

PHYSICAL ORGANIC PHOTOCHEMISTRY

NICHOLAS J. TURRO

Department of Chemistry, Columbia University, New York, NY 10027 (U.S.A.)

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Physical organic photochemistry has been concerned with the systematic investigation of structure–reactivity relationships involved in the photo-physics and photochemistry of organic molecules. The field relies heavily on the use of physical and computational methods to elucidate mechanistic pathways that allow an understanding of the molecular basis of observed or predicted structure–reactivity relationships. Determination of rate laws through kinetic analysis, syntheses of “tailor made” structures to test theories or mechanisms, and the use of product structure has been the dominant tool in physical organic chemistry and has shown similar validity in physical organic photochemistry. Reactive intermediates, which were postulated to explain observed products, have played an important role in the development of physical organic chemistry. In physical organic photochemistry these reactive intermediates have often been directly detected by time resolved spectroscopic methods.

During the 1960s the methods of physical organic photochemistry typically involved steady state kinetics, product analysis and the assumption of triplets as ubiquitous intermediates. During the 1970s time resolved methods became available and traditional reactive intermediates (carbenes, ylides, radicals, biradicals etc.) became accessible to direct spectroscopic observation, characterization and investigation. In addition, singlet states, exciplexes and radical ions were added to the list of commonly occurring reactive intermediates. There was a shift in the theoretical framework for thinking about photochemical reactions from the state diagram level to the energy surface level. During the 1980s the use of sophisticated instrumentation and time resolution of the order of nanoseconds became more common. During this period the pervasive occurrence of electron transfer processes in organic photochemical reactions became apparent, and reactive intermediates such as contact ion pairs and solvent separated ion pairs became familiar in a variety of reactions. A major change occurred as photochemists began to investigate photoprocesses occurring in microheterogeneous systems such as micelles, cyclodextrins, polymers, and porous solids. It was discovered that weak magnetic fields can strongly modify photoprocesses which occur in microheterogeneous media if radical pairs or biradicals are involved.

Since my last review in 1984, the basic paradigms for investigating organic photochemistry have not changed very much, but advances in instrumentation have continued to have a major impact on the field. For example

“multiphoton chemistry” has been made possible by the use of lasers in conjunction with computer control of instrumentation. The photochemistry of reactive intermediates such as triplet states, carbenes, radicals, and biradicals became accessible to investigation. A more subtle form of multiphoton chemistry was demonstrated in the use of microwave and radio-frequency photons to change products by inducing intersystem crossing in radical pairs and biradicals. The observation of resonance Raman of reactive intermediates is an example of the use of multiphoton chemistry as an important advance in the analytical methods for characterizing reactive intermediates. Multiphoton processes employing at least one vibrational quantum have not been successful in solution.

Among the most important developments in reaction mechanisms was the “discovery” of the Marcus theory of electron transfer by physical organic photochemists. The possibility of finding systems for which the rate of electron transfer decreased as the driving force for electron transfer increased provided the inspiration and motivation to design successful inter- and intramolecular examples of the so-called “Marcus inversion region”.

Developments in instrumentation have mainly involved improvements in time resolution. Nuclear magnetic resonance (NMR), chemically induced dynamic nuclear polarization (CIDNP), electron spin resonance (ESR) and chemically induced dynamic electron polarization (CIDEP) spectroscopy capable of nanosecond resolution have been demonstrated. The beginnings of submicrosecond IR spectroscopy have been reported, but the method will need further development of tunable diode lasers before it will be attractive as a general tool for investigating reactive intermediates. Time resolved photoacoustic spectroscopy has provided a means of directly accessing the heats of formation of reactive intermediates.

The use of computational methods to elucidate reaction mechanisms has not really made a major impact on the way organic photochemists think about such mechanisms. The Woodward–Hoffmann rules and Salem diagrams of the 1960s and 1970s still serve as the basis for the day-to-day analysis of photoreactions.

What will the 1990s bring? It seems clear that the impact of instrumentation on the investigation of reaction intermediates will continue. Time resolution in the subnanosecond domain will probably become as common and routine as is the case for nano- and microsecond spectroscopy today. FT-ESR, which operates on principles similar to Fourier Transform (FT)-NMR, could be the most powerful instrumental development for organic photochemists during the 1990s. This sensitive technique, which already is capable of routine nanosecond resolution, will be capable of investigating radical pairs and biradicals directly, and with the high resolution of magnetic spectroscopy. As pulse sequences analogous to the powerful one employed in FT-NMR are developed for FT-ESR, a wealth of dynamic and structural information is likely to emerge from this technique.

In terms of reactive intermediates, perhaps in analogy with “multiphoton” chemistry, it might be expected that “multiplexes” will emerge as

important reactive intermediates. Triplexes (adducts of an exciplex and a ground state molecule) have been convincingly demonstrated as reaction intermediates. Quadriplexes (adducts of two exciplexes) and sexaplexes (adducts of two triplexes) should begin to emerge as observable reactive intermediates as intense lasers become more commonly employed by physical organic photochemists. Such species are likely to open a new chapter of photochemical mechanisms, theory and products, since adiabatic processes on excited surfaces are known to be common for the parent exciplexes.

Investigation of various features of photoinduced electron transfer processes is likely to continue into the 1990s. Various tests of the Marcus theory, discovery of further examples of systems in the inversion region, and searches for unusual effects such as the simultaneous transfer of two or more electrons will be reported. Analogies of electron transfer with other important processes that involve electron overlap (spin exchange, electron exchange, and overall controlled reactions) will provide insights connecting all of these processes.

The investigation of photochemical processes of molecules adsorbed at interfaces (surface photochemistry) is likely to continue unabated. Based on experience over the last decade, information on both photoprocesses and interfaces will result from such studies. Owing to the inherently microheterogeneous nature of interfaces, it is certain that new approaches to handling kinetics will be developed. With more powerful computing capabilities emerging continually, methods for dealing with nonexponential decays of intermediates as well as novel methods of treating kinetic data (*e.g.* use of fractal dimensionalities, random walk simulations and statistical considerations) will be employed. A wider range of interfaces will become available for investigation and a deeper understanding of the common topological features that imbue different interfaces with similar or equivalent features at the structural level will develop. The investigation of size, shape, and site features of interfaces by photochemical probes will continue to develop as an important method to characterize the structure and dynamics of interfaces. Photoreactions will continue to be examined in novel media (supercritical fluids, the fields of superconducting materials etc.) and surprises will certainly be found.

The manipulation of the reaction dynamics and products of radical pairs by application of external magnetic fields and electromagnetic radiation may become a common and useful practice during the 1990s. The spin-off from development of instrumentation and theory of magnetic resonance should be important in this regard. It should be possible to employ these ideas and techniques to develop a new level of selectivity of photochemical reactions; triplet spin sublevel and nuclear spin sublevel specific photochemistry. The selectivity of the spin states is tied in with the assistance or inhibition of intersystem crossing in radical pairs and biradicals as a result of electron-electron or electron-nuclear spin-spin interactions.

In summary, over the past three decades physical organic photochemistry has been enriched and invigorated by a continuous infusion of more advanced instrumentation and by extension to microheterogeneous systems. The field has had an aptitude for successfully applying the classic features of systematic investigations of structure–reactivity relations to ever novel situations. The intellectual and scientific richness of the field has been apparent to external observers as it has to its “card carriers”. This situation is likely to persist into the 21st century.

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