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Supramolecular photochemistry. A paradigm for the 1990s?

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Abstract

The emerging field of supramolecular chemistry, which involves ''chemistry beyond the molecule'' and which emphasizes non-covalent intermolecular bonding and structures, also provides an intellectual basis for a new vision of photochemistry, namely supramolecular photochemistry. Supramolecular photochemistry embraces not only the principles of supramolecular chemistry, but also the principles of supramolecular physics which deal with the influence of static and fluctuating electric and magnetic fields on photochemical reactions. Thus, the combination of intermolecular forces, sometimes quite weak individually but strong cooperatively, and electrical and magnetic forces ''beyond the molecule'' provide exciting opportunities to control the course of new photochemical reactions and to investigate important examplar reactions in novel ways.

Keywords: Paradigm; Radical pairs; Supercages; Supramolecular photochemistry

1. Paradigms: a brief overview

A scientific theory may be viewed as a structure which is universally accepted by the community of practitioners and which has been termed the community's paradigm [1]. A mature science is governed by a single paradigm which sets the standards for legitimate work within the science it governs. The paradigm, which is the set of beliefs driving 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 which distinguishes a mature science from a developing science. The nature of a paradigm is to possess components and connections which are accepted as necessary and sufficient to describe all observable phenomena of interest to the practitioners.

From time to time, paradigm shifts occur when the accepted paradigms governing the way in which the practitioners view a field appear to be incapable of explaining observations and of directing new experimental situations. Fields undergoing frequent paradigm shifts are considered to be immature and not to have reached the broad consensus which characterizes the activities of a mature science. In immature fields which have not yet reached consensus on their paradigms, continuous arguments rage over the validity of very fundamental issues.

2. Molecular organic photochemistry

Molecular organic photochemistry may be considered to be a field which is controlled by mature paradigms. Practitioners do not argue over fundamental issues, such as whether electronically excited states are produced by photochemical excitation, whether singlet and triplet excited states and exciplexes exist or whether laser flash photolysis is a valuable technique for the characterization of the structure and dynamics of electronically excited states. Adherence to the paradigm allows practitioners to pose soluble problems for which methods exist for their solution.

However, it was not that long ago when photochemists would argue over many issues which are now taken as both fundamental and given. Indeed, since the late 1950s, organic photochemistry has undergone a number of important paradigm shifts. For example, in the early 1960s, the paradigm relating spectroscopy (orbital characterization of excited states) to photochemical reactivity (primary photochemical reactions) became accepted as a starting point for explaining results and directing experiments in organic photochemistry. During the 1960s, the paradigm of the triplet state dominated the thinking of the organic photochemists. Only during the 1970s did the possible involvement of singlet state reactivity and excimers and exciplexes really become an accepted part of the photochemical paradigm. Also during the 1970s the extension of orbital characterization of excited states to the

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energy surfaces connecting excited states to primary photochemical products and to ground state surfaces was added to the photochemical paradigm. During the 1980s, time-resolved techniques were developed which were capable of direct characterization of the structure and dynamics of the intermediates predicted from orbital and surface considerations. By the 1990s, molecular organic photochemistry was operating under a mature paradigm which directed the normal science activities of the field and which had settled down to the investigation of photochemical reactions in greater and greater detail under the guidance and comfort of a mature and effective paradigm of molecular photochemistry.

The paradigm of "molecular chemistry" relies on the concept of molecules and focuses on the covalent bond between atoms. Molecular chemistry has been the powerful and unifying paradigm for chemistry and photochemistry for decades. However, during the 1980s, the elements of a paradigm shift occurred as chemists and photochemists began to explore "microheterogeneous systems" and chemistry at interfaces [2]. We now consider the emerging "paradigm shift" from molecular chemistry to supramolecular chemistry [3] and its extensions from molecular chemistry to supramolecular organic photochemistry [4]. First, let us consider the emerging paradigm of supramolecular chemistry.

3. Supramolecular chemistry

The paradigm of supramolecular chemistry [3] has not yet reached a mature stage at which the practitioners agree substantially on all of the important and fundamental aspects of the field. This immaturity is reflected in the difficulty in defining supramolecular chemistry. Broad definitions might involve "chemistry beyond the molecule" or "chemistry of the intermolecular bond" or "chemistry beyond the covalent bond". Therefore, in a general way, a supramolecular system or "supermolecule" is an aggregate of two or more building blocks, each of which may be considered as a stable molecule possessing separate stability and each of which is well defined chemically and physically in isolation. Typical supramolecular systems possess intermolecular bonding which is considerably weaker than typical covalent bonds. Whereas a molecular structure may possess stability when it consists of strong covalent bonds, a supramolecular structure may possess stability by possessing many weak non-covalent bonds.

A more restricted, but useful, working definition might focus on an important class of supramolecular systems, such as guest–host complexes, of which enzymes are outstanding examples. The non-covalent bond which "connects" the component molecules of supramolecular guest–host complexes is related to the covalent bond which "connects" atoms in covalent molecules. In a supramolecular structure, the chemist can identify the molecular (covalently connected) components, but can also recognize physical and/or chemical features which are absent when considering the molecular components in either the gas phase or in a "homogeneous" solvent.

4. Supramolecular organic photochemistry

Over the last 20 years, as the paradigm of molecular organic photochemistry matured, the mechanisms of photochemical reactions became firmly established and the techniques for determining mechanisms became increasingly sophisticated, organic photochemists began moving from investigations of new reactions towards the use of well-established reactions in media other than homogeneous solutions [2,4]. The terminology for these media varied: photochemistry in microheterogeneous media, photochemistry at interfaces, photochemistry in colloidal systems, photochemistry in restricted spaces, photochemistry in self-organizing assemblies, etc. On inspection, nearly all of these terms can be subsumed by the single term, supramolecular photochemistry.

For example, pyrene fluorescence has been employed as a probe of micelles, solid surfaces, polymers, etc. [2]. The paradigm of the photophysics of pyrene was considered to be sufficiently mature to be able to provide information on the structure of complicated "host" media, such as micelles, solid surfaces, polymers, etc.

A surprise occurred when it was discovered that certain supramolecular systems possessed unexpected dynamic behavior. We consider one important example of such a system in which "dynamic resonances" can occur.

5. Supramolecular systems involving geminate radical pairs

As an example of a supramolecular system of great importance in photochemistry, let us consider a radical pair (produced, for example, by α-cleavage or hydrogen abstraction in a primary photochemical process) which is "non-covalently bound" to a host which confines the pair to a restricted space during a significant fraction of the pair's lifetime.

As a specific example of such a supramolecular system, let us consider a radical pair adsorbed in a micelle. Why should such a system be considered supramolecular? What are the experimental results that support the notion that the system is supramolecular? The term "supramolecular" is operationally effective when it is presented against a "molecular" background. For example, a micellized radical pair can be compared with a radical pair in the gas phase or in a non-viscous, non-interacting solvent. Under the latter conditions, the pair may be considered as operating independently, i.e. as independent free radicals, except for the short intervals of time when they happen to be within each other's proximity (typical of the order of several angstroms for small organic molecules).

Given these considerations, to a certain extent, even a radical pair in homogeneous solvent may be considered as "supramolecular" for a certain timescale under certain conditions [5]. For example, if a geminate radical pair is produced by an α-cleavage primary photochemical process in a non-viscous homogeneous solvent, for a certain period of time the walls of the solvent cage provide a restricted space which constrains the geminate pair. Typical lifetimes of geminate pairs in primary solvent cages of non-viscous solvents are considered to be of the order of picoseconds. During this time period, the geminate pair in the solvent cage meets the definition of a supramolecular system, since the pair is non-covalently "bonded" by the solvent cage. There is a certain small probability that the geminate pair, even after becoming solvent separated, will re-encounter and return to a solvent cage in competition with irreversible formation of free random radicals.

From this model, we can imagine the construction of supramolecular systems consisting of radical pairs in a variety of restricted spaces (liquid crystals, porous solids, polymer films, cyclodextrins, Langmuir films, etc.) [6]. The fundamental properties differentiating these restricted spaces from the solvent cage will be dynamic features involving the chemical dynamics of the geminate pair and the rotational and diffusional dynamics (molecular dynamics) of the pair within the restricted space. Since the chemical dynamics may be rate limited by spin dynamics if the initial geminate pair is a triplet, the chemistry of the supramolecular geminate pair is often determined by the interplay of chemical, molecular and spin dynamics and the size of the restricted space. From this point of view [5], there is no fundamental difference between the "molecular" radical pair in a homogeneous solvent and the "supramolecular" radical pair in a micelle when the timescale and dynamics of the system are considered explicitly!

6. Dynamic "resonances" in supramolecular systems

There are a number of straightforward effects on the chemistry of the supramolecular radical pair, such as enhancement of the probability of geminate reactions if the pair is maintained in close proximity for long periods of time as a result of the supramolecular structure. There are a number of more subtle effects on the chemistry of the pair which result from interacting dynamics. These effects may be considered as "resonances" which occur when certain dynamics possess similar "critical" timescales.

For example, let us consider the critical timescale t_{rw} for the separation of the partners of a triplet geminate pair from an origin, a random walk and return to the origin in a restricted space such as a micelle [5]. When t_{rw} is of the order of the timescale t_{isc} for intersystem crossing of the triplet radical pair to the singlet radical pair, a "resonance" between the dynamics of the random walk and the chemical reactivity of the pair occurs in the sense that, on return to the origin, an originally chemically "unreactive" triplet radical pair has been transformed into a very chemically "reactive" singlet radical pair. It is the interplay of the molecular dynamics and the spin dynamics in the restricted space which controls the chemical dynamics of reactivity of the geminate pair.

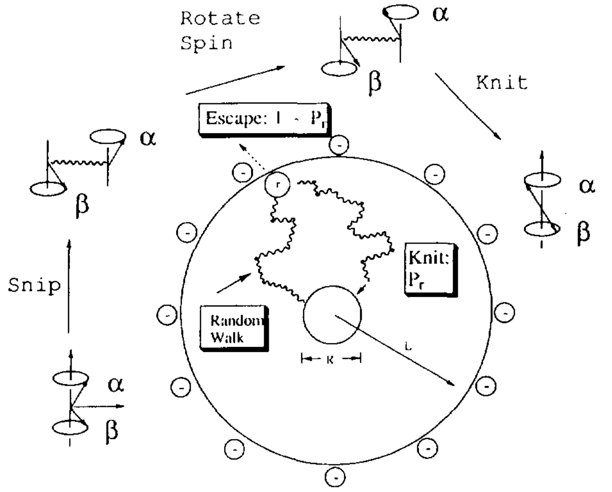

Fig. 1. Model of a radical pair in a micelle.

Fig. 1 shows a model of the supramolecular micellized triplet radical pair for which the micelle is viewed as a non-viscous, homogeneous, spherical host restricted space in which the radical pair is a guest [5].

Under the assumption that the radical fragments possess a mutual diffusion coefficient D and that the space possesses a radius R, a theory may be constructed which relates the time-dependent spatial separation r of the partners of the pair (molecular dynamics) with the ability of magnetic interactions (spin dynamics) to induce intersystem crossing in the pair from the unreactive triplet to the reactive singlet. The results of the theory are that, for small separations (less than several angstroms) of the triplet pair, the electron exchange interaction J "quenches" intersystem crossing by causing a singlet–triplet splitting which is larger than the available magnetic interactions which can induce intersystem crossing. For large separations of the pair (more than several angstroms), which occur during the random walk in the restricted space of the micelle, the value of J is near zero and the weak available magnetic interactions can induce intersystem crossing. The timescale of the random walk is of the order of $t_{rw} \sim R^2/D$ where D is the translational diffusion coefficient and R is the radius of the micelle. Since a "resonance" occurs when $t_{rw} \sim t_{isc}$, a relationship between the chemical reactivity of the guest geminate radical pair and the size of the host micelle may be deduced as $t_{isc} \sim R^2/D$.

The latter relationship implies that, when intersystem crossing determines the rate of reaction of geminate radical pairs, the rate of reaction $(1/t_{isc})$ depends directly on the square of the radius of the space accessible to the pair and inversely on the relative diffusion coefficient of the pair. To the extent that the model can be extended, it demonstrates the critical features which will distinguish a radical pair in a supramolecular system from radical pairs in the gas phase or in a non-viscous solvent.

7. Magnetic fields and supramolecular systems

Often supramolecular systems, such as radical pairs in micelles, display reactions which are sensitive to the application of both static and fluctuating magnetic fields [7]. The origin of these magnetic effects is related to the dynamic resonances discussed above. For example, the application of a weak static magnetic field can destroy the degeneracy of the triplet state and singlet state of the radical pairs. Even the oscillating magnetic photons associated with the electromagnetic field of light can be applied in "two-photon" experiments to modify the reactivity of geminate radical pairs in micelles. "Spin locking" of one of the triplet radicals in a pair can "freeze" intersystem crossing of specific isotopomers of the pair by tuning into the resonance frequency of individual hyperfine lines in the electron paramagnetic resonance (EPR) spectrum of the pair.

It may be that supramolecular systems will continue to open the doors to future novel magnetic field effects on photochemical reactions. In particular, it will be interesting to see whether supramolecular systems will be found for which electric fields exert significant control over the photoreactions of, for example, ion pairs.

8. Conclusions

It appears that a paradigm of supramolecular photochemistry is emerging and capturing the attention of many organic photochemists both because of its inherent intellectual attraction and because of the range of actual and potential practical applications involving supramolecular systems. It will be of interest to follow the development of this paradigm in future anniversary issues of this journal!

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