

## From Molecular Photochemistry to Supramolecular Photochemistry. A Paradigm for the 1990s

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### Paradigms. An Overview.

A scientific theory may be viewed as a structure that is universally accepted by the community of practitioners and which has been termed the community's **paradigm**.<sup>1</sup> A mature science is governed by a single paradigm that sets the standards for legitimate work within the science it governs. The paradigm, being the set of beliefs which drives the intellectual activities of the practitioners, coordinates and directs the puzzle solving activity of the normal everyday science. The existence of a paradigm capable of supporting a normal science tradition has been put forth as the characteristic that distinguishes a mature science from a developing science. The nature of a paradigm is to possess components and connections that are accepted as necessary and sufficient to describe all observable phenomena.

The paradigm thus dictates what entities may exist and may not exist in the Universe and in doing so determines the legitimate puzzles that practitioners may attempt to solve; it assures the practitioners of the existence of solutions to these puzzles and it guides the construction and development of instrumentation and instrumental techniques that test the theoretical aspects of the paradigm. The paradigm provides the means of certification of practitioners. A puzzle is proposed by a mentor. Since the paradigm guarantees a solution, it is the skill of the young apprentice that is being tested, not the paradigm! When one demonstrates that he/she can solve the puzzle, one obtains a card that says that you are a scientist. Normal scientists presuppose that a paradigm provides the technical means of solving puzzles posed within it, and its structure provides the discipline that must be exerted in solving the puzzle. The excitement of the hunt and the detective work accompanying the solution of the puzzle provides the passion. The student

must provide the hard work and the energy! Failure to solve a puzzle is seen as a failure of the scientist rather than an inadequacy of the paradigm. To blame the paradigm for any failure to solve a puzzle, is to play a carpenter who blames his tools for poor work.

The paradigm of molecules and the covalent bond between atoms has been a powerful and unifying principle for chemistry and photochemistry for decades. We now consider a "paradigm shift" which has been occurring during the past two decades and which may take its place along side the molecular paradigm during the 1990s, namely, the paradigm of supramolecular chemistry.

### **From Atoms to Molecules to Supermolecules. From Molecular Photochemistry to Supramolecular Photochemistry.**

Chemistry is an ever expanding "universe" at the microscopic level requiring mastery of the invisible at ever increasing levels of complexity. Starting with atoms, assemblies of a single nucleus and orbiting electrons, the chemist has learned to understand atomic structure through mastery of the principles of electronic configurations. Proceeding to molecules, assemblies of two or more atoms, the chemist has learned to understand molecular structure through mastery of the principles of the covalent bond. It is quite natural that the next level of complexity will be supermolecules, assemblies of two or more molecules, whose structure will be understood through mastery of the principles of the intermolecular bond.<sup>2</sup>

Two or more molecules which behave as a unit as the result of intermolecular bonding may be considered a "supermolecule". The investigation of the structure, dynamics and chemistry of supermolecules defines the emerging discipline of "supramolecular chemistry". As in any discipline which is emerging and developing a paradigm which will define itself and its practitioners, there is a healthy debate over terminology and the universe of what the discipline will encompass. Until recently, this situation was acute for "supramolecular photochemistry", a subdiscipline for which the practitioners have tended to focus on molecular features and to be generally uninvolved in the development of supramolecular chemistry as a field. However, beginning in the 1990s an awareness of the potential of supramolecular ideas to invigorate the field has

developed, and photochemistry is truly being transformed as supramolecular photochemistry burgeons as an important and exciting subdiscipline.<sup>3</sup>

### **Receptors and Substrates**

To a large extent, supramolecular chemistry is all about receptors and substrates (hosts and guests). Receptor is a generalized term for a molecule or aggregate of molecules that is able to bind (ionic or molecular) substrates selectively by means of various intermolecular interactions resulting in a new assembly that can be considered as a supermolecule. A useful term for the formation of an intermolecular bond between receptor and substrate is "complexation", which preserves the chemically relevant "looseness" expected of non-covalent bonds. In this regard, the receptor (host) is the partner of the complex whose complexation properties are under investigation and whose design and structural variations determine these properties. The other partner, the complexed species, is the substrate. These terms are derived from the paradigms of enzyme chemistry and provide a working basis for the discussion of supramolecular photochemistry. We now consider how to transform the features of the enzyme paradigm into a paradigm for supramolecular photochemistry. First we consider the supramolecular paradigm in general and then consider examples of a supramolecular paradigm with a specific example: the photochemistry of dibenzyl ketone and its derivatives. Extensions of the results from the specific example should be readily transferable to other photochemical systems.

### **The Supramolecular Paradigm**

Structure is at the heart of systematic scientific thinking; the paradigm of molecular structure is at the heart of virtually all chemical thinking. Any molecular structure may be decomposed into the following forms or levels: (1) composition; (2) constitution; (3) configuration; and (4) conformation. At the level of composition only the number and kinds of "elements" or atoms of the structure are of chemical interest. At the level of constitution, not only is the composition of chemical interest, but also the number of possible ways in which the atoms are connected to one another. A unique *molecular structure* at this level may be identified as one for which all of the atoms of the composition possess a unique connectivity relationship. At the level of configuration, in addition to the composition and constitution, the number of possible dispositions in three dimensional space of "neighboring atoms" about a central atom is of chemical interest.

A unique structure at this level may be identified as one for which all of the neighboring atoms surrounding a central atom possess a distribution in three dimensional space that is unique. Finally, at the level of conformation, the possible shapes of a given composition, constitution and specific set of configurations is of chemical interest. A unique structure at this level may be identified as one which differs from others in terms of shapes resulting from rotations about single bonds.

Chemists have grown so familiar with the paradigm of molecular structure that its validity and centrality to all of chemistry are no longer seriously debated. However, chemists are now seeking the development of a paradigm at a level beyond that of molecular structure, namely the **supramolecular level**. Supramolecular structures are related to molecules in the same way that molecular structures are related to atoms. Although atoms play a critical role in the paradigm of molecular structure, it is the molecular structure which is generally at the center of the chemistry of molecules. The "intellectual glue" of molecular structure is the concept of the covalent bond and the stereochemistry associated with the consequences of the covalent bonds. The paradigm of the covalent chemical bond provides the rules that govern the structures, dynamics, characteristics and transformations of molecules. We therefore expect that a paradigm of non-covalent bonds will provide the rules that govern the structures, dynamics, characteristics and transformations of supramolecular assemblies.

Just as the level of atomic structure is inadequate for understanding aspects of chemistry where molecular aspects dominate, the level of molecular structure is inadequate for understanding aspects of chemistry where supramolecular aspects dominate. The emerging paradigm of supramolecular systems emphasizes the chemistry of the **intermolecular bond which holds molecules together, rather than the covalent bond, which holds atoms together**. Non-covalent intermolecular bonds are more varied and complex than covalent intramolecular bonds. In general, intermolecular, non-covalent bonds are held together by weaker forces than intramolecular, covalent bonds. For example, the important forces holding molecules together consist of dispersion forces, hydrogen bonds, hydrophobic bonds, etc. Although these forces, **per atom contact**, are small, in many supramolecular systems many such weak bonds are formed in a cooperative manner, thereby causing the supramolecular structure to be energetically

stable; however, because each "bonding contact" is relatively weak, the bonds may be broken relatively easily so that the structure may have a certain amount of flexibility.

### **Beyond the Supramolecular Paradigm. From Atomic Chemistry to Superdupermolecular Chemistry**

With the above ideas in mind, let us not attempt to extrapolate and try to imagine the paradigm that will be used by chemists in the 21st century. Prediction is difficult, especially for the future, but it is entertaining to try. First let us review the structural basis of current atomic, molecular and supramolecular concepts and then attempt to see what is missing and what we can learn from the intellectual jumps from the atomic to the molecular to the supramolecular to the "superdupermolecular" paradigm of the next millennium!

In Chemical Physics the paradigm of the "Hamiltonian", which determines the way partitioners think about chemical problems. Chemical physicists employ an abstract mathematical Hamiltonian, based on physical models, and solve wave equations to come to conclusions concerning observables. The organic chemist uses molecular structure and chemical equations based on these structures instead of Hamiltonians to solve chemical problems. Both are useful but different representations of the **same** chemical systems. Therefore we shall use a hybrid language which attempt to extract some of the more useful features of both representations.

We take as a given the idea that representations of molecular structure are the bedrock of organic thinking and so powerful intellectually that they must be employed. However, we take as an advantage of the Hamiltonian approach its universality in including all forms of interactions and energetic considerations in a systematic manner. In the language of the organic chemistry a proper chemical structure contains all the information required to solve any chemical problem of interest. In the language of the chemical physicist, a complete Hamiltonian contains all of the information required to solve any chemical problem of interest. The problem with either is that the organic chemist and the chemical physicist do not have a "proper" structure or a "complete" Hamiltonian. Worse, they often do not realize that this is the case and are frustrated by their inability to solve the problem at hand!

For example, the organic chemist may be considering a chemical problem at the molecular level, whereas the proper structure is supramolecular. The chemical physicist may be considering a chemical problem with a Hamiltonian that is missing an interaction or is not starting from the correct energetic assumptions. Let see how the chemical physicist handles the problem and then extend it to suggest how the organic chemist can handle the problem. A key concept in setting up a Hamiltonian is the selection of a physical model that determines the overall energetic characteristics of the system of interest. This selection is based on experience and judgement in the same way that the organic chemistry selects a starting structure to attack a chemical problem. The starting Hamiltonian is called the "Zeroth" order and then direct significant interactions are added as "First Order" and indirect weaker interactions are added as "Second Order". Although second order effects may be tiny in energy, they can be important if they serve as the key to the structural changes that determine the rate of a dynamic process.

*Atomic chemistry* is a science based on premise that to Zero Order, a single atomic structure is sufficient to explain the spectroscopy, chemical dynamics and reactivity of macroscopic gases, liquids and solids. *Molecular Chemistry* is a science based on the premise that to Zero Order, a single molecular structure is sufficient to explain the spectroscopy, chemical dynamics and reactivity of macroscopic gases, liquids and solids. As a logical extension, *Supramolecular Chemistry* is a science based on the premise that even in Zero Order, more than a single molecular structure may be required to explain the spectroscopy, chemical dynamics and reactivity of macroscopic gases, liquids and solids. *Atomic Chemistry* stresses structures whose composition consists of one or more electrons and a nucleus and whose composition is determined by the bonding between the nucleus and the electrons. *Molecular Chemistry* stresses structures whose composition consists of two or more atoms and whose composition is determined by covalent bonds between atoms. *Supramolecular Chemistry* stresses structures whose composition consists of two or more molecules and whose composition is determined by intermolecular bonds between molecules.

In the language of topology, atomic chemistry, molecular chemistry and supramolecular chemistry may be viewed as topologically equivalent: In going from atomic chemistry to molecular chemistry, the structure of atoms (electrons and nuclei) are suppressed and collapsed to a single point, whose internal structure may be ignored to

Zero Order. In going from molecular chemistry to supramolecular chemistry, the structure of supramolecular systems (molecules) are suppressed and collapsed to a single point, whose internal structure may be ignored to Zero Order.

We consider in this article situations for which the Zero Order approximation for atomic, molecular and supramolecular chemistry is not sufficient to explain experimental observations. We term these situations as manifestations of Überatomic, Übermolecular and Übersupromolecular chemistry. For example, the properties of matter in the presence of an oscillating electromagnetic field or in the presence of a laboratory magnetic field often cannot be understood without explicit consideration of the interaction of the fields with the structure representing the matter. Often features explicitly absent from the atomic, molecular or supramolecular structure traditionally employed to represent matter are dominant in determining the observation. This is particularly common in the case of electron and nuclear spins, which are not explicitly represented.

The purpose of this article is to explore situations for which übermolecular effects will be important for supramolecular system and provide examples which may provide a scaffolding for extension to other systems.

### **Supramolecular Paradigm and Photochemical Paradigms**

From the above considerations, the simplest supramolecular assembly is a simple complex between two molecules. In general, chemists do not consider solvated molecules as supramolecular species, but there are many examples of solvent effects that appear to possess many of the features expected of a well defined supramolecular assembly. For example, the reactions of chlorine atoms are very solvent dependent. In a saturated hydrocarbon solvent, chlorine atoms are nonselective toward hydrogen abstraction, whereas in benzene, the selectivity is quite significant.<sup>4</sup> One interpretation of the solvent effect is that a complex is formed between a chlorine atom and benzene and that this complex is the chlorinating agent, not a "free" chlorine atom. Indeed, spectroscopic evidence for such a complex is available from laser flash photolysis and thereby gives a definite structural validity to this complex.<sup>5</sup>

Photochemists have become quite accustomed to dealing with "complexes" between electronically excited states and ground state molecules of substrates or solvent. A supramolecular assembly consisting of an electronically excited molecule and a ground

state molecule is termed an "exciplex" and can be fully characterized with a unique set of spectroscopic properties in addition to unique photochemistry.<sup>6</sup> The ubiquitousness of such species in photochemistry makes a photochemist much more receptive to supramolecular concepts even at the level of small molecules. We shall return to this theme.

### **Supramolecular Chemistry. Some Working Definitions.**

According to Lehn, "Supramolecular chemistry may be defined as *chemistry beyond the molecule*, bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces." This definition is in contrast with that of molecular chemistry, "the chemistry of the covalent bond." Lehn has emphasized aspects of supramolecular chemistry which are apparent in enzyme catalysis, chemical systems for which chemists have developed an excellent paradigm for the structure and dynamics of exceedingly complex chemical systems. Thus, appealing to the enzyme paradigm, an operating enzyme may be considered in the simplest case as a bimolecule, a supramolecular system whose composition is a receptor (or host) and a substrate (or guest). Although binding is a characteristic of the entire supramolecular assembly, usually the receptor is considered to have binding sites to which the substrate becomes noncovalently attached.

### **Zeolites and Micelles as Enzyme Models.**

Micelles have long been employed as "enzyme mimics".<sup>7</sup> The ability of micelles (in aqueous solution) to serve as "receptors" for hydrophobic substrates is a simple example of the supramolecular characteristics of these supermolecules. It is less obvious that an analogy may be made between the rigid framework structure (the "walls" of the internal surface) of a zeolite possessing internal void space of molecular dimensions (ca. 1 nm) and the cavity forming the active site resulting from the tertiary protein structure of an enzyme which operates on a molecular substrate of size ca. 10 Å. To some extent, enzymes incorporate, at the active sites, metal reagents that are relatively non-selective in their reactions with substrates in homogeneous solutions. The phenomenal selectivity of the metal when it is incorporated into the enzyme is due to the environment, which may both discipline a metal ion's tendency toward non-selectivity by modifying the redox parameters and more importantly, by providing an environment that encourages the transport of substrates to the active site and which selectively recognizes only the



"correct" substrate on which to operate at the active site. The latter molecular discrimination or molecular recognition is achieved through a stereochemical void space in the environment of the active site that is exquisitely designed to select substrate via size/shape characteristics. The important point of the above discussion is that many microheterogeneous systems may be considered within the framework of supramolecular chemistry, and intuitive information on the properties of these system may be obtained by appeal to the enzyme paradigm.

### **Enzyme Catalysis.**

One of the most important properties of enzymes is their ability to serve as catalysts for specific chemical transformations. Given the above discussion, we expect that supramolecular photochemistry will also exhibit an analogy to this property, which we now review broadly.

The overall process of an enzymatic catalysis can be viewed as a sequence including the following processes: (1) relatively indiscriminate adsorption of the substrate on the surface of the enzyme; (2) diffusion of the substrate to the region in the vicinity of the active site; (3) size/shape "molecular sieving" of the substrate into the active site; (4) selective transformation of the substrate into a new chemical species; (5) release of the transformed substrate from the active site; (6) accumulation of the transformed substrate in the bulk system. Effectively, the enzyme structure has molecular features which (1) serves as "fly paper" to which the substrate in the bulk solution becomes attached; (2) serves as a "policeman" to exert "molecular traffic control" on the diffusion of substrate to the active site; (3) serves as a "molecular sieve" allowing access to the active site only to those substrates possessing the appropriate size and shape characteristics; (4) serves to discipline the reactivity of reagents which cause the transformations that occur in the active site and orient the substrate for transformation of high selectivity; (5) serves to release the transformed substrate.

Both micelles and zeolites can exhibit the enzymatic features of catalysis in photochemical reactions in the following ways: (1) The external surface of a zeolite or micelle serves as "fly paper" to collect substrate molecules that diffuse through a bulk solvent and then adsorb on the external surface. (2) The adsorbed molecule may then diffuse on the external surface that serves as the "policeman" and directs the substrate to an internal pore of the zeolite or the internal hydrophobic core of the micelle. (3) The

size and shape of the pore or the detail of the chemical structure of the micelle is the "gatekeeper" determining which substrate molecules can enter the internal surface.

Let us now turn to the paradigm of modern molecular photochemistry and employ the reactions of radical pairs photochemically produced in micelles and zeolites as examples of supramolecular photochemistry.

### **From the Paradigm of Molecular Photochemistry to the Paradigm of Supramolecular Photochemistry.**

Molecular photochemistry has a mature paradigm that provides the practitioner with a conceptual basis for generating a "map and a clock" for examining the mechanisms of photochemical reactions. The "map" is the connectivity of the chemical entities whose structures must be characterized and the reaction steps and/or structural changes that interconvert the chemical structure, whose dynamics are of greatest importance in understanding the details of the mechanism of a photochemical reaction. In addition, the paradigms of modern molecular photochemistry provide the practitioner with (1) a blueprint whose theoretical parameters are of greatest import, (2) the way to connect the theoretical parameters with experimental parameters, and (3) techniques that will provide the appropriate data to be transformed into experimental parameters. Finally, the paradigm provides the information needed to formulate a comprehensive theoretical basis for quantitative computation to simulate experimental data.

All of the features of the paradigm of modern molecular photochemistry are automatically incorporated into the developing paradigm of supramolecular photochemistry. However, in addition, we must merge the "molecular" aspects of this paradigm with those of the paradigm of *supramolecular* chemistry.

What are the essential and critical features of a supramolecular chemical system? Although the definition of a supramolecular system still requires refinement, it is useful first to perceive a supramolecular system as "self-similar" to a molecular system in terms of structure and dynamics and then to add any features that might be unique to the supramolecular system. At the first level, the key intellectual unit of the molecular system is the covalent chemical bond. The paradigm of the covalent bond ties together the critical features of structure and reactivity of molecules. In this paradigm, intermolecular interactions are considered to be continuous and relatively weak and non-specific and to play a secondary role in determining structure and reactivity. As the

intermolecular interactions between molecules become more and more selective and stronger, the system begins to slip from one that can be well described as molecular to one that *must* be described as supramolecular. When the system becomes truly supramolecular, basic quantitative features become difficult to understand if the concepts of molecular chemistry are applied. Indeed, in some cases the basic intuition derived from molecular chemistry will fail even at the qualitative level!

All of the features of the paradigm of modern molecular photochemistry are automatically incorporated into the developing paradigm of supramolecular photochemistry. However, in addition, we must merge the "molecular" aspects of this paradigm with those of the paradigm of *supramolecular* chemistry. We mention briefly here some of the key similarities and differences between molecular and supramolecular chemistry and supramolecular photochemistry as they can serve as a superb testing ground for exploring and defining supramolecular concepts which will be useful for the chemistry of today and of the next century.

Let us now present a specific example of a supramolecular photochemical system. Geminate radical pairs are produced by photochemical reactions of ketones many photochemical reactions of ketones. We shall emphasize the production of triplet radical pairs by the  $\alpha$ -cleavage reaction of ketones. The intersystem crossing step from the triplet geminate pair to a singlet geminate pair determines the reactivity of the pair. In general, this step is inefficient in ordinary solvents (molecular photochemistry), because the diffusional separation of the pair is much faster than intersystem crossing. It has been shown that the "complexing" of the radical pair as a substrate with a micelle or zeolite as receptor enhances the efficiency of intersystem crossing in the same manner that an enzyme enhances the rate of reaction of a bound substrate.

### **Some General Features of Supramolecular Photochemical Systems.**

A supramolecular system consists of two or more molecules for which at least one property is so strongly correlated that the property cannot be deduced by consideration of the individual molecules alone. The notion of "correlation" implies that the molecules in the supramolecular structure "talk to each other" in a manner that can modify the properties of each molecule as an isolated entity. This definition attempts to capture a breadth of supramolecular systems that is considerably beyond the now "classical" host/guest concept of a supermolecule. The composition of the supermolecule in

photochemical systems is limited by the lifetime of electronically excited states and reactive intermediates produced by photoexcitation and by the time scale for exploration of the environment by these species.

In the case of radical pairs, the most important supramolecular correlations are the geminate character of the pair and the spin correlation of the pair. Both are intermolecular features that distinguish radical pairs and become therefore truly supramolecular when they influence chemical reactivity.

Consider a system for which photolysis of a supramolecular system consisting of a (guest) ketone associated with a (host) micelle produces a new supramolecular system consisting of two subunits, a triplet geminate radical pair. The micelle host has been termed a **supercage** and **the geminate pair guest in the micelle may be considered to be a stoichiometric entity or a supermolecule**. The term supercage is intended to describe a supramolecular system possessing some of the characteristics of a homogeneous solvent "cage", but in addition, possesses certain special supramolecular characteristics of a guest host complex. For example, the boundaries of the geminate pair-micelle supermolecule constrain separation of the pair, thereby discouraging long trajectories and encouraging or forcing reencounters on the pair. The supercage structure enhances the lifetime of the triplet geminate pair by orders of magnitude over that of its lifetime in a solvent cage (of a non-viscous homogeneous liquid). Depending on the details of the supramolecular structure (hydrophobic characteristics of the subunit radicals in the pair and the hydrophobicity and size of the micelle), the rate of escape of one or both radicals of the geminate from the supercage may be competitive with geminate reactions within the supercage. The radical subunits of the biradical undergo trajectories in space that are similar to those of the geminate pair in a micelle supercage, but instead of being random motions in a restricted supercage, the biradical subunits undergo motions in space that are correlated by the flexible connector of covalent bonds that hold the subunits together. An important and very intriguing supramolecular issue is whether the flexible connector of the biradical supermolecule provides an intrinsic interaction between the subunits that is absent in the geminate pair in the supercage.

Consider the photolysis of dibenzyl ketone DBK adsorbed in the inside of a micelle or in a zeolite cage. Let us assume that the usual situation for solution with respect to the photophysics of the ketone are appropriate for the complexed

ketone, i.e., the intersystem crossing from the singlet excited state produced by light absorption crosses quantitatively and rapidly to the triplet excited state which then cleaves quantitatively to a spin and composition correlated triplet geminate radical pair,  $^3[\text{C}_6\text{H}_5\text{CH}_2\text{CO}\cdot \cdot \text{CH}_2\text{C}_6\text{H}_5]\text{GP}$ . In this case the composition is correlated to that of the starting ketone, i.e., each atom in the radical pair is correlated with each atom of the parent ketone. The electron spin of the geminate radical pair is correlated to that of the starting parent ketone, i.e., the orbitally uncoupled electron spins are parallel and correspond to a triplet state. The geminate radical pair also possesses a constitution correlation which is identical to that of the starting material in all respects except for the disconnection of the bond that has undergone  $\alpha$ -cleavage. As time goes on, the three correlations of spin, composition and constitution will be lost as the triplet relaxes to singlets or to uncorrelated doublets and as the geminate composition becomes lost as the result of diffusional separation and randomization of the radicals in the global space of the solution. Finally, the constitution correlation becomes lost as the  $\text{C}_6\text{H}_5\text{C}_2\text{CO}$  radical loses CO via bond cleavage. The time scales for each correlation loss are different and, as suggested by the  $t = R^2/D$  relationship, they depend on several factors that are functions of the size (R) of the available space. In this regard, the different topological regions of a given system may have different effects on the evolution of the triplet excited state and the subsequent radical intermediates.<sup>9</sup>

The loss of spin correlation of the geminate radical pair mediates the probability of competition between primary geminate recombination and decarbonylation. The loss of spin correlation is a strong function of the intramolecular magnetic fields due to nuclear hyperfine coupling and to spin orbit coupling of the odd electrons in the radical pair, and to the separation of the radical centers in space. The strength of the hyperfine coupling in the radical pair is distance independent, but its ability to induce intersystem crossing is strongly distance dependent. The strength of the spin orbit coupling is strongly distance dependent, being related to the magnitude of orbital overlap between the two radical centers, and falling off roughly exponentially as a function of the radical pair separation. The magnitude of the singlet-triplet energy gap depends on

distance in a manner similar to that of the spin-orbit coupling. Although the situation is obviously complex, the essential points are readily comprehended and the qualitative effects are easy to identify. For example, if the size of the restricted space is very small relative to the size of the radical pair, the singlet-triplet gap will be large (enforced orbital overlap) and the intersystem crossing will be slow. Decarbonylation should occur preferentially over primary geminate coupling. On the other hand, if the size of the restricted space is large relative to the size of the radical pair, the triplet-singlet separation will tend to zero and either hyperfine or spin orbit induced intersystem crossing will be effective. If the size of the topological region is adequate, the probability of reencounter of the singlet radical pair will be correlated with the rate of intersystem crossing and the formation of geminate products will compete with decarbonylation. However, if the size of the space is too large, separated radical pairs will tend to lose their compositional correlation as they spread throughout the space and encounter radicals generated from other parent ketones. Finally, the constitutional composition will be lost if the primary geminate pair is separated long enough for loss of carbon monoxide to occur. Several situations covering these possibilities have been observed experimentally in several supramolecular systems which we discuss below.

### **The Role of the Environment on the Photochemistry of Dibenzyl Ketone.**

Different reaction media can impose different constraints on the molecular freedom of dibenzyl ketone. It is not surprising to observe completely different photochemical results in different reaction media considering that the space available to the reactant is of great importance in modulating the competition between the alternative deactivation and decay processes. These may all be characterized as supramolecular photochemical systems. Prospective reaction environments may range from the relatively tight and tailor-made medium of the crystalline solid state to the somewhat larger environments of inclusion complexes, zeolites and micelles. According to the topological regions where the reaction takes place, restricted environments and organized media can be classified as topologically closed or topologically open environments. Closed environments are those systems where the entire reaction sequence occurs under

the influence exerted by a unique topological space. Reactions occurring solely at the surface of a stretched polymer, at the external surface of a solid support, or within the boundaries imposed by the host of an inclusion complex can be all considered under this category. Topologically open environments, on the other hand, are those in which the substrates, excited states or reaction intermediates are able to partition between more than one of the topological regions available in the system.

### **Supramolecular Photochemistry of Dibenzyl Ketone in Micelles.**

Assessing the effect of the size of the environment in zeolites, micelles and other less restricted environments may become somewhat more complicated as the radical intermediates may escape from the influence of their initial topological spaces. In micelles, for instance, the competition between intersystem crossing and decarbonylation of the primary radical pair may not be completed when some of the first-formed secondary radical pairs begin escaping out into the aqueous environment. The cage effect of the micelles in the recombination of the secondary radical pair is less than 100%. Photolysis of p-MeDBK (ACOB) in hexadecyltrimethylammonium chloride (HDTCL) above the critical micelle concentration, for instance, resulted in a cage effect of only 50%. However, it should be pointed out that the rate of escape and the percent cage effect are related to the integrity of the reaction medium and not to the size of the restricted environment. The effect of the size on the reactivity of DBK can be assessed here from the relatively faster processes such as primary radical recombination in which endomicellar reactivity dominates.

Perhaps the most important supramolecular feature of the photochemistry of DBKs in micelles is the enormous sensitivity of the reactivity of the radical pair to magnetic effects. The system displays a very large magnetic isotope effect on the recombination of the geminate radical pair ( $^{13}\text{C}$  containing radicals recombine faster than  $^{12}\text{C}$  containing radicals) and very large magnetic field effects on the geminate combination of radicals. These features have been thoroughly reviewed.<sup>10</sup>

### **Supramolecular Photochemistry of Dibenzyl Ketone in Zeolites.**

Another interesting system with a topologically open environment where size effects are of clear chemical consequence relates to the zeolites X and Y (known as the faujasite zeolites).<sup>11</sup> Faujasites are microcrystalline porous aluminosilicates containing an enormous amount of internal space accessible to relatively large molecules such as DBK. The chemical composition of the X and Y zeolites differ in their relative Si/Al composition with the X zeolites containing roughly a 1:1 ratio, and the Y zeolites containing a 2:1 Si to Al ratio. Each Al atom in the framework contributes with a net negative charge that can be neutralized by a monovalent ( $M^+$ ) inorganic cation. The X and Y zeolites possess a three dimensional network of relatively large and almost spherical cavities termed supercages that are interconnected by roughly cylindrical channels. The supercages and the channels have internal diameters of approximately 13 Å and 8 Å, respectively. The space available for a chemical substrate, however, can be modulated by selection of the exchangeable cations. The ionic diameters of the alkali ions (Li 1.4 Å, Na 1.9 Å, K 2.7 Å, Rb 3.0 Å, Cs 3.4 Å) for instance, vary over a factor of two, implying a change in volume of a factor of about an order of magnitude.

Because of the internal connectivity, and because of the relatively large internal environment, the topological spaces available to the reactants can be considered in local or global terms. Locally, the topology of the faujasites can be considered in terms of the connectivity given by the supercages. Globally, the topology is given by the space available during the lifetime of the reactant and may, in principle, extrapolate to the entire lattice. The photochemistry of DBK in the faujasites compares to the photochemistry observed in the micelles because part of the reaction occurs beyond the limits of the local supercage environment.<sup>12</sup> The openness of the environment is clearly indicated by cage effects systematically lower than 100%.

The effects of the cations in modifying the supercage sizes are mostly manifested in terms of the primary recombination products. The lifetime of the primary radical pair is probably too short for allowing it to diffuse and react before losing its constitutional correlation. Escape of the primary radical should therefore result in decarbonylation and reaction of the secondary radical pair in



the global environment. The product distribution obtained from photolysis of DBK at low loading in different ion exchanged X and Y is different for different cations. Several trends relating to the effect of the size can be deduced from the product distribution. First, the major product obtained in all cases, except for KX, comes from secondary radical recombination. The amount of primary radical recombination, reporting on the feasibility of intersystem crossing and reencounter, increases substantially with increasing cation size in the X zeolites, but not in the Y zeolites.

An interesting example illustrating the contrasting chemical behavior of two topological isomers can be drawn from the photochemical behavior of p-MeDBK and o-MeDBK in pentasil zeolites.<sup>13</sup> Pentasil zeolites (ZSM-5 and ZSM-11) present a borderline situation regarding the adsorbability of DBK and its derivatives within the internal surface structure. The internal surface consists of two types of intersecting pore systems with internal diameters of approximately 6 Å. A channel with a sinusoidal path and a near circular cross section is perpendicularly intercepted by another straight channel running along the pentasil lattice. Strict size and shape considerations determine the diffusibility of organic adsorbates into the internal structure. Pentasils, for instance, are able to selectively adsorb p-xylene from a mixture containing also the ortho and meta isomers. The size and shape of the reactants determine their location on the external or internal zeolite surfaces. Substrates too large to penetrate the internal porous structure will remain adsorbed onto the external surface and will naturally experience different constraints from those able to penetrate the zeolite interior.

A very interesting aspect regarding the photochemistry of dibenzyl ketones in the pentasil zeolites comes from the fact that the smaller fragments resulting along the fragmentation sequence may be relieved of the size restrictions and tend to diffuse into the zeolite interior.<sup>13</sup> Obviously, a rational choice of substrates should be of the greatest value for exploring the consequences of the inside/outside topological isomerism within the same reacting system. Two substrates selected for the study of the pentasil zeolites were o-MeDBK (o-ACOB) and p-MeDBK (p-ACOB). This choice was based on the expectation that the ortho isomer would remain on the external surface

while the para isomer would diffuse to the zeolite interior. In this manner, o-ACOB can be considered an "outside isomer" while p-ACOB can constitute the "inside isomer". Furthermore, photolysis of these ketones was expected to generate radical fragments presenting structural resemblance and dynamic properties similar to those of ortho and para xylene.

Photolysis of oACOB and pACOB at low coverages (1% w/w) on the pentasil zeolites also led to the exclusive formation of decarbonylation products. The effect of the media was strongly manifested in terms of the recombination statistics of the secondary radical pair. The oACOB isomer, for instance, was found to give a negative cage effect by inducing the recombination of the 'like' fragments AA and BB. The major product in the case of the para isomer resulted from enhanced geminate recombination to give the normal cage effect product, AB. These results clearly support the expectations regarding the location of the reactant and the diffusibility of the radical intermediates.

It seems possible that the lack of primary radical geminate products in the two reaction systems may be the result of different influences from the medium. Restricted rotation of the primary radical pair, in the case of p-ACOB, and fast diffusion in the case of o-ACOB may explain the predominance of the decarbonylation pathway. The negative cage effect in the case of the ortho isomer arises from the preferential sieving and recombination of the benzyl radicals in the internal surface while the methyl substituted benzyl radicals remain excluded and recombine in the external surface.

The negative cage effect obtained in the case of o-ACOB provides a measure of the ratio of the rate of radical adsorption vs. recombination, **R**. Interestingly, the value of **R** was found to be dependent on the particular zeolite sample used and the magnitude of its value turned out to be inversely correlated with the amount of o-xylene adsorbed in separate experiments. Adsorption of pACOB inside the pentasil framework, in contrast, resulted in cage effects of 100%. This interesting result implies that radical diffusion within the zeolite is slow relative to the rate of recombination. A similar conclusion regarding the relatively slow diffusion rate of p-ACOB in pentasils was reached by independent solvent extraction and radical scavenger experiments.

Further evidence regarding the importance of the local topological environment on the chemical reactivity was obtained by studying the effect of added water. Although water can be considered an unreactive spectator, addition of water to the pentasil system results in a dramatic change of the topological structure of the system. With water being a stronger adsorbate, p-ACOB is displaced to the external surface where random diffusion of the photogenerated radicals occurs. In the case of the oACOB system, the effect of water is one of blocking the zeolite entrances and preventing the sieving of the benzyl radicals. Both radical fragments are in this manner confined to the external surface also causing radical randomization. The cage in both systems is therefore reduced to zero.

### **Conclusion**

Photochemistry has long possessed the richness of multidimensionality in time, space and energy. Photochemists must keep track of time scales, energy surfaces, magnetic effects, etc. in examining the mechanisms of photoreactions. The concepts of supramolecular photochemistry are therefore not very far from those commonly employed to interpret conventional photochemistry. Perhaps the reason for this is that the photochemist has been long forced by the complexity of his discipline to view nature in a supramolecular manner. The ubiquitousness of exciplexes is an excellent example of the ordinariness of supramolecular effects in photochemical systems.

Perhaps the most important consequences of "thinking supramolecularly" is the ability to "see" apparently disparate chemical systems as "the same thing" in the sense that techniques and strategies for mechanistic investigation can be mapped from a well established supramolecular system onto a new one, once the topological supramolecular connections have been established. In this respect the move from molecular chemistry to supramolecular chemistry has the flavor of moving from "static molecular structures" to conformationally flexible structures. The rewards for adopting such an approach should be as great as those achieved when considering conformational structures.

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