Photochemistry in Organized and Confining Media: A Model

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Introduction

There are many examples which demonstrate that organized and constraining media[1] influence the abilities of guest molecules to change their shapes during the course of photoreactions,[2] but few in-depth explanations delineating the responsible factors.[3] In this Account, we present a general qualitative model which identifies what we believe to be the principal host-related factors determining the nature of the environment experienced by a guest molecule undergoing a photochemical reaction in a constraining medium.[4] In spite of our emphasis on photochemical processes, many of the conclusions derived from the model are applicable to thermal reactions also. Although examples are chosen mostly from our own studies, the work of many others[2] is the foundation upon which we have built.

The point at which a host environment begins to constrain the molecular motion of a guest (so that reactivity is influenced) is somewhat subjective. Any species will have an effect on another, but the magnitude of the interactions and their consequences may be imperceptibly small. Central to the complexity of describing reaction sites in isotropic media is the initial spatial distribution and temporal redistribution of free volume which must be present at a site in sufficient quantity if reactant molecules are to be able to undergo the shape changes required for their transformation to products.

At room temperature important relaxation modes of low-viscosity, nonpolar solvents can occur more rapidly than the rates normally encountered for deactivation of S_1 and T_1 excited states.[5] Under such conditions, temporal fluctuations in microscopic solvent structure may permit all molecules in the solution to be exposed to a "single effective environment" during their excited lifetimes. An average of stochastic site morphologies can be inferred from observed rate constants, photoproduct distributions, or optical spectra. In many cases, the average may not correspond closely to the mean site type, nor does it allow the breadth of the distribution of site types to be ascertained. For example, macroscopically homogeneous polar media like water and water–alcohol mixtures can offer microscopic sites to reacting excited-state solutes.[6,7] These sites may have a disproportionate influence on the net photochemical behavior of the solute. As a consequence of their long relaxation times and microscopic inhomogeneities, even extremely viscous isotropic nonpolar solvents, polymers, or glasses of low molecular weight host molecules can provide a wide variety of effective site types, each with differing constraints, to a photosensitive guest molecule.[8-10]

This Account deals with media which are thought to offer a limited number of sites to reactants and whose reaction cavities possess limited free volume in specific locations. It should be noted that many potential sites

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(3) Turro, N. J.; Garcia-Garibay, M. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991; p 1.

(4) A more detailed presentation of the model has appeared elsewhere: Ramamurthy, V.; Weiss, R. G.; Hammond, G. S. In *Advances in Photochemistry*; Volman, D. H., Neckers, D., Hammond, G. S., Eds.; Vol. 18; Wiley-Interscience: New York, 1993; pp 67–234.

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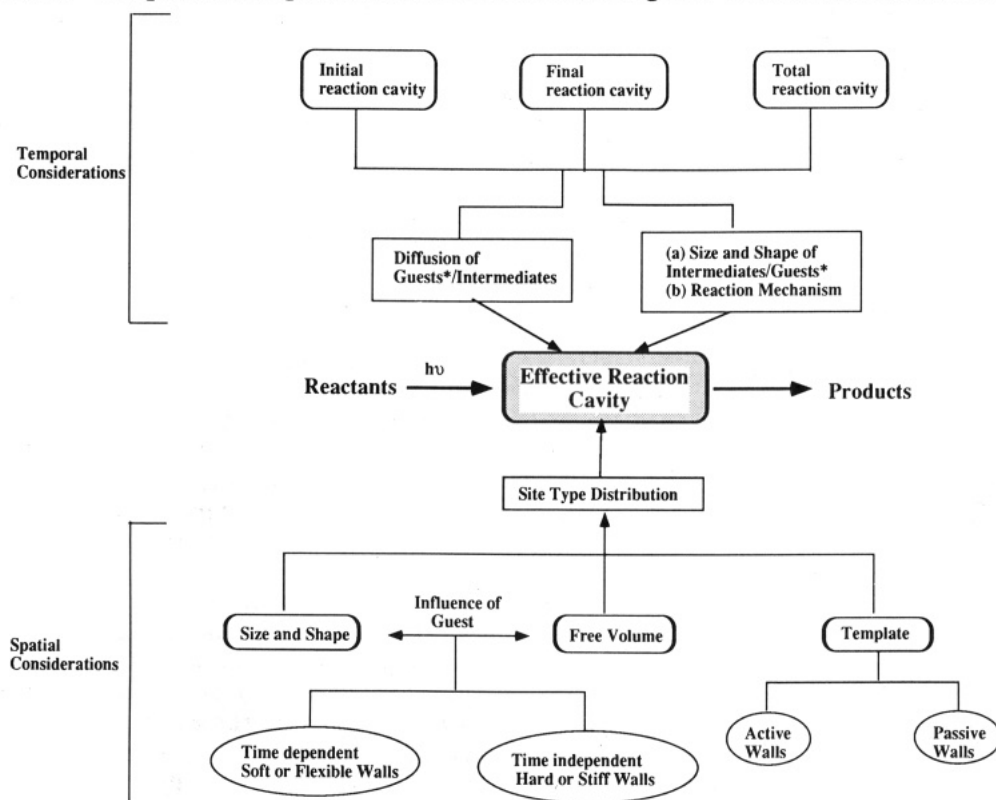
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Chart I.   Temporal and Spatial Considerations Affecting the "Effective Reaction Cavity"[a]

[a] See text for explanation of entries.

may be intrinsic to a medium or created by the presence of guest molecules, but, by definition, information regarding only the occupied sites can be accessed by this model.

The Model

The model should be recognized as no more than *a* model, that is, a point of departure for further refinement and experimentation which requires that the site at which photoreactions of guest molecules occur be categorized according to several dynamic and structural parameters. These parameters are included in the form of a flow chart (Chart I) which focuses on the characterization of the "effective reaction cavity" (*vide infra*). Each parameter will be discussed separately and then integrated with other related ones. Time is measured within the model according to the period required for a reactant molecule to be transformed to its photoproducts; space is defined by the relative dimensions and shape of the reaction cavity as compared to those of the reactants and photoproducts and the motions linking them.

Reaction Cavity. We expand the concept of a "reaction cavity", originally developed by Cohen to

describe reactions in crystals,[11] to include a number of organized and constraining media (Figure 1). The dimensions of the reaction cavity may be measurable and static, as in the case of some zeolites, or may be less well-defined and transitory, as in the case of liquid crystals. The volume of a reaction cavity may be very small (as in crystals and cyclodextrins), potentially very large (as in micelles), or undefinable because of the lack of a boundary in at least one dimension (as on surfaces of silica). Cavities may be separated into three temporal categories: an "initial reaction cavity", defined by the space in which the excited states of the reacting molecules are generated; a "total reaction cavity", which encompasses the space and molecular environment which the excited molecules and their intermediates explore from the time of their inception to the moment of their final product-determining steps; and a "final reaction cavity", which includes only the sites in which the product-determining steps occur. The space which controls the product distribution and the reactivity of the excited guest and/or the intermediates, the "effective reaction cavity", may be any one of the three.

The exact size and shape of an effective reaction cavity are related to a number of factors (Chart I), including the nature of the guest molecues' reaction mechanisms. In certain cases, especially those which involve the probability of encounters by two or more species, all of the space explored by excited molecules and their intermediates before they yield final products may be included in the effective reaction cavity. When the distribution of specific product types is being probed, knowledge of only the final cavity may be necessary to define the effective reaction cavity. These two cases are illustrated by the photobehavior of α-alkyl dibenzyl

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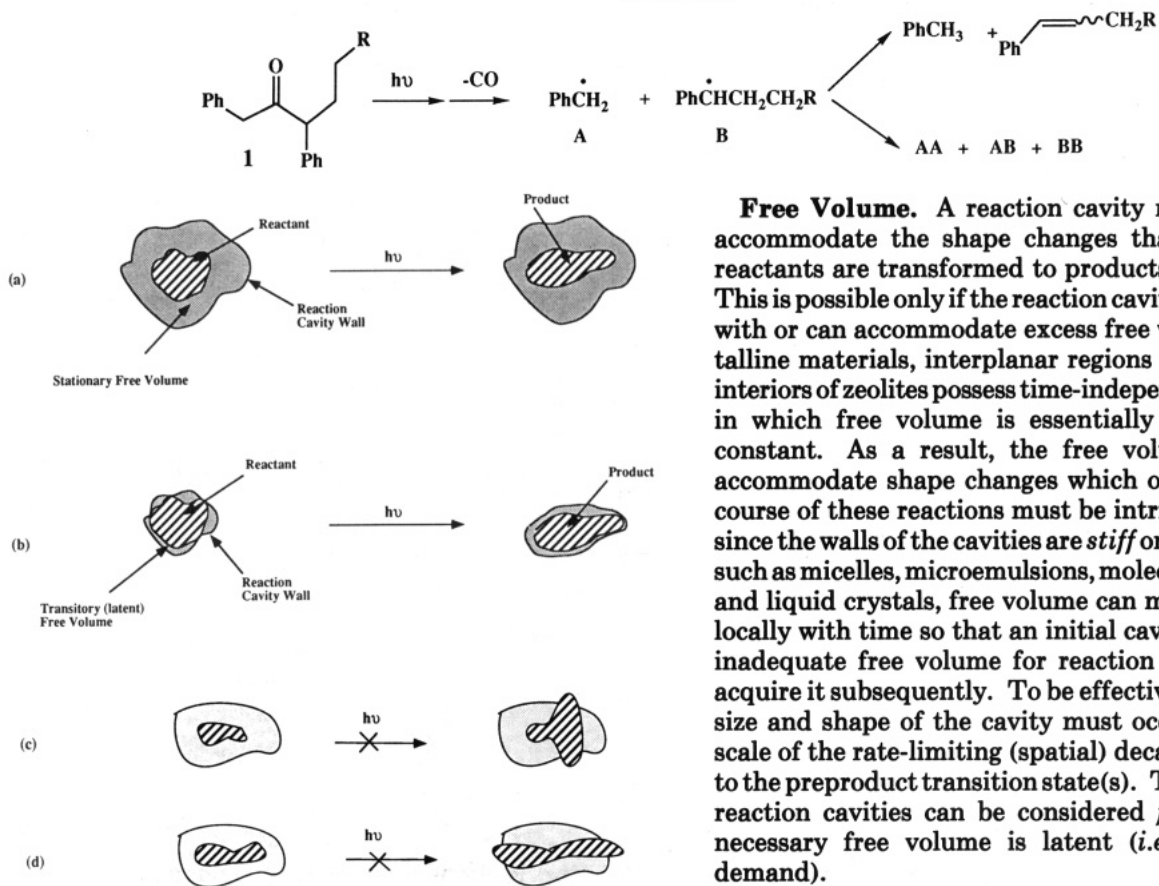
Scheme I

Figure 1. Cartoon representation of a hard (a, c, and d) and a soft (b) reaction cavity. In (a) the shape and size of the reaction cavity does not change during the reaction. In (b) the free volume required for the reaction becomes available as the reactant transforms to the product. Cavities (shaded) with stiff walls and which do not possess adequate free volume in specific directions to permit transformation of guest molecules (striped) to their photoproducts are represented in (c) and (d).

ketones (**1**) included within zeolites.[12] Excitation of **1** is followed by α-cleavage (in addition to γ-hydrogen abstraction) and subsequent decarbonylation to yield the geminate radicals A and B (Scheme I).[13] Reaction of two A radicals can yield only coupling products (AA) whereas reaction between two B or an A and a B radical yield both coupling (AB and BB) and disproportionation products. The ratio of encounters of A/A, A/B, and B/B pairs, as discerned from the photoproduct distributions within zeolites, depends upon the *total* space explored by A and B during their transient lifetimes; the effective reaction cavity, defined in this reaction as the space explored by two radicals from the moment of their creation until they react with each other, is required to explain the product distribution. On the other hand, the ratio of coupling to disproportionation products depends only upon the "final reaction cavity" experienced by each of the A/B and B/B encounter partners.

Free Volume. A reaction cavity must be able to accommodate the shape changes that occur as the reactants are transformed to products (Figure 1b–d). This is possible only if the reaction cavities are endowed with or can accommodate excess free volume.[14] Crystalline materials, interplanar regions of clay, and the interiors of zeolites possess time-independent structures in which free volume is essentially stationary and constant. As a result, the free volume needed to accommodate shape changes which occur during the course of these reactions must be intrinsic to the host since the walls of the cavities are *stiff* or *hard*. In media such as micelles, microemulsions, molecular aggregates, and liquid crystals, free volume can migrate and vary locally with time so that an initial cavity may include inadequate free volume for reaction to proceed but acquire it subsequently. To be effective, the change in size and shape of the cavity must occur on the time scale of the rate-limiting (spatial) decay paths leading to the preproduct transition state(s). The walls of such reaction cavities can be considered *flexible* or *soft*; necessary free volume is latent (*i.e.*, provided on demand).

A striking relationship between the stiffness of the walls of a reaction cavity and the ability of a guest molecule to be influenced by it is observed in the Norrish II reactions of 2- and *sym*-alkanones (**2**) in several layered phases with similar packing arrangements. These include the hexagonally-packed interdigitated and normal bilayer gel phases of 50% aqueous potassium stearate (KS) and 50% aqueous KS/1-octadecanol (KSO),[15] the layered hexatic B and orthorhombically-packed solid phases of *n*-butyl stearate (BS),[16] and the hexagonally-packed (less stiff rotator) phase II and orthorhombically-packed (very stiff) phase I layered solids of heneicosane (C21).[17] Although each set of hexagonal and orthorhombic layered phases is very similar in its packing arrangement, the stiffness of the walls associated with the reaction cavities they provide is quite different; qualitatively, stiffness increases in the order KS < KSO < BS < C21. The solid phases of C21 are most restrictive and incorporate within their layers only the homologues of **2**, which are very near in length to the host molecules. The fragmentation/cyclization (E/C) photoproduct selectivities (defined as the E/C ratios from the ordered phase of the host divided by the E/C ratios from the isotropic phase of the host) show that the *sym*-**2** homologues most easily

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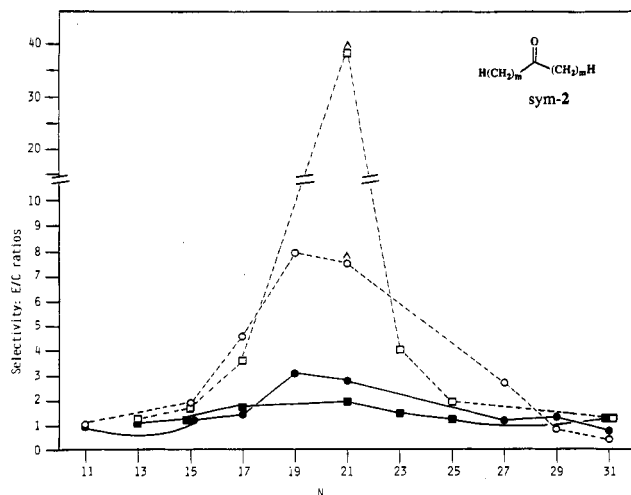
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Figure 2. E/C selectivities from irradiation of *sym-2* in BS (●, ○) and C21 (■, □) versus N ($=2m + 1$), the number of carbon atoms in the ketone chains: (●) from 20 °C/30 °C (hexatic B/isotropic) data; (○) from 0 °C/30 °C (orthorhombic solid/isotropic) data; (■) from 35 °C/45 °C (phase II/isotropic) data; (□) from 25 °C/45 °C (phase I/isotropic) data. Carats indicate lower limits to selectivities.

(isomorphously) incorporated into phase I of C21 experience reaction cavities with stiffer walls and less free volume than they do in the analogous orthorhombically-packed, layered solid phases of BS (Figure 2). However, the range of molecular lengths of the *sym-2* over which appreciable nonunity values of selectivity are found is much narrower for the C21 than the BS host. By comparison, the selectivities of the Norrish II photoreactions of all *sym-2* homolouges are small in the soft cavities of the KS and KSO gel phases.[15]

In addition to an adequate quantitiy, an appropriate spatial distribution of free volume within a cavity must be available if a reaction is to occur (Figure 1). Crystalline 7-chlorocoumarin (3) has two potentially reactive pairs of molecules in a unit cell: one which favors the formation of the *syn* head-to-head dimer is translationally related and has a center-to-center distance of 4.54 Å, and one which is oriented to yield the *anti* head-to-tail dimer is centrosymmetrically related and has an even closer center-to-center distance of 4.12 Å. The presence of appropriately placed free volume near the translationally-related pair and its absence near the centrosymmetrically-related pair as inferred from lattice energy calculations can explain why only the *syn* head-to-head dimer is obtained.[18]

The distribution of reduction (R) and Paterno–Buchi cycloaddition (C) products from irradiation of the conformationally-labile 10-undecenyl benzophenone-4-carboxylate (4, Scheme II) is sensitive to the quantity and distribution of free volume of the reaction cavities afforded by low-density polyethylene (LDPE) films.[19] Thus, irradiation of 4 in stretched LDPE films gives photoproduct mixtures which contain more than twice the relative yield of cycloadduct (C) than unstretched films. This result is interpreted to be a consequence

Scheme II
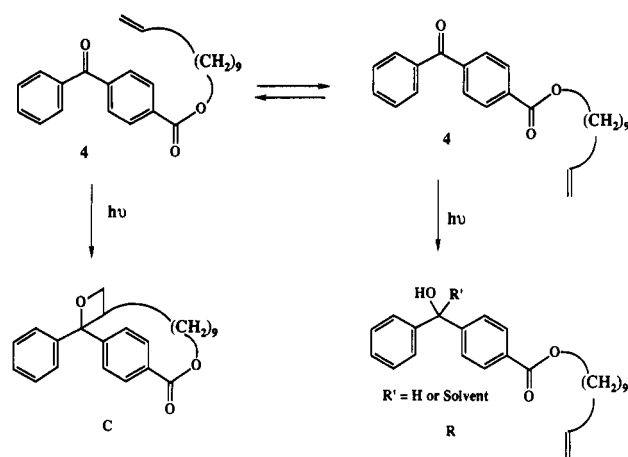
of the smaller reaction cavities of stretched LDPE[20] favoring conformations of 4 which place its ω-vinyl group in the vicinity of the carbonyl group.

Both the photochemical and the photophysical behavior of *trans*-stilbene and longer *all-trans-α,ω*-diphenylpolyenes critically depend on the zeolite type in which they are included.[21] In pentasil zeolites ZSM-5, -8, and -11 (channel diameter ~5.5 Å), wherein these polyenes are tightly held with virtually no free volume near the double bonds, enhanced fluorescence, protracted singlet lifetimes, and no photoisomerization occur. In the larger chambers of faujasites (supercage diameter ~12 Å), the same guest molecules do undergo photoisomerization. The limiting factor here and in many cases such as on the surface of silica is the cross-sectional area provided by host sites rather than the total free volume.

Active and Passive Reaction Cavities. A reaction cavity is considered "*passive*" and predictions concerning the behavior of the excited guest molecules can be made solely on the bases of cavity size, shape, and flexibiilty when there are no significant differences in the interactions of a guest molecule and a host at various points along its walls. The cavity is considered "*active*" and predictions concerning the course of photoreactions require consideration of different (and, perhaps, time-variable) orientations of the guest within the cavity when there is significant directionality to interactions between the walls and the guest. Interactions may vary from weak van der Waals forces to strong hydrogen bonds or electrostatic forces between charged centers. For example, a number of hosts such as cyclodextrins, silica surfaces, and urea and deoxycholic acid channels possess functional groups which can form hydrogen bonds which may orient guest molecules; surfaces of clays and zeolites often carry a large number of cations which can interact electrostatically with guests; and micelles, monolayers, and related assemblies of surfactant molecules have interfaces at which guest molecules can be oriented through hydrophobic–hydrophilic interactions.

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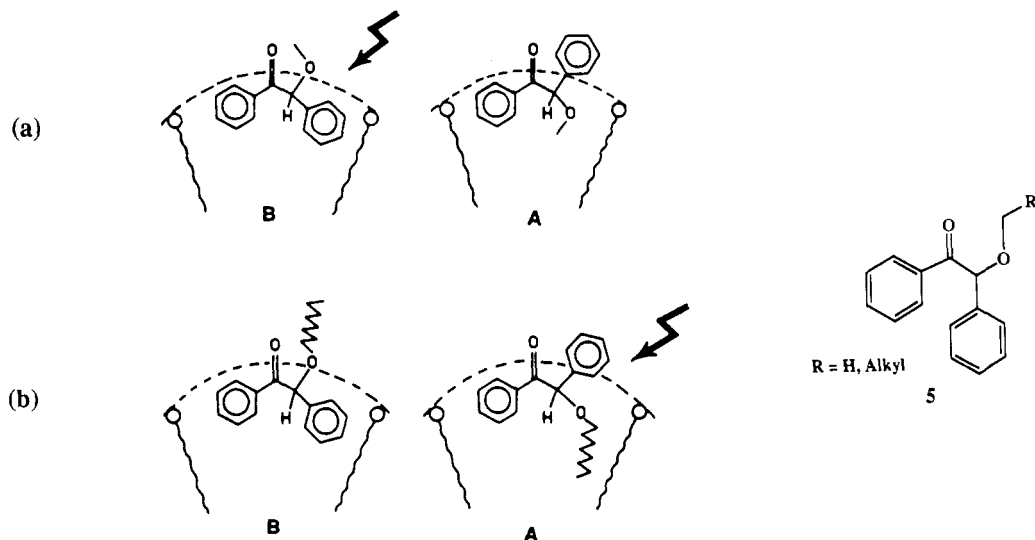
Figure 3. Representation of the probable solubilization modes of 5 with methyl (a) and long alkyl (b) ether chains at micellar interfaces (dashed lines). The long chain of 5 in (b) favors conformation A, which permits only Norrish Type I photoreaction, while the methyl groups of 5 in (a) favor conformation B, which permits both Norrish Type I and Type II photoreactions.

If the walls of an active reaction cavity are also "stiff" and there is a paucity of free volume, even weak interactions may be sufficient to force specific wall–guest orientations. Conversely, if the walls of an active reaction cavity are "flexible" and there is a large amount of free volume, the preorientation existing in the ground state may be lost upon excitation unless the wall–guest interactions remain strong throughout the course of the photoreaction. Thus, the walls of a reaction cavity, in addition to their other characteristics, may act as *templates* during critical moments along a reaction coordinate.

For example, benzoin alkyl ethers (5), independent of their alkyl chain length, yield predominantly Norrish Type I (α-cleavage) photoproducts in isotropic solvents.[22] When incorporated into sodium dodecyl sulfate or cetyltrimethylammonium bromide micelles, 5 can be directed to either Norrish Type I or Type II photoproducts depending on the magnitude of hydrophobic–hydrophilic interactions at the micellar–aqueous interface experienced by benzoin ethers with various alkyl chain lengths (Figure 3). Additionally, new potentially stronger or weaker interactions may develop between the cavity walls and functional groups created in intermediates during the course of a reaction. An example is found in the Norrish II reactions of *p-n-*alkylalkanophenones (6) in the ordered phases of *n*-butyl stearate (BS).[23] The proximity of carboxyl groups on BS molecules constituting the cavity and the carbonyl group of a molecule of 6 whose total length does not exceed that of a BS layer thickness ($m + n = 21$) will depend upon the values of m and n. The m, $n = 3, 18$ and $15, 6$ isomers are especially well-suited according to this model to permit dipolar interactions between the carboxyl and the carbonyl groups. After excitation of 6 and γ-hydrogen abstraction, the resultant triplet BR can donate a hydrogen bond to the same carboxyl groups, thereby increasing the strength and specificity of the guest interactions with the cavity wall.

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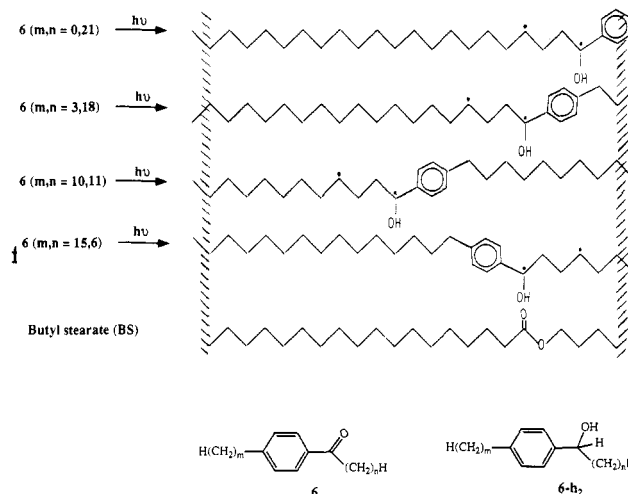(23) He, Z.; Weiss, R. G. *J. Am. Chem. Soc.* 1990, *112*, 5535.

Figure 4. Representation of extended *transoid* 1,4-biradicals (BR) from selected homologues and their probable orientations in a BS layer. Note the approximate distances of the hydroxyl groups of the BRs from a layer boundary (shaded areas) and their relative locations with respect to the carboxyl group of a BS molecule.

Infrared experiments in BS with 6-h₂, models for the BR, demonstrate that the purported hydrogen bonding does occur.

Indeed, the fragmentation to cyclization (E/C) product yields from 6 isomers clearly are maximal when *m*, *n* = 3, 18, but not when *m, n* = 15, 6! Examination of Figure 4 shows that while the hydroxy groups of the BR from both the isomers are well-suited to form hydrogen bonds, the biradical centers from the *m, n* = 3, 18 isomer are nearer a layer center (which provides the stiffest cavity walls) than those from the 15, 6 isomer. The proximity of the biradical centers from the BR of the *m, n* = 15, 6 isomer to the cylinder ends (which provide the most flexible walls) must allow the untethered BR chain end to adopt easily the conformations associated with both fragmentation and cyclization.

Microheterogeneity in Organized Media. All reaction cavities in an organized medium are rarely equivalent. Even perfect crsytals provide different reaction cavities at interior and surface sites. Similarly,

Scheme III
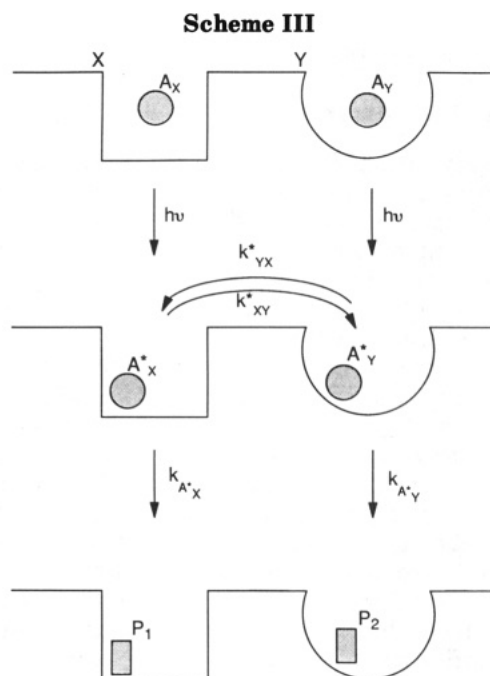
guests may reside at either the aqueous interface or the interior of micelles, and they usually coexist within a host such as cyclodextrin in a number of orientations. Generally, the relationship between the rates of hopping by molecules among various sites and the rates of reactions of excited states determines the probability that single molecules will experience multiple reaction cavities and, therefore, the distribution of various products derived from them.

Scheme III illustrates this potential complication with a reactant molecule (A) capable of inhabiting either a cubically-shaped (X) or a spherically-shaped (Y) site type. Excitation of molecules in the two site types, A_X and A_Y, gives A_X^* and A_Y^* initially. They will behave in the same way if they equilibrate between X and Y before yielding photoproducts (P_1 and P_2). In media with time-independent structures, equilibration requires that excited-state or preproduct intermediate lifetimes be very long since molecular diffusion is slow; in media with time-dependent structures, equilibration can be accomplished *via* fluctuations in the microstructure of the initial reaction cavities as well as translational motion of A to new sites. Additionally, *apparent* migration between X and Y sites may occur if A* molecules are capable of transferring their excitation energy to A molecules by any of a number of mechanisms (*e.g.*, energy hopping by exciton migration, Forster energy transfer, or trivial energy transfer).

Several limiting cases can be envisioned for Scheme III: For instance, (1) the rate of excited-state reaction may be much slower than the rate of site exchange so that equilibrium is established between A_X^* and A_Y^* before decay (k_{XY}^* and $k_{YX}^* \gg k_{A_X}^*$ and $k_{A_Y}^*$); (2) the rate of excited-state reaction may be faster than or comparable to the rate of site exchange so that only the initial site need be considered primarily in assessing a photoproduct distribution; (3) reaction from only one site can be detected despite the initial site occupancies so that only the final site is important. In one scenario for (3), $k_{A_Y}^* \gg k_{YX}^*$ and $k_{XY}^* \gg k_{A_X}^*$.

Mechanism 1 corresponds to the situation expected in fluid isotropic solutions. One consequence of mechanism 2 is that both the quantum efficiency and the photoproduct distributions may vary with the extent of conversion of A if the rate of exchange of ground-state molecules between sites A and B is slow enough to permit depletion of those sites in which reaction is faster. Another consequence is that it should not be possible to fit the excited-state decay of A* to a single-exponential function. In fact, systems involving micelles, the surfaces of silica and alumina, the channels and the cages of zeolites, and the toruses of cyclodextrins may be described best by more complicated versions of mechanism 2.[24] The presence of more than one reaction site and a mechanism 2 case is indicated by the excitation wavelength-dependent phosphorescence from *trans*-stilbene adsorbed onto the channels of zeolite Tl X[25] and by the multiexponential decay of excited singlets of aromatic molecules adsorbed onto zeolites.[26] Another apparent example of a mechanism 2 type system is found in the phase-dependent head-to-head/head-to-tail photodimer ratios from irradiation of *n*-alkyl *trans*-cinnamates in the isotropic, hexatic B, and crystalline phases of BS.[27]

According to mechanism 3, even if the initial ground-state concentration of A in site Y is much smaller than that in X, appreciable photoreaction from A_Y may occur through rapid $A_X^* \rightarrow A_Y^*$ molecular or energy transport. Thus, head-to-head photodimers are predicted from the crystal structure of 9-cyanoanthracene, but the head-to-tail dimer is isolated.[28] Reactions at defect trap sites, which are initiated by exciton migration from electronically excited molecules in the bulk, have been invoked to explain the results.

Potential Complications. Just as a host can influence the favored conformations and mobility of guest molecules, the guests can play a major role in defining their immediate environments. In many media, especially those whose sites have soft walls, it is not possible to describe a reaction cavity independent of the nature of the guest molecule(s). Even the most benign isomorphous substitution of a guest molecule into a host matrix must result in some disruption to the local environment; the electronic and shape changes which accompany the guest along its reaction course will induce analogous modifications to the cybotactic region. In all but sites offered by zeolites and other highly prestructured rigid hosts, the properties of the initial and effective reaction cavities are dependent upon both the host and the guest. Therefore, information derived from the photochemical or photophysical properties of the guest does not provide an accurate picture of the unadulterated host to the extent that guest-based disruptions to their local environment occur.

The disturbing influence of a pyrenyl group [as part of ω-(1-pyrenyl)alkanoic acids, *n*-**7**, where *n* is the

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number of carbon atoms in the acid chain] on the ability of polymethylene chains in the probe's vicinity to maintain their normal close-packing arrangement below the melting transition can be indicated by the depression in the melting temperature detected *microscopically* by fluorescence measurements at the reaction cavity, but not in the bulk.[29,30] Thus, it was shown that pyrenyl probe sites [whose distance from the aqueous interfaces of small unilamellar vesicles and microtubules of 1,2-bis(tricosa-10,12-diynoyl)-*sn*-glycero-3-phosphocholine or the layered phases of 50% aqueous KS, KSO, and rubidium stearate can be approximated from the value of *n*] are somewhat more available to water molecules at temperatures immediately below the host chain-melting transition than above them. The stiff, rodlike unmelted chains of the host find it more difficult than the melted chains to maintain close contact with a pyrenyl group, whose width is more than twice the cross-sectional diameter of a methylene group. As a result, lifetimes of excited singlet states of pyrenyl groups experience a pronounced increase as temperature is raised in the region of the transition; the melted chains of the vicinyl host molecules wrap themselves around pyrenyl units more efficiently, diminishing the probability that water molecules (as polarity quenchers) will be near a pyrenyl singlet.

Concluding Remarks

The very nature of this Account precludes more than inferential substantiation of our model at this time. In all but the crystalline media, detailed information representing molecular interactions of all molecules in a system is lacking; and even in those cases, we can make only "intelligent" guesses about how the structure of the medium changes as reactions of individual molecules progress. If our ultimate goal—to design reaction cavities *a priori* which lead to specific transformations of guest molecules—is to be achieved, it will be necessary first to learn how to quantify the features of a reaction cavity in empirical forms like the linear free energy relationships developed by physical organic chemists to describe the influence of substituents or isotropic bulk solvent properties on the rates of solute reactions.[31] Even the concepts of "change" and "order", which are fundamental to the evaluation of the influence of a medium on the reactions of its guest molecules, are subjective and qualitative since they must be referenced to a set of conditions which vary between experiments and laboratories. Clearly, the underlying quantitative bases are outside our understanding at this time. Our dissection of the subject into principal components hopefully will aid us and others to attack the parts to solve the whole. We expect (and hope) that the model will be scrutinized and modified based upon future experiments.[32]

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