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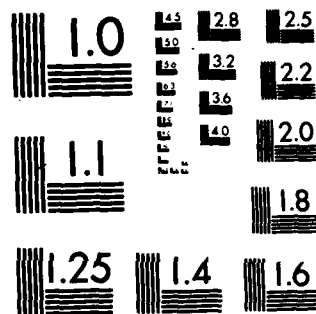
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STRUCTURAL AND DYNAMIC STUDIES OF MATERIALS

POSSESSING HIGH ENERGY CONTENT

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by-
Nicholas J. Turro

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<p>→ This final report updates and summarizes the research accomplished under this grant during the period of November 1, 1980 through October 31, 1983. We have emphasized investigations in the following areas: (1) photochemical mechanisms through the use of time-resolved laser flash spectroscopy; (2) Carbenes, radical pairs, ylides, singlet molecular oxygen and other high energy species; (3) Detailed and systematic determination of the absolute rate constants for the addition of carbenes to ethylenes; (4) Application of weak magnetic fields for</p>																	

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controlling the reactivity of radical pairs in colloidal systems; (S) Ability of weak magnetic fields to dramatically influence the rate and molecular weights in emulsion polymerization. *⌘*

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FINAL REPORT OF RESEARCH ACCOMPLISHMENTS SUPPORTED BY GRANT AFOSR-81-0013
DURING THE THREE YEAR PERIOD - 1 November 1980 through 31 October 1983.

The research supported by this Grant has produced knowledge in several areas concerned with the structure and dynamics of materials possessing high energy content. Our major emphasis has been directed toward the determination of absolute rate constants of the reaction dynamics of carbenes and radical pairs via time resolved laser flash spectroscopy, toward the elucidation of the structure and dynamics of microheterogeneous spaces produced in aqueous environments by species such as micelles and cyclodextrins, toward the establishment of the nature of oxygen as a quencher of photochemical processes, and toward the development of an understanding of the nature of magnetic effects on the reactions of radicals. In addition, reviews of magnetic field effects on chemical reactions and of the time resolved laser flash spectrometric studies of singlet carbenes were prepared.

1. Laser Flash Spectroscopy

The use of laser flash spectroscopic techniques allows the detection, identification, and dynamic analysis of biradicals and caged radical pairs in fluid solution at ambient temperatures. The conventional flash spectroscopic device has been advanced with the advent of the Excimer Laser, as an excitation source of the optical multichannel analyzer (OMA) as a detector system, and of the transient digitizer (TD) as a data collector and analyzer. The excimer laser, in addition to serving as an excitation source, may also induce novel photophysical and/or photochemical events as a result of the unusually high intensities produced by such devices. Examples are given¹ of the use of excimer laser-OMA and excimer laser-TD systems to study the dynamics of radical pairs which are caged in micelle aggregates and to study novel emissions produced by photoexcitation of benzophenone and substituted benzophenones.

STUDIES OF SINGLET CARBENES RESEARCH (AFSC)
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At high laser intensities, excitation of benzophenone and certain substituted benzophenones in nonpolar, inert solvents results in the observation of a novel emission that is attributed to an electronically excited complex produced by triplet-triplet interactions.² We have also found that the diphenyl ketyl radical, which is formed upon photolysis of α -phenyl benzoin, is produced in its excited state upon intense pulsed laser irradiation.³ Using techniques of time-resolved absorption and emission spectroscopy, reaction rate constants for the ground and excited states of this radical were obtained. For the radical quenchers employed, the excited state reactivity is found to be typically several orders of magnitude greater than that of the ground state. It is concluded that the excited state of diphenyl ketyl radical reacts predominantly by electron transfer processes.

We used laser flash photolysis to determine the rate constants and Arrhenius parameters for decarbonylation of phenylacetyl ($C_6H_5CH_2CO$), phenylmethylacetyl ($C_6H_5CHCH_3CO$), and phenyldimethylacetyl [$C_6H_5C(CH_3)_2CO$] radicals in isooctane. The variation of the rate constant for decarbonylation follows the pattern expected from radical stabilities, but the activation energies do not. We propose that previously unrecognized conformational restrictions may be significant in determining decarbonylation rates.⁴

In collaboration with Professor Richard S. Givens of the University of Kansas, we investigated the mechanism of photodecomposition of aryl sulfones using both steady-state and time-resolved techniques.⁵ We found direct evidence for radical and triplet state intermediates and a correlation between the dynamics of reaction of the intermediate triplet states with the stabilities of the intermediate radicals. In a similar study (in collaboration with Professor Gary Griffin and associates at the University of New Orleans) we found that N,N,N',N'-tetramethylbenzidine (NTMB)

photosensitizes the cis-trans-isomerization of stilbene oxiranes (SO) and the extrusion of SO_2 from dibenzyl sulfone (DBS).⁶ In acetonitrile solution and in the absence of SO or DBS, singlet NTMB undergoes three processes: intersystem crossing to triplet NTMB ($\phi_{\text{ISC}} = 0.63$, $k_{\text{ISC}} = 6.3 \times 10^7 \text{ s}^{-1}$), fluorescence ($\phi_{\text{f}} = 0.30$, $k_{\text{f}} = 3 \times 10^7 \text{ s}^{-1}$), and formation of a cation by electron ejection ($\phi_{\text{ion}} = 0.09$). Both singlet and triplet sensitization were observed; a charge transfer or reversible electron transfer mechanism is proposed to explain these results.

2. The Role of Molecular Oxygen in Photoreactions

Two separate studies were conducted in this area: (1) We evaluated the relative lifetimes of singlet molecular oxygen as a function of solvent and deuterium substitution via measurements involving the direct emission of singlet oxygen at $1.27 \mu\text{m}$.⁷ (2) We discovered that the phosphorescence on the 4-bromo-1-naphthoyl group was readily quenched by molecular oxygen in homogeneous solvents.⁸ However, when this lumophore is complexed with γ -cyclodextrin in aqueous solution at room temperature, its phosphorescence is observed even under 1 atm of oxygen. Phosphorescence decay data indicated that two types of probe/cyclodextrin complexes are formed with lifetimes of 600 μs and 3.5 ms. Oxygen completely quenches the fast decay, but only partially quenches the slow decay.

3. Magnetic Field Effects on Reactions in Heterogeneous Spaces

The photolyses of dibenzyl ketones in aqueous micellar solution have been shown to greatly enhance both geminate radical pair recombination and the enrichment of ^{13}C in recovered ketone compared to homogeneous solution. These observations have been attributed to the combined effects of the reduced dimensionality imposed by micellization and hyperfine induced intersystem crossing in the geminate radical pairs. This latter effect is the basis of Chemically Induced Dynamic Nuclear Polarization (CIDNP), a phenomenon

which is well known in homogeneous solution. The photolyses of 1,2-diphenyl-2-methyl-1-propanone and its ^2H and ^{13}C derivatives in micellar solution further demonstrate the enhanced cage and magnetic isotope effects of micellization. We observed CIDNP during the photolyses of micellar solutions of several ketones further demonstrating the validity of the radical pair model to these systems.⁹ Analyses of the CIDNP spectra in the presence and absence of aqueous free radical scavengers (e.g., Cu^{2+}) allow us to differentiate between radical pairs which react exclusively within the micelle and those that are formed after diffusion into the bulk aqueous phase. In some cases this allows us to estimate a lifetime associated with the exit of free radicals from the micelles.

The photochemistry of dibenzyl ketone (DBK) and other molecules capable of producing benzyl radicals and substituted benzyl radicals has been investigated in micellar systems.¹⁰ The cage effect (percent of unscavengeable radical pairs produced by photolysis) was measured under a variety of conditions, and the results were compared with those obtained in homogeneous organic solvents. For example, parameters such as mean occupancy of ketone, detergent type and concentration, O_2 concentration, additives, temperature, applied magnetic field and pressure have been varied and investigated as to their influence on the magnitude of cage effect. In addition to modifying its environment, structural modification of the DBK by incorporation of ^2H and ^{13}C isotopes, hydrophobic groups, and heavy atoms was performed to investigate the impact of these variations on the cage effect in micellar systems. Isotopic substitution of ^2H or ^{13}C leads to results on both the quantum yields for reactions and on the percent cage that were consistent with expectations of magnetic isotope effects. Hydrophobic groups substituted in the 4-position of DBK were found to cause

a substantial increase in the cage effect and yet retain the magnetic-field-dependent character found in the parent DBK. Incorporation of Br in the 4-position of DBK was found to enhance the cage effect, but at the same time causes the cage effect to become magnetic field independent. Substitution of α -naphthyl for phenyl in DBK also produced magnetic-field-independent behavior, in addition to a dramatic decrease in the efficiency of photolysis.

The course of chemical reactions involving radical pairs may depend on the occurrence and orientation of nuclear spins in the pairs. The influence of nuclear spins is maximized when the radical pairs are confined to a space which serves as a cage which allows a certain degree of independent diffusional and rotational motion of the partners of the pair, but which also encourages reenounters of the partners within a period which allows the nuclear spins to operate on the odd electron spins of the pair. Under the proper conditions, the nuclear spins can induce intersystem crossing between the triplet and singlet states of radical pairs.¹¹

In our continuing studies on emulsion polymerization we have found that the efficiency of emulsion polymerization and the average molecular weight of the polymers formed are significantly increased by the application of laboratory magnetic fields when photoinduced initiation is sensitized by oil-soluble ketones, but not when aqueous soluble thermal initiators are employed.¹² No magnetic field effects are observed for photoinitiated polymerization of styrene in toluene solution. These results are interpreted in terms of the postulate that for oil-soluble photoinitiators, micellized radical pairs are produced at the initial stages of polymerization and that micellized triplet pairs are required for the effective operation of external magnetic field effects because the efficiency of radical escape out of the micelle aggregate in the early stages of polymerization is significantly influenced by the application of weak magnetic fields.

The photochemically induced emulsion polymerization of styrene, methyl methacrylate, or acrylic acid is photosensitized by oil-soluble ketone initiators (e.g., dibenzyl ketone) to conversion and average molecular weights which are comparable to those achievable by employing conventional aqueous-soluble thermal initiators such as persulfates. The efficiency of polymerization and the average molecular weight of the polymers formed are significantly increased by the application of laboratory magnetic fields when photoinduced initiation is sensitized by oil-soluble ketones, but not when aqueous-soluble thermal initiators are employed.¹³ With 1,1'-diphenyl-1,1'-azoethane as initiator, triplet-sensitized initiation, but not thermal or direct photoinduced initiation, shows magnetic field effects on the average molecular weight and the yield of the products. No magnetic field effects are observed for photoinitiated polymerization of styrene or methyl methacrylate in toluene solution. With dibenzyl ketone that is enriched with ¹³C-enriched and natural-abundance, DBK changes the relative yield of the lower and higher molecular weight fractions. It is concluded that external magnetic fields decrease the efficiency of triplet to singlet radical-pair intersystem crossing within micelles, and, accordingly, increase the fraction of radical pairs which escape without terminating polymerization chains.

Concomitant with this research, the tacticity of poly(methyl methacrylate) (PMMA) samples made by emulsion polymerization has been determined by NMR spectroscopy at higher resolution than any previous study.¹⁴ When photo-initiation was employed at room temperature, the polymer obtained was highly syndiotactic and more stereoregular than that obtained in homogeneous radical polymerization under the same conditions. The percentage of racemic dyads and the length of racemic sequences vary significantly with the degree of conversion and the temperature, but not with variation of the hydrophobic

or the hydrophilic part of the detergent molecules. A magnetic field of 5 kG or less accelerates the polymerization reaction, and increases the polymer molecular weight when dibenzyl ketone is employed as oil-soluble photoinitiator, and has an indirect influence on the polymer tacticity. From measurements of the temperature dependence of the polymer steric composition, the difference of activation enthalpy and entropy of the meso and racemic additions have been calculated. The values do not follow the correlations from precedent literature for radical polymerization in solution if the reaction is considered a first-order Markov process. The persistence ratio depends on the detergent and the temperature of the EP; in some cases its difference from unity exceeds the experimental error. These results are interpreted as a conformational effect of the locus of the polymerization in the first stage of the EP (when micelles are present) which favors the racemic addition more than is expected in a homologous solvent such as an alkane, e.g., at the same temperature.

REVIEW ARTICLES

Three review articles were prepared during the Grant period:^{15,16,17} (1)

Magnetic Field and Magnetic Isotope Effects on the Products of Organic

Reactions. The crucial requirements for the observation of magnetic effects on chemical reactions were extracted from a large number of well-documented literature examples, which we found to be as follows: (a) An intermediate in which exchange interactions are sufficiently small as to allow intersystem crossing and thus production of a different spin state for the intermediate;

(b) A reaction of the intermediate which is in competition with the magnetic field influenced intersystem crossing process, which enables a sorting of the reaction products of the different spin states of the intermediate to take place; and (c) A proper balance of the rates of the intersystem crossing, electron exchange, and the competition process.

(2) Flash Photolysis Studies on the Reactions of Singlet Carbenes

The results of time-resolved laser flash spectrometric studies of singlet carbenes was reviewed. In particular, the absolute rate constants for reactions of phenyl chloro carbene and related carbenes with alkenes were summarized and systematized. The experiments described provide the basis for a detailed examination of carbene reactivity selectivity principles. The results of studies of the influence of variable temperature on the absolute rate constants for carbene reactions provided evidence for the existence of transient carbene/alkene intermediates. (in collaboration with Professor Robert A. Moss and co-workers at Rutgers University).

(3) Singlet-Triplet Interconversion of Diphenylmethylene. Energetics,

Dynamics, and Reactivities of Different Spin States. A combination of picosecond and nanosecond laser spectroscopy measurements, chemical quenching experiments, and triplet sensitization experiments has allowed the determination of the rapid singlet to triplet and slower triplet to singlet intersystem crossing rates for diphenylmethylene in fluid solution at room temperature. It is shown that under the conditions of the kinetic measurements, singlet and triplet diphenylmethylene (^1DPM and ^3DPM , respectively) are in rapid equilibrium relative to reactions, so that knowledge of the values of k_{ST} and k_{TS} allows determination of the equilibrium constant and change in free energy for the $^1\text{DPM} \rightleftharpoons ^3\text{DPM}$ process. The absolute reactivity of ^1DPM toward a series of alcohols has been determined and is discussed in terms of other current investigations of carbene reactivity. (in collaboration with Professor Kenneth Eisenthal, Columbia University).

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