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ORGANIC PHOTOCHEMICAL MECHANISMS

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At the onset, it must be stated that this article is concerned with a discussion of organic reaction mechanisms in fluid solution near room temperature. During the decade of the 1960s, organic photochemical mechanisms began at a primitive level but rapidly developed to achieve a respectable level of maturity in the late 1960s. During this decade mechanistic photochemists struggled with the development and validity of organic photochemical mechanisms at the *state level*. The first chore in any mechanistic analysis must be the proper identification and characterization of the starting reagents. From the (mellow) field of electronic spectroscopy, concepts and terms such as excited singlet, triplet, n,π^*, π,π^* and Kasha's rule for emission spectroscopy were utilized to develop a starting paradigm for organic photochemical reactions. The typical mechanistic questions of the 1960s were as follows. (1) Is the reacting state S_1 or T_1? (2) What is the electronic configuration of the reactive state? (3) How can the reactions of an electronically excited state be correlated with state configuration and spin? (4) What are the rate constants for the reaction?

The experimental methods employed to investigate organic photochemical mechanisms during the 1960s relied heavily on product analyses, sensitization and quenching studies and extrapolation of the results of emission spectroscopy at low temperatures to reactions at room temperature. During this period several styles of investigating reaction mechanisms were developed, and a few model systems were thoroughly investigated and well defined. The 1960s were also a period of great activity and excitement in simple discovery of new reaction types. The Woodward–Hoffmann rules for concerted photoreactions served as an important mechanistic classifier but, by the end of the decade, it was clear that a simple "electron count" was not sufficient to guarantee the applicability of the rules to a given system. It was becoming clear that the rules had their dominant applicability to singlet state π,π^* reactions.

During the 1970s the theory of organic mechanisms began to shift from an emphasis on *reactive states* to an appreciation of *reaction surfaces*. The concept of surfaces began to inject important ideas from the field of radiationless transitions into the interpretation of organic photochemical mechanisms. The critical link between nuclear geometric changes and motion of a representative point on a surface became a very important tool to

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resolve mechanistic paradoxes or dilemmas that occurred when only the properties of the initial state were employed to interpret mechanisms.

The Woodward–Hoffmann rules took on a new dimension when surfaces were considered and the relationship between diradicaloid geometries and the transition state for ground state symmetry-forbidden reactions emerged.

Discussion of reaction mechanisms in terms of surfaces added not only a new richness to the intellectual aspects of organic reaction mechanisms but also served to stimulate experimental activity in areas which were "forbidden" by or ill defined by the paradigms of the 1960s. For example, "upper" state photoreactions (reactions initiated in an electronically excited state other than S_1 or T_1), adiabatic photoreactions (reactions which proceed on an electronically excited surface all the way to a product) and chemiluminescent organic reactions (reactions in which an electronically excited state is produced as a result of thermal excitation of a reagent) all could be mechanistically interconnected via the framework of a theory of reaction surfaces.

The interpretation of photochemical mechanisms in terms of surfaces began to lead to new typical questions such as the following. (1) What are the nuclear geometries at which a system jumps from an initial electronic excited surface to a lower electronic surface? (2) What are the mechanisms by which these jumps occur? (3) How is the movement on a surface (crossing over barriers, jumps between surfaces etc.) correlated with state structure and the structure of intermediate geometries along the reaction profile?

The experimental methods employed during the 1970s to investigate organic photochemical mechanisms began to incorporate direct spectroscopic detection of initial states and of reaction intermediates. Single-photon counting became a useful tool for the determination of the dynamics of fluorescent systems. The discovery of phosphorescence of certain compounds in fluid solution allowed the direct and convenient determination of the rate constants of triplet states. Toward the end of the 1970s time-resolved laser flash spectroscopy employing optical absorption and emission as a means of detection was beginning to become part of the experimental tools of the mechanistic organic photochemists.

During the early 1970s major mechanistic breakthroughs occurred in the areas of electron transfer reactions and singlet oxygen chemistry. Photosensitization of organic reactions by electron transfer (often a highly reversible process) developed into a powerful adjunct to direct photochemical triplet photosensitization. The development of sensitive detectors in the near-IR region allowed the direct measurement of emission from singlet molecular oxygen and expanded greatly the areas for which quantitative information could be obtained on the dynamics of this important excited state.

The use of time-resolved laser flash spectroscopy to investigate organic reaction mechanisms increased dramatically during the early 1980s. Investigations of diradicals, radicals, ions, carbenes and other reactive intermediates, in addition to singlet states, triplet states and exciplexes, have become standard in an ever increasing number of laboratories.

There was a noticeable trend during the 1970s away from conventional homogeneous solvent systems to "microheterogeneous" systems such as aqueous solutions of micelles, cyclodextrins and water-soluble polymers. These systems have been shown to exert significant influences on the course of photoreactions as a result of "supercage" effects on conformational selection. In particular, radical pairs held by such supercages were found to be susceptible to exceptionally large effects of applied magnetic fields and to the magnetic moments of nuclei contained by the radical fragments.

Conformational analysis of excited state reactivity became an important paradigm for the interpretation of organic reaction mechanisms involving flexible systems. Conformations that are rapidly interconverting in the ground state may be "frozen" in a single conformation during the lifetime of an excited state. As a result, "single excited states" (*i.e.* S_1 or T_1) were found to exhibit photoreactions which depend on ground state conformation populations.

The extensive role of exciplexes (species considered as mechanistically suspect during the 1960s) and ion pairs in many organic photoreactions became widely appreciated during the mid-1970s. "Simple" reactions such as electron transfer, hydrogen abstraction and cycloadditions were often found to be complicated by exciplex precursors to the primary reaction products.

During the 1970s photoexcitation was employed to produce as transients or as species stabilized indefinitely in matrices, molecules, diradicals, zwitterions and other reactive intermediates whose structures and energy content were incredible by the standards of the 1960s.

What advances in the science of organic photochemical mechanisms might we expect for the duration of the 1980s? One of the clearest trends, which will certainly continue, is the impact and incorporation of increasingly sophisticated instrumental techniques and methods to attack problems of interest to the mechanistic photochemist. At the forefront of many instrumental approaches will be the laser in its varied aspects. The expanded use of time-resolved laser methods, the development of "routine" picosecond devices and the development of continuous wavelength pulsed and continuous lasers are almost certain. The concepts of selective multiphoton chemistry and of utilization of "low energy" photons (for IR to excite overtones, IR to excite vibrations, microwave to excite electron spins etc.) are likely to be developed to the point of maturity and experimentally practised by photochemists by the end of this decade.

New methods of detection will allow for increasing amounts of structural information on transient species. Resonance Raman spectroscopy, a detection method capable of picosecond resolution, is established as a viable and powerful method for the study of electronically excited states and reactive intermediates derived from primary and secondary processes. Time-resolved flash nuclear magnetic resonance (NMR) spectroscopy has been extended to the microsecond time scale by use of chemically induced dynamic nuclear polarization signal intensity enhancements. Although a

relatively "slow" method, the enormous structural information and versatility of NMR methods will provide a powerful tool for mechanistic study of both structure and reaction mechanisms. Time-resolved flash electron spin resonance spectroscopy has undergone steady development and, as for time-resolved flash NMR, provides great promise for studying structure and dynamics of radical transients.

In the 1980s continued investigation of the well-studied conventional model systems that provided the basis for paradigms of the 1960s and 1970s are likely to be witnessed, except that these systems will be investigated under unconventional conditions, *i.e.* with multiphoton laser excitation, in microheterogeneous environments, with novel detection methods etc.

In summary, the investigation of organic photochemical reaction mechanisms has been invigorated by the continued injection and expansion of modern instrumental methods as everyday tools of the organic photochemist, and by the extension of photochemical studies from conventional homogeneous solvents to microheterogeneous systems. The richness and excitement of the field is as apparent to casual observers as it is to its practitioners.

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