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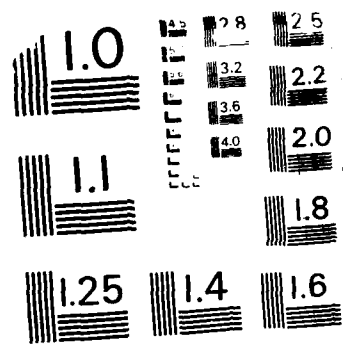
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The accomplished research has centered about the construction of new instrumentation for the investigation of transient high energy materials and the exploration of how the chemistry of transient high energy materials and the dynamics of these species respond to systematic variations in structure, environments, and experimental variables. Particular emphasis has been given to reactions in microheterogeneous environments and interfaces provided by micelles, polymers and porous solids, using resonance Raman spectroscopy, Nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, optical absorption and optical emission. The use of external magnetic fields on the reactivity of carbenes, of radical pairs and of biradicals, and of adsorption of reactive intermediates at interfaces has been explored as methods which may be capable of extending the lifetimes of these transient species.

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FINAL REPORT.

Dynamics and Stabilization of Materials Possessing High Energy Content

Principal Investigator: Professor Nicholas J. Turro

Chemistry Department

Columbia University, New York, New York 10027

Accomplished Research

General comments: The accomplished research has centered about the construction of new instrumentation for the investigation of transient high energy materials and the exploration of how the chemistry of transient high energy materials and the dynamics of these species respond to systematic variations in structure, environments and experimental variables. Particular emphasis has been given to reactions in microheterogeneous environments and interfaces provided by micelles, polymers and porous solids.

The executed research has achieved some significant accomplishments and progress toward the syntheses and investigations of a range of high energy reactive intermediates and transients such as carbenes, radical pairs, biradicals, ylides and electronically excited states. A battery of analytical techniques, such as resonance Raman spectroscopy, nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, optical absorption and optical emission have been employed to characterize the structures and to define the dynamics of high energy transients. The use of external magnetic fields on the reactivity of carbenes, of radical pairs and of biradicals, and of adsorption of reactive intermediates at interfaces has been explored as methods which may be capable of extending the lifetimes of these transient species.

FUNDAMENTAL INVESTIGATIONS OF MATERIALS CAPABLE OF HIGH ENERGY CONTENT, STORAGE AND RELEASE

Preface

The development of the field of chemical kinetics over the past 50 years has been driven by the new experimental techniques which provide improved methods for the investigation of ever faster reactions in ever increasing structural and energetic detail. In the early part of the 20th century experimentalists were able to identify only the final, stable products of chemical reactions which took place over a time scale of minutes or hours. Today, on the other hand, the most advanced experimental methods are aimed at investigations of highly reactive and transient intermediates (the precursors to the final products of a chemical reaction), and the attainable experimental time scale has shrunk by more than 15 orders of magnitude from hours to femtoseconds (10^{-15} second, a quintillionth of a second). Technical and instrumental improvements, which rely heavily on the development of fast electronic detectors, lasers, and computer technology, are significantly advancing our understanding of combustion processes involving energetic and chemically unstable materials. Modern experimental studies of chemical reactions can now follow the generation, preservation and release of chemical, vibrational and electronic energy, and clarify the exact mechanism whereby reactants are transformed into the final products. The Principal Investigator, Professor Nicholas J. Turro, is a physical organic photochemist specializing in the synthesis, characterization and dynamics of molecules possessing high energy content. His research group has had extensive experience and expertise in the investigation of energy capture, storage and release involving electronically excited states and highly energetic ground states.

Photochemical Reactions at Interfaces and in Microheterogeneous Environments

Cyclodextrins

We have exploited the hydrophobic internal cavity of cyclodextrins in aqueous systems to create unusual photophysical situations. For example, an unusual intramolecular exciplex emission was observed from aqueous solutions of an aromatic hydrocarbon/amine substrate, even though such emission had never before been detected

in aqueous solutions (307). In another system we were able to employ fluorescence polarity probes to examine the polarity of the cyclodextrin cavity (313), and examine the influence of binding to a cyclodextrin cavity on the acid-base properties of a substrate (318). We have also explored the use of inclusion complexes as a means of controlling the reactivity of electronically excited guest molecules. The behavior of dibenzyl ketone in deoxycholic acid in the solid state and in aqueous solutions of cyclodextrin has been examined (357). Employing the cage effect as a probe we have found that the translational motion of the benzyl radical pairs is severely restricted in these microheterogeneous environments. In the case of cyclodextrins we have been able to observe the ESR spectrum of radical pairs produced by photolysis at ambient temperatures. In a second system involving aryl alkyl ketones, the competition between Type I and Type II reactions of ketones included in cyclodextrins was investigated and it was found that moderate effects on the products ratios relative to those found in homogeneous fluid media could be achieved (363).

Reactive Intermediates

Time resolved laser flash spectroscopy has been applied to a variety of carbene, ylide and biradical systems to provide quantitative information on the chemical dynamics of these systems by measurement of the absolute rate constants of the reactions of carbenes with alkenes. During the grant period we have measured for the first time a large number of absolute rate constants for reaction of carbenes to ethylenes. The electrophilicity of phenyl halo carbenes has been established by determination of Hammett constants of these systems (368). For a novel system of cyclophane diaryl carbenes, the structural control of the reactivity by means of the singlet triplet equilibrium was determined (376). A detailed study of the temperature of the absolute rate constants for additions of carbenes to alkenes showed that these reactions are generally dominated by entropies of activation. Indeed, negative enthalpies of activation were observed with the faster reacting alkenes, a result that provided evidence for a reversibly formed alkene-carbene complex (377). One of the

simplest nitrile ylides, methyl nitrile ylide, was generated by the reaction of methylene and acetonitrile, and the rate constants for cycloaddition of this ylide with a variety of 1,3-dipolarophiles were determined by time resolved laser flash spectroscopy (378). The singlet triplet intersystem crossing of methylene in fluid solution was investigated by chemically induced dynamic nuclear polarization (CIDNP) and by time resolved laser flash spectroscopy (383, 394). The quantitative chemical reactivities of a sulfur substituted diaryl carbene (thioxanthenylidene-S,S-dioxide) and a cyclic carbene (carbenadibenzocycloheptane) were established by time resolved laser spectroscopy (389, 390). Direct spectroscopic evidence for the formation of a carbonyl ylide from the reaction of methylene and carbonyl compounds was reported (401). Since diazirines are often the precursors for the carbenes we have investigated by photochemical excitation, we have studied the direct photochemical population of triplet diazirines and established their triplet energies by an energy transfer method (396).

Radicals and Biradicals

The primary Type I photocleavage of dibenzyl ketones and the subsequent decarbonylation of phenacyl radicals have been investigated and the rate constants for loss of carbon monoxide established (388). Nanosecond transient absorption studies of the lifetimes of several substituted biradicals elucidated the mechanisms which determine the lifetime of these reactive intermediates (399). It was established that spin-orbit coupling provided the major mechanism for intersystem crossing, which is the rate determining step for the biradicals investigated. In addition to these reports, we have (1) demonstrated the difference between the dynamics observed for reactive intermediates when intense laser light rather than conventional lamp irradiation is employed for photochemical excitation (308); (2) performed mechanistic studies of the photodecomposition of arylmethyl sulfone in homogeneous and micellar solutions; (3) investigated the photochemistry of radical pairs in liquid crystalline media (323, 326); (4) observed the first CIDEP spectrum from reactions in micellar systems (332); (5) reported the first in-depth analysis of the dynamics

of radical pair reaction in micelles (342); and (6) studied the photodissociation of cyclooctatetraene and styrene in the gas phase (348).

Polymers

We have employed photochemical and photophysical probes to investigate polymer dynamics and structure. For example, we (1) have developed fluorescence probe for aqueous solutions of non-ionic micelles (328), (2) investigated the proton transfer reaction of poly-2-vinyl pyridine by fluorescence an dexcimer formation (331), (3) shown how fluorescence probes can serve as convenient detectors of the critical micelle concentration (340) and (4) investigated the quenching of pyrene fluorescence in micellar systems (343). In addition, a review of the use of photophysical probes for understanding the structure and dynamics of polymer systems was published (367) and a report employing the chemiluminescent formation of acetone to investigate the role of triplets in the initiation of vinyl polymerization was reported (380).

Reactive Intermediates Adsorbed on Porous Solids

The photochemistry of ketones adsorbed on porous solids such as silica and zeolites was found to vary dramatically from that observed in homogeneous solution (309, 319, 321, 329, 334, 336, 345). The basis for the differing behavior was traced to the diffusional properties of the intermediate radicals produced by photolysis of the ketones. For example, it was found that the product formation was sensitive to the size and shape of zeolite pores (395) and that pore size was a significant factor in determining the behavior of radical pairs adsorbed on porous silica (400). These results provide important new methods and techniques for stabilizing reactive intermediates. For example, it may be possible to design systems in which radical intermediates are kinetically stabilized by adsorption on a porous solid and for which addition of an inert displacing material (water, nitrogen) will kinetically trigger the reactions of the radicals and the release of energy. Such concepts could be useful in increasing fuel efficiency or the initiation of ignition of fuels.

Singlet Molecular Oxygen and Oxidation

In a fruitful collaboration with Professor K. B. Eisenthal of the Chemistry Department of Columbia University the picosecond dynamics of two isomeric endoperoxides were investigated (375). From the results it was concluded that the photoexcited endoperoxide undergo extrusion of singlet molecular oxygen in a non-concerted reaction the steps of which are in the picosecond time domain. A review of AFOSR supported research on oxidations has appeared (338).

Review Publications

Reviews of organic photoreaction mechanisms (314), magnetic isotope effects on organic photoreactions (317), laser spectroscopy of carbenes (324, 337), magnetic field effects on organic photoreactions (327), spin effects on oxidation reactions (338), photochemistry in micelles (341), photosensitization by reversible electron transfer (361) and of the topological bases for scientific thinking in organic chemistry (379) have been published.

Coupling Activities and Professional Activities of the Principal Investigator

The Principal Investigator has attended and presented a lecture at the AFOSR contractors meeting in Bedford, Massachusetts in November 1986 and has delivered a paper at the AFOSR sponsored meeting on Porous Microstructures in San Diego in February, 1987. He visited the Office of Scientific Research at Bolling Air Force Base in October 1986 and met with several program managers to discuss ongoing research and future directions for research.

The Principal Investigator has been honored with two major awards during 1986: The Harrison Howe Award of the Rochester Section of the ACS, and the Cope Scholar Award of the ACS. He was also selected to present the Fahs Smith Lecture (University of Pennsylvania, April, 1986) and the Cherry Emerson Lecture (Emory University, Atlanta, Georgia, April, 1987). He was a plenary lecturer at the IUPAC Symposium on Photochemistry (Lisbon, Portugal, July, 1986) and at the ACS Polymer Division Symposium on Photochemistry in Polymer Systems (Anaheim, California, September, 1986). He was also selected to be a participant in NSF sponsored workshops on Solar Energy Conversion (Hawaii, March, 1987) and on Reactive Organic Intermediates (Holderness, New Hampshire, June, 1987).

The Principal Investigator has presented lectures on AFOSR supported research at a number of institutions since the last annual report: Wesleyan University (January, 1986), Exxon Corporate Research Laboratory (February, 1986), University of Florida (February, 1986), Cornell University (March, 1986), University of Pennsylvania (April, 1986), University of Rochester (November, 1986), University of California, Santa Barbara (February, 1987), and the University of Toronto (May, 1987).

The Principal Investigator has been and continues to be a member of the National Academy of Sciences Board on Chemical Sciences and Technology and he serves on an Advisory Committee to the Chemistry Division of the Office of Naval Research and on the Science Advisory Committee of the Council for Chemical Research. He also serves on the Advisory Board of the Journal of the American Chemical Society, the Journal of Photochemistry, the Journal of Reactive Intermediates and the Encyclopedia of Physical Science and Technology.

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October 31, 1987.

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2. G.L. Duveneck, E.V. Sitzmann, K.B. Eisenthal and N.J. Turro, "Photoisomerization of trans-Stilbene upon Complexation to Cyclodextrins".
3. N.J. Turro, C.H. Tung, and I.R. Gould, "Electron Transfer Photoinduced Decomposition of Benzyl Esters."
4. R.A. Moss and N.J. Turro, "Laser Flash Photolytic Studies of Arylhalocarbenes," submitted to Plenum Press as a chapter in a book.
5. J.F. Wang, K.M. Welsh, K.C. Waterman, P. Fehlner, C. Doubleday, Jr. "Dynamics of Interaction between a 1,9-Biradical and Lanthanide Ions", submitted to J. Am. Chem. Soc.
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