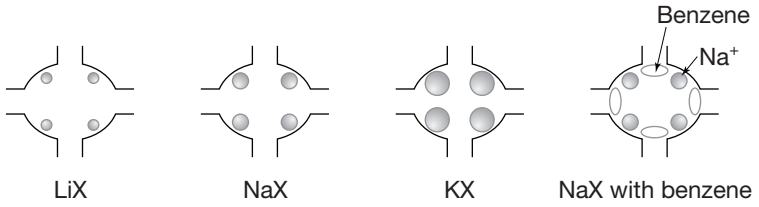
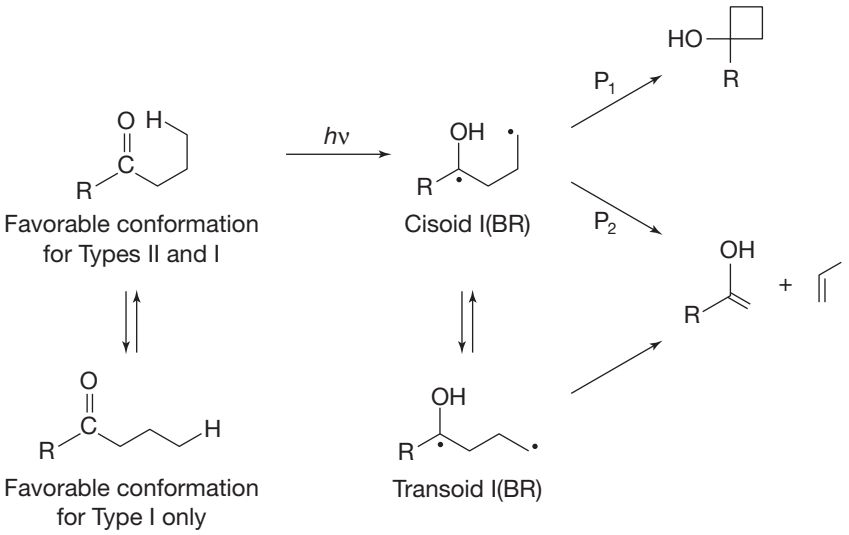


Figure 13.28 Schematic representation of how the free space within the supercage varies with the size of the cation. Also, the free space could be controlled with adsorption of organic molecules, such as benzene.

selectivity for ortho-coupling product **56** over para-coupling product **57** is similar to the observations in the case of naphthyl ester (**46**) (Schemes 13.24 and 13.25) and its origin once again is related to the restricted rotation in a supercage with very little free space. On further reduction of the free space within the supercage by adsorption of benzene as a coguest in a **54**/C_6H_6@NaX complex (Fig. 13.28), rearrangement products **56** and **57** form in 95% yield![100–103]

From the above examples in porous solid zeolites, it is clear that for supermolecular complexes a decrease in the free space of the reaction cavity favors rearrangement products of I(RP). This trend is also achieved in aqueous solution. For example, when the capsule **54**@OA_2 was irradiated in water, *p*-RP (**57**) was obtained in 49% yield, a significant improvement from 0.2% in water.[104,105]

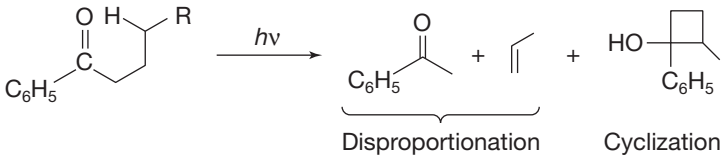
Now, we consider a 1,4-BR intermediate, I(BR), yielding products via two processes (P_1 and P_2). As an exemplar of I(BR) consider the 1,4-BR derived via Type II reaction of carbonyl compounds (Scheme 13.27). As shown in Scheme 13.27, the 1,4-BR derived via the γ-hydrogen abstraction can undergo two processes (P_1 = coupling and P_2 = disproportionation) that yield different products. The intermediate I(BR), although initially formed in a cisoid geometry, can adopt a transoid geometry through conformational rearrangement. The reactivities of these conformationally distinct



Scheme 13.27 Intermediates and possible products during Norrish Type II reaction of a ketone with an abstractable γ-hydrogen. Conformational effects emphasized.

rotomers differ (Section 9.18). The cisoid rotomer can plausibly yield both cyclobutanol and olefins via cyclization and disproportionation; on the other hand, the transoid rotomer can give only olefins via cleavage. The scenario here is similar to the benzoin ether photochemistry where the two conformations of R and *R underwent different primary photoreactions (Types I and II) (Section 13.14 and Fig. 13.4). In the current example, it is the two conformations of I (1,4-BR) undergoing different reactions. Can the same reasoning used in Fig. 13.4 be used here to control the chemistry of I(BR)?

In solution, generally the transoid BR conformation is preferred and the disproportionation products (P_2) are formed in larger amounts. How can we increase the amount of cyclobutanol (cyclization product) with supramolecular techniques? The essential preservation of the 1,4-BR intermediate in the cisoid conformation is possible in a rigid reaction cavity with little free space for the BR to rotate to the transoid conformer. This preservation of the 1,4-BR intermediate was achieved within NaX, NaY, and ZSM-5 zeolites and β-cyclodextrin.[106,107] Two such examples, butyrophenone (**58**) and valerophenone (**59**), are shown in Scheme 13.28. Irradiation of these ketones as complexes in these reaction media gave cyclobutanol in large amounts. In these supramolecular assemblies, most likely the cisoid I(BR) cyclized without relaxing to the more stable transoid I(BR). In principle, cisoid I(BR) can also disproportionate, which is likely when the cyclization product does not fit within the reaction cavity. For example, only cleavage products result upon irradiation of **58**@ZSM-5 and **59**@ZSM-5. It is very likely that within the smaller cavity of ZSM, the cisoid I(BR) was forced to undergo only the cleavage as the cyclobutanol (product of cyclization) would not fit in the channels of ZSM-5 (Fig. 13.12). This would represent a supramolecular steric effect on the formation of the cyclobuanol.

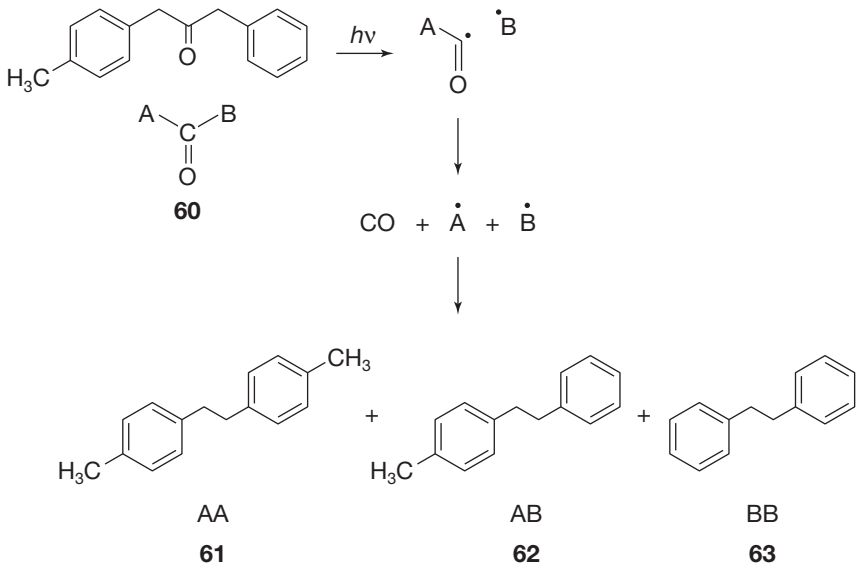


	Ketone	Medium	Ratio of the Products of Disproportionation–Cyclization
R = H	Butyrophenone (**58**)	Methanol	13.6
		NaX	2.7
		NaY	3.2
		ZSM-5	73.0
		β-Cyclodextrin–water	3.8
R = CH_3	Valerophenone (**59**)	Methanol	3.5
		NaX	1.2
		NaY	1.1
		ZSM-5	>100.0
		β-Cyclodextrin–water	2.9

Scheme 13.28 Products of disproportionation and cyclization controlled by the shape and size of the reaction cavity.

13.21 Time-Dependent Supramolecular Effects on Reaction Intermediates (I)

The examples discussed in Sections 13.14–13.20 were concerned with supramolecular effects that control the primary photochemical $^*R \rightarrow I$ and secondary thermal $I \rightarrow P$ processes, where the R, $^*R$, I, and P remained within the supramolecular host during the entire reaction. In the time scale of the overall reaction ($^*R \rightarrow P$), the reaction cavity served as a carcerand and R, $^*R$, I, and P did not exit the reaction cavity. In other words, the guest@host complex remained a time-independent carceplex. This situation may not apply when the lifetime of an excited state ($^*R$) or an intermediate (I) is fairly long and exit of the guest from the host becomes important. Now, we describe supramolecular effects on reactions where some fraction of the reaction intermediates exit the reaction cavity before yielding the final products. Under such conditions, the prediction of the observed products must take into consideration the time the reaction intermediates spend in the different environments, that is, in a carcerand, hemicarcerand, or solvent cage (Section 13.8). For example, consider the carceplex–hemicarceplex assignments for $^*R$@micelle for an SDS micelle for R = naphthalene: The lifetimes of $^*R(S_1)$, $^*R(T_1)$, and an SDS micelle are $\tau_S \sim 0.1\ \mu s$, $\tau_T \sim 1000\ \mu s$ and $\tau_{Micelle} \sim 10\ \mu s$, respectively. Thus, since $\tau_S < \tau_{Micelle}$, $^*R(S_1)$@SDS the micelle is considered a carceplex; however, since $\tau_T > \tau_{Micelle}$, $^*R(T_1)$@SDS micelle is considered a hemicarceplex. The consequences of this distinction are considerable. For example, for the carciplex $^*R(S_1)$@SDS micelle, $^*R(S_1)$ is strongly protected from



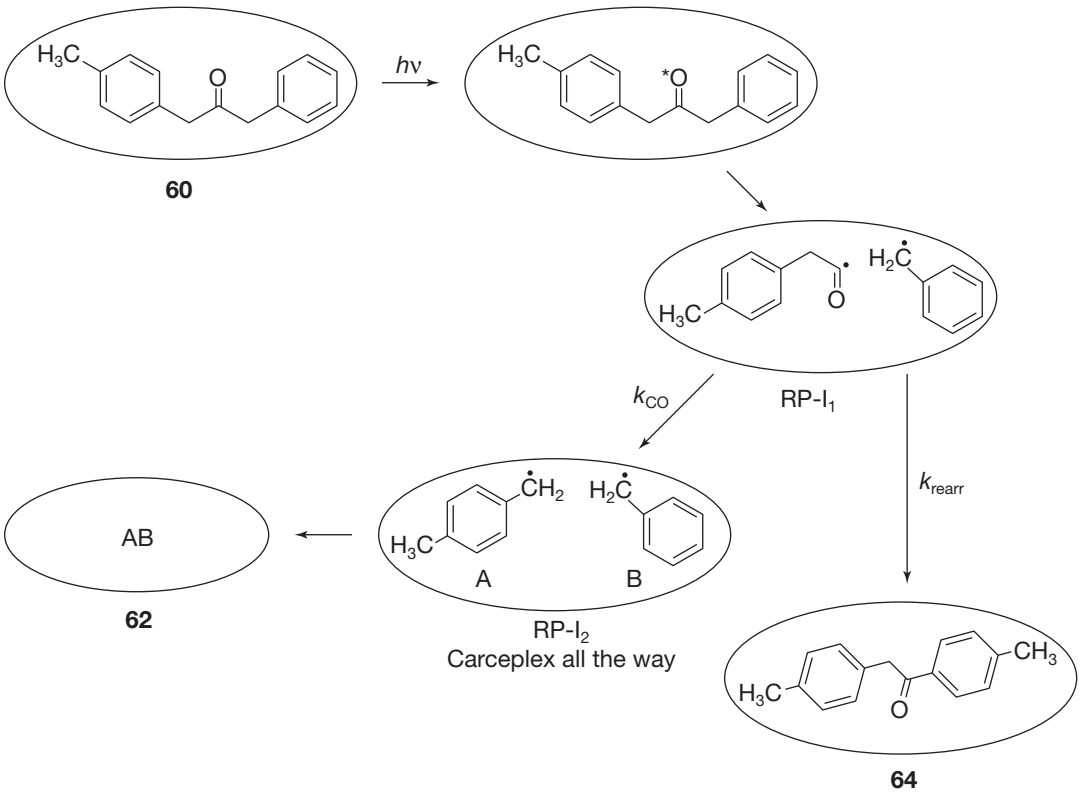
$$\text{Cage effect (\%)} = \frac{[AB] - ([AA] + [BB])}{([AB] + [AB] + [BB])} \times 100$$

Scheme 13.29 Possible products during Norrish Type I reaction of the unsymmetrical 4-methyl DBK.

bimolecular quenching by oxygen during its entire lifetime, whereas for the hemicarceplex $^*R(T_1)$@SDS micelle, $^*R(T_1)$ is only protected while it is incarcerated in the host. When $^*R(T_1)$ exits the host, strong quenching by the oxygen in the bulk aqueous phase can occur. Under conditions where the quenching by oxygen is faster than the return of $^*R(T_1)$ to a micelle, the rate of exit from the micelle determines the lifetime of $^*R(T_1)$.

In this section, we illustrate this feature with the photochemistry of an unsymmetrical DBK **60** represented as ACOB as an exemplar (Scheme 13.29)[108,109]

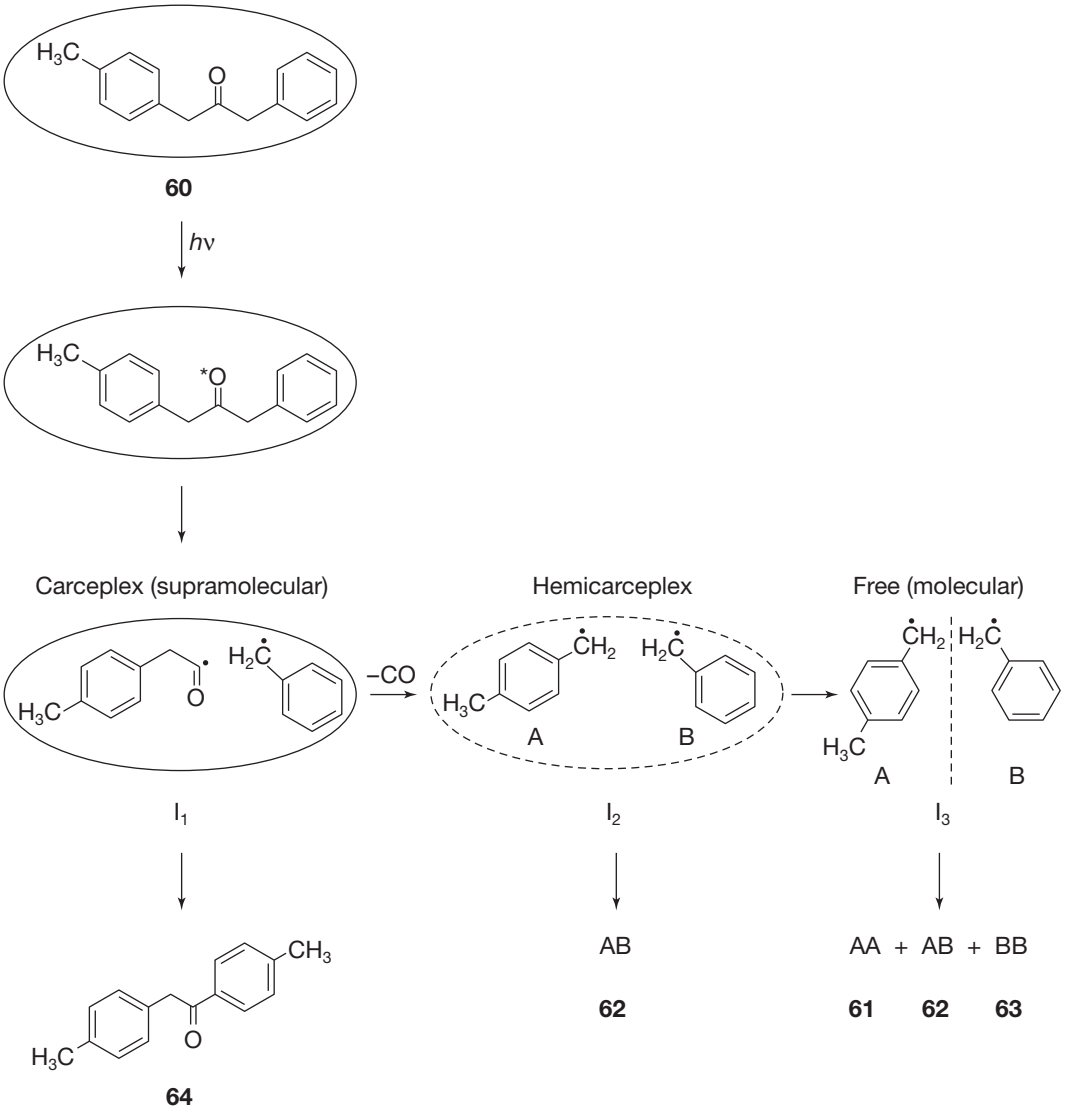
In homogeneous solution, all unsymmetrical DBKs (ACOB, where A and B are different groups) undergo photolysis to produce a primary ACO$^\bullet$ $^\bullet$B triplet geminate radical pair, $^3I(RP)_{gem}$, that decarbonylates to A$^\bullet$ + B$^\bullet$. The latter produce AA + AB + BB coupling products in a statistical 1:2:1 molar ratio through free radical–radical combinations (Scheme 13.29). In other words, the cage effect for these radical–radical reactions in nonviscous homogeneous solution is zero. A priori, we can imagine that depending on the type of supercage in which the primary product of α-cleavage, $^3I(RP)_{gem}$, is produced, the geminate radical–radical coupling products ACOB, ACOB' (B' is an isomeric group of B; ACOB and ACOB' are two molecules with the same molecular formula, but with different structures (see **60** and **64** in Scheme 13.30) or AB could be selectively formed for appropriately selected hosts. For example, in a very rigid and tight reaction cavity re-formation of the original



Scheme 13.30 Photochemical behavior of 4-methyl dibenzyl ketone in a carceplex environment. No radicals escape. Only AB and rearranged products are obtained.

ACO-B bond, which is broken, might be the only pathway allowed if translational and rotational motions are strongly inhibited. This process could be the case, for example, in tightly packed crystals.

As the host cavity becomes more flexible, the separation of the B$^\bullet$ radical from the ACO$^\bullet$ radical will occur, and recombination to form regioisomers (ACOB′) of the initial ACOB is possible. If the host allows considerable separation of the B$^\bullet$ and ACO$^\bullet$ radicals, but provides a strong boundary preventing them from becoming free radicals, decarbonylation may occur to produce a secondary geminate pair of A$^\bullet$ and B$^\bullet$ radicals. As discussed in Section 13.20, this occurs in zeolites and in an OA capsule where the rearrangement product is formed in a significant amount ($\sim$ 50%) and after decarbonylation only AB is obtained. In these cases, both the primary and secondary radical pairs are incarcerated during their entire lifetimes. As illustrated in Scheme 13.30, in these hosts R, *R, I, and P remain within the same reaction cavity until the end of the reaction. In other words, the products of the reaction could be predicted assuming the guest@host complex is a carceplex during the entire course of reaction *R $\rightarrow$ P.



Scheme 13.31 Photochemical behavior of 4-methyl dibenzyl ketone in a hemicarceplex environment. Some of the radicals escape. A mixture of AA, AB, and BB and rearranged products are obtained.

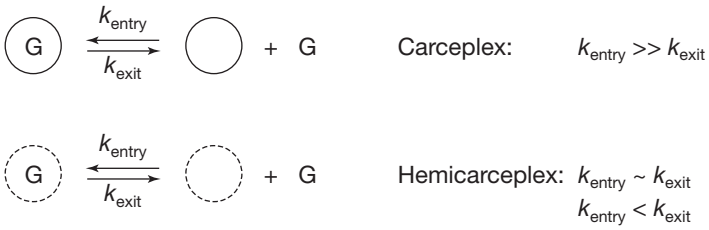
However, if the host structure is fluid and has a weak boundary for incarcerating the guest, a fraction of the radicals A and B exit the A/B@host complex and become free radicals. These free radicals undergo random radical–radical reactions resulting in the formation of AA + AB + BB. An exemplar of this situation is provided by the **60**@SDS micelle, as illustrated in Scheme 13.31.

The photochemistry of **60**@micelle was discussed in some detail in Sections 8.41 and 8.42, as well as in Section 13.20. Examples of supramolecular effects on the I(RP)@micelle → P@micelle were discussed in connection with magnetic effects on the products of photoreactions that involve an $^{*}R(T_1)$@micelle → $^{3}I(RP)$@micelle process. In particular, magnetic effects on the cage effect for radical–radical reactions

in micellar systems were described. Therefore, here we will only emphasize the supramolecular control of possible products from the I → P step.

Photolysis of **60** in nonviscous solvents results in a 1:2:1 mixture of products AA, BB, and AB (Scheme 13.29). However, photolysis of the **60**@micelle (e.g., HDTCl) gives AB as the product in a yield higher than that expected for a random 1:2:1 coupling of the free radicals $A^{\bullet} + B^{\bullet}$.[110−113] This significant change in product distribution favoring the formation of AB is due to the restriction of the mobility for the geminate radical pair provided by the host micellar structure. This change only occurs at or above the critical micelle concentration (the minimum concentration at which micelles are formed). The predominant formation of AB in a micelle is consistent with the entrapment and restriction of translational motion of the geminate radical pair in a small hydrophobic reaction cavity. If all the coupling between $A^{\bullet}$ and $B^{\bullet}$ radicals occurred within the micelle, the cage effect should have been 100% to yield only AB. The fact that this is not the case suggests that some fraction of the radicals $A^{\bullet}$ and $B^{\bullet}$ escape the micellar supercage. As illustrated in Scheme 13.31, the coupling reaction possibly occured both within the micelle and in the aqueous exterior. Therefore, with respect to the fraction of escaping $A^{\bullet}$ and $B^{\bullet}$ radicals, the supramolecular complex is considered a hemicarceplex. Thus, although the reaction starts as an *R@carcerand → I@carcerand, as a function of time, some fraction of the intermediate I@carcerand has become I@hemicarcerand. The extent to which the complex is a hemicarceplex depends on the relative rate of exit for the radical pair from the micelle to the aqueous exterior with respect to rate of coupling for the geminate $A^{\bullet}$ and $B^{\bullet}$ radicals. For example, for a carceplex the exit rate is expected to be much lower than the entrance rate while for the hemicarceplex both could be almost the same or the exit rate could be faster (Scheme 13.32; Section 13.8). As indicated above, just because R forms a carceplex there is no guarantee that *R, I, and P would form a careceplex with a given host.

The rate of exit for the radical pair depends on both the hydrophobicity of the radicals and the hydrophobicity of the micelle supercage. It is predicted and found that the cage effect increases with the number of methyl groups (increasing hydrophobicity) in the radical pair $A^{\bullet}$ and $B^{\bullet}$. For example, the cage effect within the hexadecyl trimethyl ammonium chloride micelle for DBK is 31%, whereas the cage effect for 4,4'-di-*tert*-butyl dibenzyl ketone is 95%. The results of photolysis of **60** in micelles



Scheme 13.32 Dynamics of exit and entrance of a guest from a hemicarceplex and carceplex. The full circle represents a carceplex and the dashed circle represents a hemicarceplex.

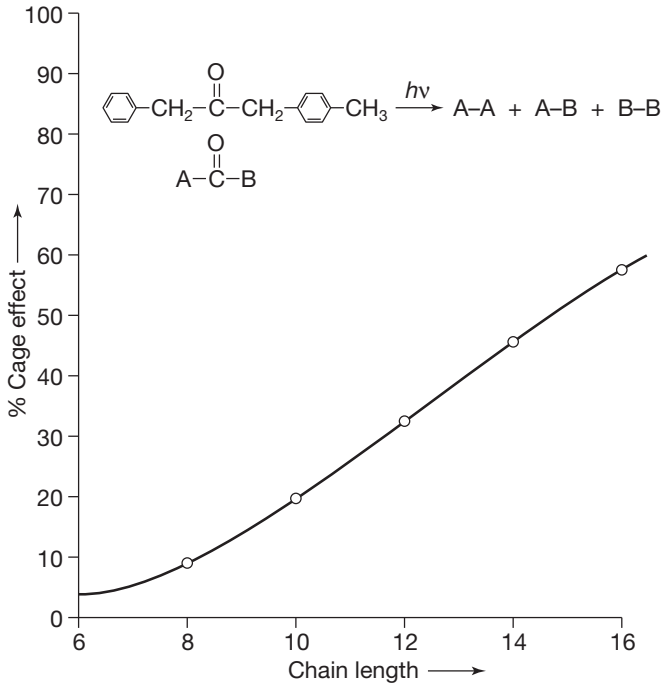


Figure 13.29 Dependence of the cage effect on the micellar size that is controlled by the alkyl chain length of the detergent.

of alkyl chain length between 6 and 14 (shown in Fig. 13.29) suggests an inversely proportional relationship between rate of radical escape from a micellar cage and the size of the micelle. The larger the micelle, the greater the hydrophobicity of the host and the greater the retention of the geminate radical pair. The estimated exit rates for the benzyl radical ($C_6H_5CH_2^{\bullet}$) from micelles of different sizes (sodium decyl sulfate: $2.7 \times 10^6\ s^{-1}$; SDS: $1.8 \times 10^6\ s^{-1}$, and sodium tetradecyl sulfate: $1.2 \times 10^6\ s^{-1}$) correlate well with the observed trend in the cage effect; that is, a larger micelle has a greater cage effect and because of its greater hydrophobicity slows the benzyl radical escape accordingly.

To summarize, the extent to which the geminate radicals ($A^{\bullet}$ and $B^{\bullet}$) can escape the micellar reaction cavity depends on both the size of the reaction cavity (micellar size) and the hydrophobicity of the RP. The more hydrophobic the radical, the slower its ability to venture outside the micellar reaction cavity. The larger the micelle, the lesser the radical pair's escape of the reaction cavity.[114,115]

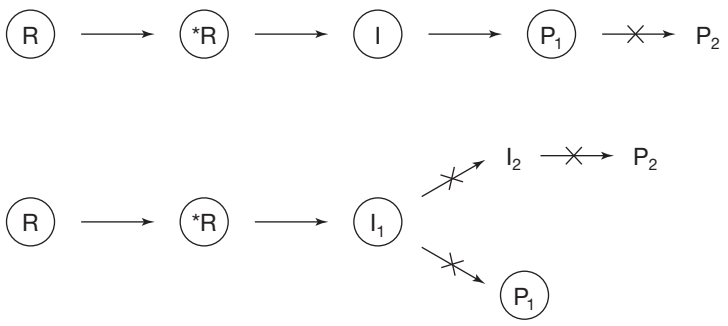
From the above presentation, it should be clear that consideration of the guest@host complex as carceplex or hemicarceplex depends on both the guest and the host, as well as on the time scales of the steps along the pathway $^*R \rightarrow P$. For example, hexadecyl trimethyl ammonium chloride micelle is a carceplex for photolysis of 4,4'-di-*tert*-butyl dibenzyl ketone (cage effect ~100%), but a hemicarceplex for DBK (cage effect ~30%). Thus, while analyzing photoreactions in a supramolecular assembly, the nature of the reaction cavity varies, depending on the lifetime of guests, reactions, intermediates, and the cavity.

13.22 Supramolecular Effects on Products (P@carcerand): Stabilization of Reactive Product Molecules (P)

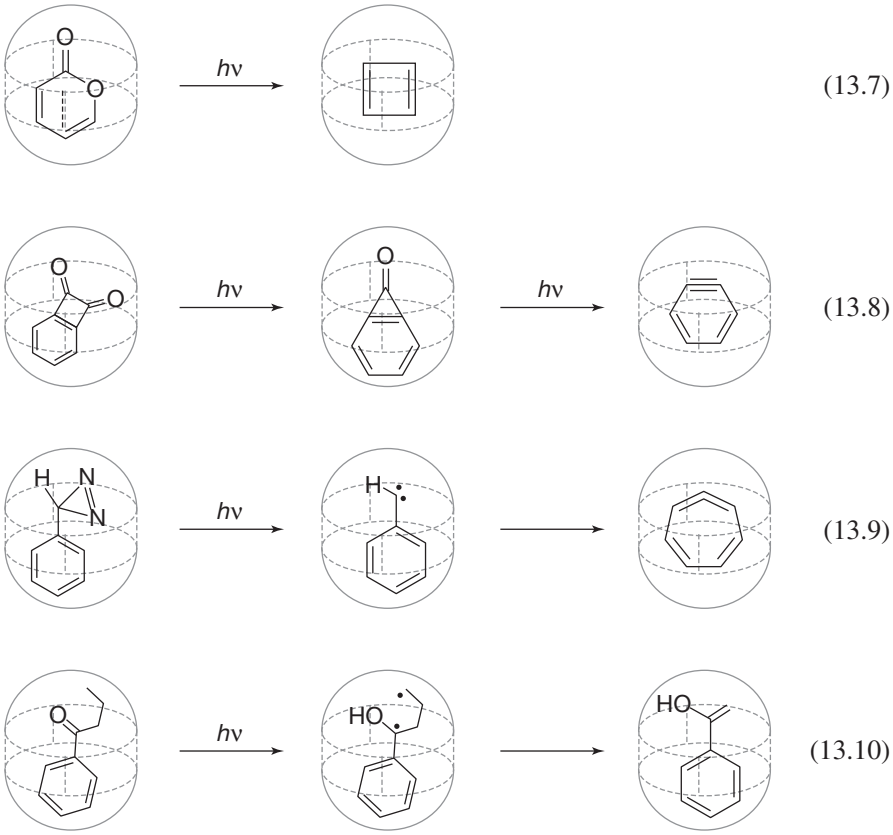
Preorganization of the reactant molecule(s) and continued influence of the host on R, *R, I, and P are essential for achieving selectivity in a supramolecular photochemical process. In a homogenous solvent, a primary photoproduct (P) could sometimes be reactive enough to transform itself to a different product. Similarly, a reactive intermediate (I), as the name implies, would further react to yield a stable product, (P). Supramolecular hosts have been used to "tame" the reactivity of unstable molecules and reactive intermediates (Scheme 13.33). Thus, the supramolecular host could prolong the life of a highly reactive primary photoproduct (P), such as cyclobutadiene and primary reactive species (I), such as radicals, carbenes, carbocations, and ion radicals. Examples of such stabilization are highlighted in this and the following sections. As illustrated in Schemes 13.33 and 13.34, extended incarceration of R, *R, I, and P is crucial to prolonging the life of reactive molecules and intermediates.

Photochemical reactions are often capable of producing highly energy-rich and transient intermediates (I) and reactive products (P). For example, molecules, such as cyclobutadiene, benzyne, benzocyclopropanone, and 1,2,4,6-cycloheptatetraene (Scheme 13.34), generally have a fleeting existence in solution at room temperature, as they often dimerize and/or react with oxygen. In contrast, when genertaed within a supramolecualr assembly in solution, these molecules are stable for hours to days at room temperature. A class of supramolecular carcerand hosts originally synthesized by Cram is very useful for this purpose (for one such example see Fig. 13.21).[116] Variations of the original Cram's hosts were also used, but for simplicity we represent all of them as a generic cage, (see Scheme 13.34).

As for cyclobutadiene, self-dimerization of the highly strained intermediate made characterization in fluid solutions impossible. However, upon irradiation of α-pyrone@carcerand, cyclobutadiene is generated as the product (Eq. 13.7).[117] Cyclobutadiene, very reactive toward self-dimerization, when generated and trapped within the carcerand under oxygen-free conditions is indefinitely stable at room temperature.



Scheme 13.33 Schematics of stabilization for reactive intermediates and highly reactive products through supramolecular architectures.



Scheme 13.34 Highly reactive molecules made stable with Cram's carcerand.

Benzocyclobutenedione serves as a precursor for both benzocyclopropanone and benzyne (Eq. 13.8). Photolysis (> 400 nm) of benzocyclobutenedione@carcerand yields the highly strained benzocyclopropanone (Eq. 13.8). This molecule, normally unstable at room temperature, once incarcerated, can even be subjected to X-ray crystallographic studies.[118,119] Benzyne produced by irradiation (> 300 nm) of benzocyclopropanone@carcerand through elimination of carbon monoxide, stable only at cryogenic temperature in inert matrices (< 10 K, $< -263°$ C), is stable for several hours at $-78°$ C within the confined space of a carcerand.

Usually, highly strained 1,2,4,6-cycloheptatetraene (Eq. 13.9) is characterized by generating it by photolysis of a diazo precursor at 15 K ($-258°$ C) in an Ar matrix. It was found to dimerize at higher temperatures when the matrix melted. As shown in Eq. 13.9, upon triplet sensitization, phenyl diazirine@carcerand yielded the 1,2,4,6-cycloheptatetratriene via rearrangement of phenyl carbene and the 1,2,4,6-cycloheptatetraene@carcerand was stable at room temperature as long it remained incarcerated.

A final example in this category is the stabilization of acetophenone enol produced by Type II reaction of butyrophenone (Eq. 13.10). Acetophenone enol, when free in solution, even in the absence of acid or base, readily tautomerizes to the keto form.

However, when generated by photolysis of butyrophenone@carcerand it was found to be stable for at least 3 days even in the presence of trifluoro acetic acid.[120]

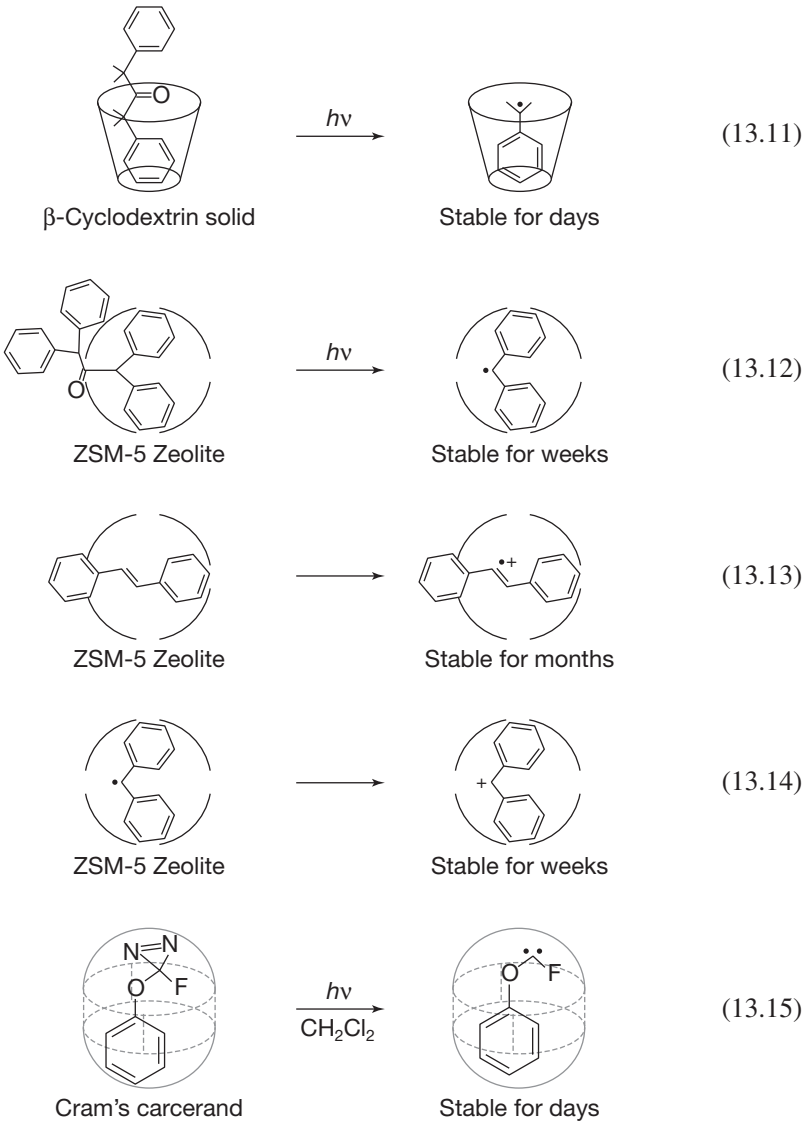
13.23 Supramolecular Effects on Reactive Intermediates (I@carcerand): Making Transient Intermediates (I) Persistent through Incarceration

Quite often the reactive intermediate I is a reactive carbon-centered free radical. Due to the diffusion controlled radical–radical reactions, the lifetimes of these radicals in isotropic solutions are on the order of microseconds or less. For example, benzyl radicals, when generated in isotropic solutions, by photolysis of DBKs undergo radical–radical combination reactions in times on the order of a few microseconds. Thus, these reactive carbon-centered radicals are transient reactive intermediates in solution. Dibenzyl ketones form complexes with solid cyclodextrins and zeolites. Carbon-centered radicals generated by photolysis of DBK@cyclodextrins or DBK@zeolites can have lifetimes of days.[121–124] For example, photolysis of α,α'-dimethyl dibenzyl ketone included in β-cyclodextrin generates a phenylethyl radical that when trapped in solid cyclodextrin is stable for 3 days or longer (Scheme 13.35, Eq. 13.11). Similarly, the diphenylmethyl radical generated in the channels of ZSM-5 zeolite by photolysis of tetraphenyl acetone persists for weeks (Eq. 13.12). These examples show how the supramolecular inhibition of diffusion arrests radical–radical reactions to the extent that the transient free radicals in solution become persistent in radical@carcerand complexes.

In this context, note that radical cations of stilbene and other polyenes produced by photolysis could be stabilized for months in the channels of ZSM-5 zeolite. 1,*n*-Diphenylalkene cation radicals, which have a nanosecond lifetime in solution, are stable for months in the channels of ZSM-5 (Eq. 13.13)[125,126] Similarly, organic carbocations remain unreactive for days within zeolites. One such example is the diphenylmethyl carbocation generated during photolysis of the diphenylmethyl radical trapped in ZSM-5 zeolite (Eq. 13.14).[124,127]

The final example in this category is the stabilization of fluorophenoxy carbene@carcerand. This carbene intermediate, a normally transient species, persists for days when generated by photolysis of 3-fluoro-3-phenoxydiazirine@Cram's host. Incarceration prevents carbene–carbene dimerization and reaction with water and oxygen (Eq. 13.15).[128]

From the examples above (Schemes 13.34 and 13.35), it should be clear that the concept of time scale and transience of reactive intermediates within supramolecular assemblies is different from that in isotropic solution. Intermediates normally considered transient, short-lived species persist within the above assemblies. Characterization of radicals and other transient species (radical ions, carbocations, etc.) requiring time-resolved laser techniques in solution can be carried with simpler methods when their reactivity is arrested by incarceration by a host. In supramolecular assemblies, intermediates and products, which based on solution behavior would be defined as highly reactive, become "tame" and have lifetimes several orders longer



Scheme 13.35 Examples of incarcerated reactive intermediates in zeolites, cyclodextrins, and Cram's carcerand.

than that in solution. Supramolecular assemblies stabilize the products by restricting their mobility and accessibility by other reactants.

13.24 Summary

Chemistry involves the mastery of an ever increasing universe of complexity. The chemist has mastered atoms, assemblies of a single nucleus and orbiting electrons held together through electrostatic interactions, and preorganized electronic configurations

that define the structure and control the reactivity of atoms. Proceeding to molecules, assemblies of two or more atoms, the chemist has mastered the molecular structure through an understanding of the covalent bond. The natural extension of molecular structure is the "supermolecule," an assembly of two or more molecules whose structure and control requires an understanding of intermolecular noncovalent bonds. Supermolecules are the building blocks of supramolecular chemistry. Although the level of complexity is much greater for supramolecular systems than for molecular systems, the principles described in this chapter allow a means of guiding expectations and classifications for a merging of supramolecular chemistry and photochemistry. Supramolecular chemistry is a work in progress concerned with mastering the rules of noncovalent bonds as they apply to the understanding and control of photochemical reactions.

Using the guest@host complex as a paradigm, this chapter describes how the journey from the solvent cage to the supramolecular cavity provides a systematic and useful means of understanding and controlling the chemistry of *R@host and I@host complexes, the key reactive intermediates of the fundamental paradigm for organic photochemistry. In the next decades, chemists will seek the development of a powerful paradigm of the noncovalent, intermolecular bond and apply this knowledge for the ever increasing complex structures ranging from materials sciences to chemical biology. Such knowledge will open new horizons for the photochemist to continue to harness and exploit the supramolecular features of *R@host and I@host complexes.

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