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RADIATION LABORATORY
UNIVERSITY OF NOTRE DAME

QUARTERLY REPORT

October 1 - December 31, 1993

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ISSUED

February 17, 1994

MASTER

The Notre Dame Radiation Laboratory is a facility of the Department of Energy operated for DOE by the University of Notre Dame under contract No. DE-AC02-76ER00038. The majority of the programs within the Laboratory are supported by the Office of Basic Energy Sciences of DOE and, unless otherwise noted in the following, support can be attributed to the Office of Basic Energy Sciences. Certain additional programs, so indicated, are supported by the Standard Reference Data Program of the National Institute of Standards and Technology.

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Prof. J. Vargas completed his radiolysis studies in the Laboratory and returned to the Universidad Metropolitana de Ciencias de la Educación, Santiago, Chile, in December.

Dr. Y.-M. Wang concluded his postdoctoral appointment with Dr. L. K. Patterson in December, and took a similar position with Prof. G. Jones at Boston University.

Dr. K. Bobrowski concluded his sabbatical term in the laboratory in December, and returned to the Institute of Biochemistry and Biophysics in Warsaw, Poland.

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Visitors during the quarter included the following:

Dr. G. Mallard of NIST visited the Radiation Chemistry Data Center in October to collaborate with Dr. A. B. Ross on production of databases.

Prof. C. Schöneich visited the Laboratory from the University of Kansas in October to further his collaboration with Dr. K. Bobrowski.

Dr. S. P. Mezyk and Mr. G. Glowa visited the Laboratory from the AECL Laboratory at Pinawa, Manitoba, during November to conduct some experiments on the LINAC.

Prof. V. Talrose of the Russian Academy of Science spent part of November in the Laboratory holding discussions with members of the staff.

Dr. S. Gallagher of Solvay Enzymes, Elkhart, Indiana, visited the Laboratory in November to make use of the gamma radiolysis facilities.

Publications

P.V. Kamat and K. Vinodgopal

The Role of Support Material in the Photodegradation of Colored Organic Compounds.

Chapter 31, Aquatic and Surface Photochemistry, G.R. Helz, R.G. Zepp, D.G. Crosby, Eds.; Lewis Publishers. pp. 443-450 (1993) [NDRL 3435]

K. Vinodgopal and P.V. Kamat

Photosensitization of Semiconductor Colloids by Humic Substances.

Chapter 30, Aquatic and Surface Photochemistry, G.R. Helz, R.G. Zepp, D.G. Crosby, Eds.; Lewis Publishers, pp. 437-442 (1993) [NDRL 3450]

I.B. Duncanson

A Bubble Trap for ESR Spectroscopy.

Fusion, Vol. XL, No. 4, p. 26 (1993) [NDRL 3501]

J.A. LaVerne and S.M. Pimblott

Diffusion-kinetic Modelling of the Cooperative Effect of Scavengers on the Scavenged Yield of the Hydroxyl Radical.

Faraday Trans. 89, 3527 (1993) [NDRL 3530]

K. Bobrowski and B. Marciniak

The Kinetics of the Acid-base Equilibrium of 4-carboxybenzophenone Ketyl Radical. A Pulse Radiolysis Study.

Radiat. Phys. Chem. 43, 361 (1994) [NDRL 3536]

P.V. Kamat and K. Vinodgopal

TiO₂ Mediated Photocatalysis Using Visible Light: Photosensitization Approach.

Photocatalytic Purification and Treatment of Water and Air, D.F. Ollis and H. Al-Ekabi, Eds.; Elsevier Science Publishers, p. 83 (1993) [NDRL 3537]

S. Hotchandani, I. Bedja, R.W. Fessenden and P.V. Kamat

Electrochromic and Photoelectrochromic Behavior of Thin WO₃ Films Prepared from Quantum Size Colloidal Particles.

Langmuir 10, 17 (1994) [NDRL 3549]

S.M. Pimblott

Stochastic Modelling of the Influence of an Applied Electric Field on the Ion Recombination Kinetics of Multiple-ion-pair Spurs in Low-permittivity Liquids.

Faraday Trans. 89, 3533 (1993) [NDRL 3553]

K.P. Madden, H.J.D. McManus and R.W. Fessenden

Computer Controlled in situ Radiolysis Electron Spin Resonance Spectrometer Incorporating Magnetic Field-microwave Frequency Locking.

Rev. Sci. Instrum. 65, 49 (1994) [NDRL 3561]

K.A. Gray, U. Stafford, M.S. Dieckmann and P. Kamat

Mechanistic Studies in TiO₂ Systems: Photocatalytic Degradation of Chloro- and Nitrophenols.

Photocatalytic Purification and Treatment of Water and Air, D.F. Ollis and H. Al-Ekabi, Eds.; Elsevier Science Publishers, p. 455 (1993) [NDRL 3568]

- R.H. Schuler
Three Decades of Spectroscopic Studies of Radiation Produced Intermediates.
Radiat. Phys. Chem. 43, 417 (1994) [NDRL 3571]
- I. Carmichael, D.M. Chipman, C.A. Podlasek and A.S. Serianni
Torsional Effects on the One-bond ^{13}C - ^{13}C Spin Coupling Constant in
Ethylene Glycol: Insights into the Behavior of $^1J_{\text{CC}}$ in Carbohydrates.
J. Am. Chem. Soc. 115, 10863 (1993) [NDRL 3576]
- G. Ferraudi
Magnetic Field Effects in Rates of Reactions between Radicals and Transition
Metal Coordination Complexes of Co(II) and Mn(II): Probes for Spin Polarization.
J. Phys. Chem. 97, 11929 (1993) [NDRL 3580]
- K.P. Madden and H. Taniguchi
An in-situ Radiolysis EPR Study of Spin Trapping by 2-Methyl-2-nitroso-
propane: Steric and Electronic Effects Influencing the Trapping of
Hydroxyalkyl Radicals Derived from Pentanols and Substituted Pentanols.
Perkin Trans. 2, p. 2095 (1993) [NDRL 3588]
- B. Marciniak, K. Bobrowski and G.L. Hug
Quenching of Triplet States of Aromatic Ketones by Sulfur-Containing Amino
Acids in Solution. Evidence for Electron Transfer.
J. Phys. Chem. 97, 11937 (1993) [NDRL 3590]
- Y. Wang
Slow Decay of Space-Charge-Limited Current in CdS.
J. Appl. Phys. 75, 332 (1994) [NDRL 3607]
- G.N.R. Tripathi and R.H. Schuler
Structure of the p-aminophenoxyl Radical.
Faraday Trans. 89, 4177 (1993) [NDRL 3611]
- Y. Wang
Spectrum of Anomalous Random Telegraph Noise.
J. Appl. Phys. 74, 7609 (1993) [NDRL 3612]
- S. Das, T.L. Thanulingam, K.G. Thomas, P.V. Kamat and M.V. George
Photochemistry of Squaraine Dyes. 5. Aggregation of Bis(2,4-dihydroxyphenyl)-
squaraine and Bis(2,4,6-trihydroxyphenyl)squaraine and Their Photodissociation
in Acetonitrile Solutions.
J. Phys. Chem. 97, 13620 (1994) [NDRL 3624]
- K. Bobrowski, D. Pogoćki and C. Schoneich
Mechanism of the $\cdot\text{OH}$ Radical-Induced Decarboxylation of 2-(Alkylthio)ethanoic
Acid Derivatives.
J. Phys. Chem. 97, 13677 (1993) [NDRL 3638]
- S. Das, K.G. Thomas, R. Ramanathan, M.V. George and P.V. Kamat
Photochemistry of Squaraine Dyes. 6. Solvent Hydrogen Bonding Effects on the
Photophysical Properties of Bis(benzothiazolylidene)squaraines.
J. Phys. Chem. 97, 13625 (1993) [NDRL 3641]

K. Bobrowski, G.L. Hug, B. Marciniak and H. Kozubek
4-Carboxybenzophenone-Sensitized Photooxidation of Sulfur-Containing Amino
Acids in Alkaline Aqueous Solutions. Secondary Photoreactions Kinetics.
J. Phys. Chem. 98, 537 (1994) [NDRL 3643]

P.V. Kamat
What Makes Semiconductor Colloids Unique as Photocatalysts?
The Spectrum 6, 14 (1993) [NDRL 3657]

External Talks and Presentations

Simon M. Pimblott, "Theoretical Studies in Radiation Chemistry and
Radiation Biology", Rochester University, Rochester, NY, Nov. 4, 1993.

The following reports were issued during the period of the quarter:

1. (NDRL-3652) A Photocatalytic Approach for the Reductive Decolorization of Textile Azo Dyes in Colloidal Semiconductor Suspensions¹

(K. Vinodgopal,² I. Bedja,³ S. Hotchandani³ and P. V. Kamat)

Two representative commercially used textile azo dyes, Acid Orange 7 and Direct Blue 1, have been decolorized using colloidal TiO₂ and WO₃ photocatalytic systems. Under UV irradiation, these dyes undergo rapid decolorization as they are reduced at the semiconductor surface by the trapped electrons. The trapping of electrons in irradiated semiconductor colloids and their participation in the dye reduction process have been probed by steady-state and laser flash photolysis techniques. The quantum efficiency for such a reductive process has been determined to be 4.7%. The rate constant for the electron transfer between the excited semiconductor colloid and the dye is of the order of $10^8 \text{ M}^{-1} \text{ s}^{-1}$. This simple approach of photocatalytic decolorization represents a significant new advance in the treatment of textile dye wastes.

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- (1) Submitted for publication in Environmental Science and Technology.
 - (2) Indiana University Northwest, Gary.
 - (3) Université du Québec à Trois Rivières.
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2. (NDRL-3653) Interaction of Semiconductor Colloids with J-Aggregates of a Squaraine Dye¹

(S. Hotchandani,² S. Das,³ K. George Thomas,³ M. V. George and P. V. Kamat)

The role of bis(2,4,6-trihydroxyphenyl)squaraine, Sq, in sensitizing large-bandgap semiconductors has been investigated in the present study. The dye in its aggregate form readily interacts with the TiO₂ colloids giving rise to a new charge-transfer band in the red region. The apparent association constant for the dye aggregate and TiO₂ colloid as determined from a Benesi-Hildebrand plot is 1600 M^{-1} . Nanocrystalline semiconductor films prepared from TiO₂, ZnO, and SnO₂ colloids have been modified with Sq to probe the photosensitization effects. Both dye monomers and aggregates were found to participate in the charge injection

process. An incident photon-to-photocurrent efficiency up to 0.7% has been observed.

- (1) Submitted for publication in Research on Chemical Intermediates.
 - (2) Université du Québec à Trois Rivières.
 - (3) Regional Research Laboratory, Trivandrum, India.
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3. (NDRL-3654) Ion Recombination Kinetics in High LET Regions of Electron Tracks in Hydrocarbons¹

(S. M. Pimblott and N. J. B. Green²)

Stochastic techniques have been devised for modeling ion recombination kinetics in low-permittivity solvents like hydrocarbons. Previously, these methods have been used to study the reaction in spurs initially containing small numbers of reactive ion pairs. As spurs represent only 80% of the energy loss events of an energetic electron in a hydrocarbon, a significant proportion of the radiation-induced reactants are found in spatially extended clusters. The chemistry of these extended entities may have a considerable effect on the observed kinetics and has to be incorporated in any realistic theoretical treatment.

Random flights simulation and the Independent Reaction Times (IRT) model have been used to study the recombination kinetics in spatially extended cation-anion (C^+/A^-) and cation-electron (C^+/e^-) systems. The modeled kinetics are found to depend on (i) the distribution of the separations between the adjacent C^+ s, (ii) the relative orientation of the cations, i.e., the $C^+-C^+-C^+$ angle, and (iii) the relative values of the cation and anion diffusion coefficients. While the long time yields predicted by the two simulation methods are in good agreement, the time dependence of the decay kinetics predicted by the IRT model is often slower than that of the more accurate random flights method. The magnitude of the discrepancy observed is determined by the initial spatial distribution of the system.

- (1) Submitted for presentation at 42nd Annual Meeting of the Radiation Research Society, Nashville, TN, May 1-5, 1994.
 - (2) King's College London.
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4. (NDRL-3655) Theories for Spur Chemistry¹

(S. M. Pimblott)

Synchrotron radiation produces isolated spurs of specific energy. In contrast, fast electron radiolysis gives tracks of well-separated spurs of different energies. The distribution of spurs produced in fast-electron radiolysis has been evaluated using Monte Carlo methods. The most probable energy loss is 22 eV in water and 16 eV in hydrocarbon. The majority of energy loss events in both media are smaller than 100 eV and so are in the regime accessible to synchrotron studies. Because of the variety of different spurs along a fast electron track, the theoretical treatment of fast-electron radiation chemistry is difficult. Consequently the potential for the use of synchrotron studies as models for studying radiation damage is significant.

Typically a spur is made up of a cluster of reactive radicals and ions derived from several ionization or excitation events. The chemistry of spatially nonhomogeneous systems like spurs is complex. It reflects the spatial relaxation of the cluster by diffusion and the reaction of the short-lived transients. A number of different stochastic and deterministic techniques for modeling spur kinetics have been developed and these methods have been used to examine the reaction and diffusion in multiple ionization/excitation spurs like those produced in synchrotron and in fast-electron radiolysis. Calculations for aqueous solutions show a significant stochastic effect on the modeled kinetics for spurs containing relatively few reactants (1, 2 or 3 ionizations/excitations). This effect is most noticeable in the yields of the molecular products. The influence of statistics on the chemistry of larger spurs is less marked. It depends on the initial spatial distribution of the reactants and frequently reaction can be modeled adequately using deterministic methods.

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- (1) Submitted for presentation at 42nd Annual Meeting of the Radiation Research Society, Nashville, TN, May 1-5, 1994.
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5. (NDRL-3656) Magnetic Hyperfine Coupling Constants in Free Radicals¹

(D. M. Chipman)

Electronic spin densities that determine experimentally observed magnetic hyperfine coupling constants are calculated for several representative hydrocarbon free radicals. Requirements for design of Gaussian basis sets suitable for computation of contact spin

densities are described. Focus is primarily on the leading terms in the wavefunction that provide direct and spin polarization contributions. Effects of nondynamical electron correlation and its spin polarization are also included in those situations where they are significant.

Results are presented for a variety of representative hydrocarbons, including the methynyl (CH), methyl (CH_3), and ethyl (C_2H_5) nonconjugated π -radicals; the vinyl (C_2H_3), ethynyl (C_2H), and cyclopropenyl (C_3H_3) σ -radicals; and the larger allyl (C_3H_5), pentadienyl (C_5H_7), and cyclohexadienyl (C_6H_7) conjugated π -radicals. Appropriate corrections are made in cases where large-amplitude vibrational or vibronic effects occur.

The spin-polarization level results are often found to compare favorably with experiment, although some systematic deviations are identified that implicate additional important contributions arising from dynamical electron correlation effects. These include systematic underestimates of all β -hydrogen couplings and overestimates of σ -radical α -carbon couplings. This survey enhances our understanding of the quantitative importance of various contributions to spin densities in free radicals.

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- (1) Submitted for presentation at 34th Sanibel Symposium, Ponte Vedra Beach, FL, Feb. 14-19, 1994.
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6. (3657) What Makes Semiconductor Colloids Unique as Photocatalysts?

(P. V. Kamat)

During the past decade, the utilization of semiconductor particulate systems as photocatalysts has seen a tremendous growth in carrying out photochemical transformations of organic and inorganic compounds. By making use of the principles of photoelectrochemistry, semiconductor colloids have been employed in the conversion of light energy. The application of semiconductor systems in initiating and controlling various photocatalytic processes has been reviewed in this paper.

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- (1) Submitted for publication in Spectrum.
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7. (NDRL-3658) Stochastic Simulation of Transient Free Radical Attachment on DNA¹
 (C. E. Bolton,² N. J. B. Green² and S. M. Pimblott)

Stochastic simulation techniques have been widely developed for the modelling of transient kinetics in radiation tracks over the last decade. In this paper we report the application of two such techniques, Monte Carlo Random Flights simulation and the approximate Independent Reaction Times method, to the competition kinetics of geminate radical recombination and scavenging by a DNA molecule, modelled as a uniform, reactive cylinder.

Both the reaction kinetics and the spatial distribution of hits show effects which are ascribed to the competition between recombination and scavenging; these are true three-body correlations, seen for the first time. The main effect is that the distance between hits on the cylinder is larger in the random flights simulation than the IRT results. The origin of this effect is analyzed in detail.

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- (1) Submitted for presentation at 42nd Annual Meeting of the Radiation Research Society, Nashville, TN, May 1-5, 1994.
 - (2) King's College London.
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8. (NDRL-3659) Photon-Stimulated Desorption of H⁻ from a BaO Surface¹
 (D. H. Baker,² R. L. Champion,² L. D. Doverspike² and Yicheng Want)

Photon-stimulated desorption of H⁻ ions has been observed from a BaO surface for photon energies in the range of 3 to 5 eV, with a yield that increases sharply for energies above the threshold at 3 eV. A possible explanation is that a chemisorbed H atom captures a photoemitted electron and desorbs as H⁻ via the Menzel-Gomer-Redhead mechanism.

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- (1) Submitted for publication in the Journal of Applied Physics.
 - (2) College of William and Mary.
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9. **(NDRL-3660) Structure and Fundamental Vibrations of Phenoxyl Radical¹**

(D. M. Chipman, R. Liu,² X. Zhou² and P. Pulay²)

The geometry and harmonic force field of phenoxyl radical are determined by *ab initio* calculations of the electronic structure. All the π electrons are involved in strong nondynamical correlations, which are treated in a complete π active space wavefunction. Results from using multiconfigurational self-consistent-field orbitals in the active space are found to be closely approximated by use of the more economical unrestricted Hartree-Fock natural orbitals. Large polarized basis sets are also required to obtain qualitatively correct results. Properties of the carbonyl chromophore are particularly interesting. Compared to closed-shell analogs, the equilibrium geometry indicates the CO bond in phenoxyl to be nearly as short as a typical double bond, whereas the scaled quantum mechanical force field shows it to have strength intermediate between those of typical single and double bonds. The calculated fundamental vibrational frequencies general confirm current interpretations of the major features of the observed experimental resonance Raman spectra, while leading to reassignments of some minor features. Some limited theoretical characterization of valence excited states provides qualitative explanation of the observed intensity pattern. Calculations carried out at lower levels of theory consistently find the CO bond to be too long and too weak, leading to misassignment of the observed vibrational spectrum.

(1) Submitted for publication in the Journal of Chemical Physics.

(2) University of Arkansas.

10. **(NDRL-3661) Chlorophyll *b*-Modified Nanocrystalline SnO₂ Semiconductor Thin Film as a Photosensitive Electrode¹**

(I. Bedja,² R. Carpentier,² S. Hotchandani,² R. W. Fessenden and P. V. Kamat)

Nanocrystalline thin SnO₂ semiconductor films (thickness $\leq 1 \mu\text{m}$) have been modified with chlorophyll *b* (Chl-*b*) by electrodeposition and adsorption methods for use as novel photosensitive electrodes in photoelectrochemical cells. Excitation of Chl-*b* with monochromatic light produced photocurrents with an incident photon-to-photocurrent efficiency (IPCE) of around 8.5%. The charge injection from excited Chl-*b* into the conduction

band of the semiconductor SnO_2 crystallites has been probed by time-resolved microwave absorption.

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- (1) Submitted for publication in Applied Physics Letters.
 - (2) Universite du Québec à Trois Rivières, Québec, Canada.
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11. (NDRL-3662) Preparation and Photoelectrochemical Characterization of Thin SnO_2 Nanocrystalline Semiconductor Films and Their Sensitization with Bis(2,2'-bipyridine)(2,2'-bipyridine-4,4'-dicarboxylic acid) ruthenium (II) Complex¹

(I. Bedja, S. Hotchandani² and P. V. Kamat)

Thin, transparent films of SnO_2 semiconductor have been prepared from 30 Å diameter colloids. Scanning electron microscopy and X-ray powder diffraction studies indicate a three dimensional network of SnO_2 nanocrystallites of particle diameter ≤ 50 Å. These thin nanocrystalline films exhibit reversible electrochromic effects. The electron trapping process in SnO_2 particles has been investigated by both spectroelectrochemical and laser flash photolysis techniques. These electrodes are photoelectrochemically active in the UV region with incident photon-to-photocurrent conversion efficiency of 20% at 280 nm. The photocurrent increases with increasing film thickness, but attains a limiting value at thickness greater than 0.75 μm . The migration of charge across the grain boundaries is a limiting factor for the photocurrent generation in thicker films. These SnO_2 films are highly porous and exhibit strong affinity for adsorption of sensitizer molecules such as Bis(2,2'-bipyridine)(2,2'-bipyridine-4,4'-dicarboxylic acid)Ru(II)perchlorate ($\text{Ru}(\text{bpy})_2(\text{dcbpy})^{2+}$). SnO_2 films modified with $\text{Ru}(\text{bpy})_2(\text{dcbpy})^{2+}$ exhibit excellent photoelectrochemical response in the visible with a power conversion efficiency of $\sim 1\%$ at 470 nm. The rate constant for the charge injection process as measured from the analysis of luminescence decay of $\text{Ru}(\text{bpy})_2(\text{dcbpy})^{2+*}$ on a SnO_2 surface, is in the range of $7.6 \times 10^7 \text{ s}^{-1}$ - $0.82 \times 10^7 \text{ s}^{-1}$.

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- (1) Submitted for publication in the Journal of the American Chemical Society.
 - (2) Universite du Québec à Trois Rivières, Québec, Canada.
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12. (NDRL-3663) Diffusion-Kinetic Theories for LET Effects on the Radiolysis of Water¹
(S. M. Pimblott and J. A. LaVerne)

Diffusion-kinetic methods are used to investigate the effects of incident particle linear energy transfer, LET, on the radiolysis of water and aqueous solutions. Analytic results obtained from simple track models show that the limiting long-time kinetics associated with high-LET particle tracks have time dependences which vary as $(\ln(T))^{-1}$. These long-time kinetics are considerably slower than those found for low-LET particle radiolysis which have a $t^{-1/2}$ dependence. Naturally, the predictions of the simple models suggest a significant reduction in the long-time yields of radicals in high-LET particle radiolysis compared to radiolysis with particles of low LET. More realistic deterministic diffusion-kinetic calculations examining the scavenging capacity dependences of the scavenged yield of e_{aq}^- and of OH demonstrate that the scavenged yields are related to the underlying time-dependent kinetics in the absence of the scavenger by a simple Laplace transform relationship. This relationship is also shown to link the effect of an e_{aq}^- scavenger on the formation of H_2 with the time dependence of H_2 production in the absence of the scavenger. The simple Laplace relationship does not work well when applied to H_2O_2 formation in high-LET particle tracks even though such a relationship is valid with low-LET particles. It is found that while the secondary reaction of H_2O_2 with e_{aq}^- can be neglected in low-LET particle radiolysis, it is of considerable significance in the tracks produced by high-LET particles. The increased importance of this reaction with increasing LET is the major reason for the failure of the Laplace relationship for H_2O_2 . It is also the cause of the larger yields of OH compared to e_{aq}^- at long times (small scavenging capacities).

(1) Submitted for publication in the Journal of Physical Chemistry.

13. (NDRL-3664) Theoretical Investigation of Spin-Trapping Reactions¹
(J. Bentley and K. P. Madden)

Quantum chemical calculations at the MP2/6-31+G level are used to examine the energetics of spin-trapping and related reactions using nitrosomethane as a model spin trap. It is established that nitrosomethane is a satisfactory model for the commonly employed spin trap 2-methyl-2-nitrosopropane. Free energy differences are reported for the reactions considered,

using theoretically determined molecular structures and vibrational frequencies to make the necessary temperature corrections. The effects of solvation are estimated by means of a self-consistent reaction field approach. The level of theory applied here is not expected to be quantitatively predictive, but is expected to be of value in establishing energetic trends among possible reactions. Results reported here indicate that nitrosomethane dimer and the anion of the monomer are capable of reacting as spin traps, although less effective than the monomer. In all cases, the ultimate product appears to be the nitroxide.

(1) Submitted for publication in the Journal of the American Chemical Society.

14. (NDRL-3665) Simulation of Geminate Ion Recombination Kinetics in Anisotropic Media¹

(C. E. Bolton,² N. J. B. Green² and S. M. Pimblott)

A Monte Carlo random flights technique is presented for simulating ion-pair recombination kinetics in systems with diffusional and dielectric anisotropy, and is applied to geminate electron-hole recombination in anthracene and naphthalene. While the importance of the anisotropy is evident in the dependence of the escape probability on the orientation of the initial inter-ion vector, it is found to be more significant in determining the time-scale of the reaction kinetics, which can vary by a factor of up to two in the systems studied. Comparisons for pairs with the same escape probability indicate that reaction in anthracene is likely to be considerably faster than in naphthalene.

(1) Submitted for publication in Chemical Physics Letters.

(2) King's College, London.

15. (NDRL-3666) Time-Resolved Resonance Raman Observation of Protein-Free Riboflavin Semiquinone Radicals¹

(Y. Su and G. N. R. Tripathi)

This communication reports the first time-resolved resonance Raman observation of riboflavin semiquinone anion, neutral and cation radicals in aqueous solution. These species

are short-lived in their unbound state. Therefore, their detection by conventional CW laser excitation, used in previous studies, was not possible. Information on vibrational frequencies, provided by this work, is essential for probing chemical interactions, such as protein and ligand interactions, in the redox intermediate states of flavin molecules using Raman spectroscopy.

(1) Submitted for publication in the Journal of the American Chemical Society

16. (NDRL-3667) Hyperfine Splitting in N_4^+ from *Ab Initio* Calculation¹

(I. Carmichael)

A quadratic configuration interaction calculation of the structure and magnetic hyperfine splitting constants in the tetranitrogen cation is reported. The species is determined to be linear and splittings in close accord with experimental findings are calculated despite the large amount of spin contamination in the UHF reference wavefunction. Indeed, reasonable agreement is attained even with a modest double- ζ description of the single-particle space in the molecular orbital treatment, provided that the effect of amplitudes due to single replacements in the reference wavefunction is included in the cluster expansion. Improvements in the quality of the basis set lead to improved predictions of the unpaired spin density, indicating that such agreement is not fortuitous. An analysis is given of the contributions from various levels of excitation, up to quadruples, in the UHF determinant.

Analogous results are also presented for various ionic states of atomic nitrogen and the dinitrogen radical cation.

(1) Submitted for publication in the Journal of Physical Chemistry.

17. (NDRL-3668) One-Bond ^{13}C - ^1H Spin-Coupling Constants as Probes of Furanoxyl Ring Conformation in Oligonucleotides¹

(A. S. Serianni² and I. Carmichael)

$^1\text{J}_{\text{CH}}$ has been studied in the model furanose, 2-deoxy- β -D-glycero-tetrafuranose 1, as a function of ring geometry in order to assess the utility of these couplings as conformational probes in oligonucleotides. *Ab initio* molecular orbital (MO) calculations were conducted on the

ten envelope forms and the planar form of **1** using the second-order Møller-Plesset (MP2) electron correlation treatment with a polarized split-valence (6-31G*) basis set. These data were used to compute $^1J_{CH}$ values in conformers of **1** at the Hartree-Fock and MP2 levels of theory using a basis set specifically designed for the reliable description of spin-spin coupling constants. The results of these calculations were subsequently scaled using a factor derived from accurate quadratic configuration interaction (QCISD) calculations on a number of simpler species. MO results indicate that C-H bonds in **1** vary with ring geometry, with a given C-H bond longest when quasi-axial and shortest when quasi-equatorial. Computed $^1J_{CH}$ were found to be sensitive to C-H bond orientation, with greater couplings observed when a C-H bond is equatorial. Couplings varied by as much as 13 Hz with changes in C-H bond orientation. These results suggest a role for $^1J_{CH}$ in the conformational analysis of furanose rings which will complement current methods based on $^3J_{HH}$, $^3J_{CH}$ and $^2J_{CH}$.

(1) Submitted for publication in the Journal of the American Chemical Society.

(2) Department of Chemistry, University of Notre Dame.

18. (NDRL-3669) Radiolytic and TiO₂-Assisted Photocatalytic Degradation of 4-Chlorophenol. A Comparative Study¹

(U. Stafford,² K. A. Gray³ and P. V. Kamat)

Mechanistic and kinetic details of 4-chlorophenol (4-CP) oxidation have been elucidated by radiolytic and photocatalytic techniques. When 4-chlorophenol is oxidized by γ -radiolysis in conditions favoring hydroxyl radical oxidation ($\bullet OH$), significant concentrations of 4-chlorocatechol (4-CC) and hydroquinone (HQ) are formed as intermediates. Phenol is the only major intermediate when conditions favoring reduction by hydrated electrons are employed. No aromatic intermediates are detected when 4-chlorophenol is oxidized in the presence of oxide. Oxidative degradation rates of 4-CP are similar at pH 3.0 and pH 6.1. The 4-CP degradation rate is relatively slower at pH 9.1 and no aromatic intermediates are detected. These results confirm the proposal that hydroxyl-mediated 4-CP oxidation follows at least 3 separate degradation pathways, forming 4-CC, HQ, and unidentified non-aromatic compounds, as reaction intermediates en route to complete mineralization. Pulse radiolysis experiments have also been carried out to characterize the radical transient species formed during the

oxidation of 4-CP (pH 6 and 10), and for 4-chlorocatechol (pH 6). The second order rates for scavenging of $\bullet\text{OH}$ radicals at pH 6 are measured as $9.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for 4-CP and $7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for 4-CC.

Photocatalytic degradation produces intermediates consistent with hydroxyl radical oxidation, but the concentration of aromatic intermediate is lower than in the radiolysis experiments, especially at higher concentrations of TiO_2 . This indicates that the course of photocatalytic transformation of 4-CP does not involve hydroxyl radical oxidation exclusively. Direct electron transfer and surface chemical reactions also contribute significantly to the disappearance of 4-CP and its reaction intermediates in TiO_2 slurries.

- (1) Submitted for publication in the Journal of Physical Chemistry.
- (2) Also Department of Chemical Engineering, University of Notre Dame.
- (3) Department of Civil Engineering and Geological Sciences, University of Notre Dame.

19. (NDRL-3670) Raman Estimate of Phenoxyl and Semiquinone Radical Yields in the Hydroxyl Radical Oxidation of *p*-Hydroxybenzoic Acid¹

(Y. Su and G. N. R. Tripathi)

Redox reactions of *p*-hydroxybenzoic acid (HBA) play a vital role in many chemical and biochemical processes. In this work, time-resolved resonance Raman spectroscopy has been used to examine one-electron oxidation of *p*-hydroxybenzoic acid by $\text{OH}\bullet$ radicals in aqueous solution. The $\text{OH}\bullet$ radicals were prepared by pulse radiolysis of N_2O -saturated aqueous solutions. These radicals react with HBA at a rate constant of $6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Formation of the transient products was probed by resonance Raman excitation in the 400-450 nm region. The Raman spectrum obtained 100 ns after electron pulse irradiation of a solution containing HBA at pH ~ 11 shows Raman signals due to *p*-carboxy phenoxyl radical at $\sim 1515 \text{ cm}^{-1}$, and also those of *p*-benzosemiquinone anion at 1620 cm^{-1} . This spectrum was compared with the Raman spectrum of carboxy phenoxyl radical obtained by $\text{N}_3\bullet$ oxidation, in which reaction occurs by electron transfer, and the radical yield is similar to the yield of $\text{OH}\bullet$ radical produced on radiolysis of water. The yield of *p*-carboxy phenoxyl radical formed on $\text{OH}\bullet$ oxidation of HBA was found to be $\sim 12\%$ of the OH radicals at pH ~ 7 . The maximum yield of *p*-benzosemiquinone anion was estimated as $\sim 3\%$ of the $\text{OH}\bullet$ radicals. Kinetics of the

semiquinone formation was monitored by the 1620 cm^{-1} band of the radical, which gave a formation rate constant of $1 \times 10^6\text{ M}^{-1}\text{s}^{-1}$. The phenoxyl and semiquinone radicals are formed due to $\text{OH}\cdot$ attack on ring carbon positions linked to OH and CO_2^- groups, respectively. This study is an illustration of the application of Raman spectroscopy for quantitative estimation of the transient products while reactions are in progress.

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- (1) Submitted for presentation at Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Chicago, IL, February 27-March 4, 1994.
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20. (NDRL-3671) Thin Nanocrystalline SnO_2 Films as New Electrode Material for Photoelectrochemical Cells: Preparation, Characterization and Photosensitization¹

(I. Bedja,² S. Hotchandani² and P. V. Kamat)

The approach of using semiconductor colloids for the design of optically transparent thin semiconductor films has been fascinating in the sense that this technique is relatively simple and inexpensive compared to other commonly employed techniques such as molecular beam epitaxy or chemical vapor deposition. The present study focuses on the method of preparation and characterization of nanocrystalline SnO_2 films for developing new electrode materials for photoelectrochemical cells. Scanning electron microscopy and X-ray diffraction have shown the nanocrystalline structure of SnO_2 colloids (30 Å diameter) employed for the preparation of the films. These transparent thin SnO_2 film electrodes have been shown to possess excellent photoelectrochemical properties with incident photon-to-photocurrent conversion efficiency (IPCE) of 20% at 280 nm. The thin films prepared from colloidal suspensions are quite porous and can be readily modified with sensitizing molecules such as $\text{Ru}(2,2'\text{-bipyridine-4,4'-dicarboxylic acid})^{2+}$. A maximum IPCE of 22% was observed around 460 nm with this sensitizer.

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- (1) Submitted for presentation at 1994 Florida Advanced Materials Chemistry Conference, Palm Coast, FL, March 27-30, 1994.
- (2) Université du Québec à Trois Rivières.
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21. (NDRL-3672) Photochemistry of Textile Azo Dyes. Spectral Characterization of Excited State, Reduced and Oxidized Forms of Acid Orange 7¹

(K. Vinodgopal² and P. V. Kamat)

Special characterization of singlet triplet excited states of an azo dye, Acid Orange 7 (AO), have been made using picosecond and nanosecond laser flash photolysis. The excited singlet lifetime as estimated from the bleaching recovery is around 135 ps. The triplet excited state generated by T-T energy transfer method shows a difference absorption maximum at 650 nm with a lifetime of 20 μ s. The oxidized and reduced forms of the dye have been generated by reacting AO with pulse radiolytically generated azide ($N_3\bullet$) and e_{aq}^- radicals. These radicals were also detected as the primary intermediates in the visible-laser-induced photoionization. The photoelectrochemical reduction of the dye in UV-irradiated TiO_2 colloidal suspension results in the irreversible decoloration of the dye.

(1) Submitted for publication in the Journal of Photochemistry and Photobiology A: Chemistry.

(2) Indiana University Northwest, Gary, Indiana.

22. (NDRL-3673) The Excited Triplet State of N-(9-Methylpurin-6-yl) Pyridinium Cation as an Efficient Photosensitizer in the Oxidation of Sulfur-Containing Amino Acids. Laser Flash and Steady-State Photolysis Studies¹

(B. Marciniak, G. L. Hug, J. Rozwadowski² and K. Bobrowski)

Laser flash photolysis studies have been carried out on the N-(9-methylpurin-6-yl)pyridinium chloride/sulfur-containing amino acid systems in neutral aqueous solutions. Rate constants were determined for the quenching of the pyridinium cation triplet state by five sulfur-containing amino acids, and, for contrast, 2,2'-thiodiethanoic acids, alanine, and ammonium acetate. The quenching rate constants were found to be 2.1×10^8 - 7.8×10^9 $M^{-1} s^{-1}$ for the sulfur-containing compounds and three to four orders of magnitude lower for ammonium acetate and alanine. Time-resolved transient absorption spectra accompanying the quenching events were assigned to the excited triplet state of pyridinium cation ($\lambda = 550$ nm), the $(S\cdots S)^+$ radical cation for some of the amino acids ($\lambda = 480$ nm), and the N-(9-methylpurin-6-yl)pyridinyl radical ($\lambda = 610$ nm). The presence of the latter species was separately confirmed in

complementary pulse radiolysis experiments. The formation of the pyridinyl radical occurs for some amino acids (methionine and thiaproline) in two temporally distinct processes. A fast component that occurred on a nanosecond time scale is ascribed to electron transfer from the sulfur atom to the triplet state of pyridinium cation, followed by the diffusion apart of the CT-complex. A slower formation of pyridinyl radicals that occurred on a microsecond time scale, is characterized by pseudo-first-order rate constants, which depend linearly on the pyridinium cation ground-state concentration ($k = 2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). This dark reaction is assigned to the one-electron reduction of the pyridinium cation ground state by the α -aminoalkyl radicals produced from the radical cation of the amino acids as a result of intramolecular electron transfer from the carboxyl group to the sulfur-centered radical cation, followed by decarboxylation. Steady-state photolysis studies led to the identification of the water-insoluble 4,4'-dimeric, reduced pyridine compound formed by the dimerization of pyridinyl radicals. A detailed mechanism for the pyridinium cation-sensitized photooxidation of sulfur-containing amino acids is proposed and discussed.

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- (1) Submitted for presentation at XV IUPAC Symposium on Photochemistry, Prague, Czech Republic, July 17-22, 1994.
 - (2) A. Mickiewicz University, Poznań, Poland.
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23. (SR-159) Theory of Spin Effects in Radiation Chemistry¹

(C. E. Bolton)

Most existing theories of radiation chemistry completely ignore the effects of spin on reactivity by assuming that reactions are all diffusion-controlled or nearly so. We have developed a theoretical methodology of radiation chemistry to study spin effects. This investigation involved the modification of existing techniques such as Monte Carlo random flights and Independent Reaction Times simulations. The modified techniques were tested by performing calculations for systems where the solutions were already known or could be found by an alternative method.

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- (1) Submitted as project report to King's College, London for summer program at Radiation Laboratory.
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24. (SR-160) Simulation of Indirect Radiation Damage to DNA¹

(C. E. Bolton)

Radiation damage to DNA can take place by two distinct mechanisms: the direct effects occur when the radiation particle deposits its energy directly in the DNA and the indirect effect involves the chemical attack of free radicals induced in the surrounding medium. There have been few studies to date of the competition between radical recombination within radiation induced spurs and attack upon a DNA molecule in the vicinity of the spur. Since spurs contain several free radicals in a clustered distribution, such a mechanism has the potential to produce several "hits" on the DNA in close proximity. In this project the competition between recombination of a radical pair and attack on the DNA is studied using Monte Carlo random flights and Independent Reaction Times simulation methods. The aim was to examine both the kinetics and the spatial distribution of hits on the DNA, including correlations between hit positions when two hits occur.

- (1) Submitted as project report to King's College, London for summer program at Radiation Laboratory.
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25. (SR-161) Simulation of Electron-hole Recombination and Triplet-Triplet Annihilation in Quasi-one-dimensional Solids¹

(C. E. Bolton)

The aim of this study is to simulate the energy transfer and charge migration in columnar systems of molecules such as porphyrins, phthalocyanines and their derivatives. These compounds are highly anisotropic with migration taking place along essentially one-dimensional closely packed columns of molecules. Extremely high mobilities are exhibited along these columns, with low mobilities for the process of inter-columnar hopping. Analytic solutions and Monte Carlo random flights simulations for modeling the geminate reaction of a pair of particles have been developed. These models are based upon the assumption that the relative motion of the reactive particles is diffusive and can therefore be described by a diffusion equation. In addition Monte Carlo methods have been devised that are capable of simulating the migration and recombination processes in quasi-one-dimensional systems. Calculations

were performed for neutral species (energy migration) and are in progress for the charge migration study.

- (1) Submitted as project report to King's College, London for summer program at Radiation Laboratory.
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26. (SR-162) Supplementary Fitting Programs for NDRL Nanosecond Laser Traces¹
(G. L. Hug)

Two supplementary FORTRAN programs are available for fitting decay traces that have been stored in the special format of the data files from the NDRL nanosecond lasers or the NDRL linac. The fitting function for one of the programs is a two-exponential decay (four parameters: two positive pre-exponential factors and two rate constants). The other function is a three-parameter growth-decay function with two exponentials and one pre-exponential factor. The basis of both programs is a nonlinear least-squares method based on the Marquardt algorithm. Documentation for the use of these programs on VAX computer systems is available.

- (1) Internal report.
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Other investigations in progress include:

27. Geminate Ion-Pair Recombination in Pseudo-One-Dimensional Media
(S. M. Pimblott, C. E. Bolton¹ and N. J. B. Green¹)

Monte Carlo simulation methods are being developed for studying the recombination kinetics of geminate electron-hole pairs in porphyrins and phthalocyanines. In these systems, which are often referred to as pseudo-one-dimensional, the molecules are stacked in columns and the electron-hole mobility tensor, μ , and dielectric permittivity tensor, ϵ , are highly anisotropic. Consequently, the motion along a columnar stack of molecules is rapid while the frequency of inter-column hopping is small. The simulation technique devised treats motion up and down a column as diffusive while it models the hopping between stacks using a random

walk on a hexagonal lattice. Proper account of the Coulombic inter-ion potential is included in the method.

The predictions of the Monte Carlo simulation technique suggest that the probability of geminate escape essentially depends upon the stacks on which the two ions are initially situated, and not upon the relative positions on these stacks. For a typical phthalocyanine, a geminate pair initially on the same stack has a recombination probability of 0.99, while a pair on the same stack has a recombination probability of 0.75. Except when the two ions are initially situated on the same stack, the time dependence of the geminate recombination also does not depend on the relative positions of the ions on the stacks.

Comparisons of the results obtained using the Monte Carlo simulation model with the solution of the anisotropic backward equation show significant discrepancies. The differences show that a completely diffusive treatment of the relative inter-ion motion is not appropriate. Further calculations are in progress.

(1) King's College London.

28. The Influence of Temperature and Scavenging Capacity on the High-Energy Electron Radiolysis of Water

(S. M. Pimblott and J. A. LaVerne)

Recent studies have shown that deterministic diffusion kinetic modeling is a powerful tool for probing the nonhomogeneous radiation chemistry of aqueous solutions. Calculations are in progress to elucidate the effects of elevated temperature on the radiolysis of solutions of e_{aq}^- scavengers. A comparison of the predictions of the modeling studies with experimental data for SF_6 solutions at 200 °C shows excellent agreement. At room temperature previous studies showed that the scavenged yield of e_{aq}^- increases from a limiting escape yield, G^{esc} , to the initial radiation-induced yield, G^0 , as the scavenging capacity of the solution is increased. The same behavior is also observed at elevated temperatures, but the escape yield depends upon temperature. The calculations show that in a solution of given scavenging capacity as the temperature is increased the yield of e_{aq}^- that is scavenged increases.

At room temperature, the dependence of the observed yield scavenger experiments on the scavenging capacity of the irradiated solution, $G(k[S]0)$, provides information about the underlying kinetics in the absence of the scavenger, $G(t)$, by a simple Laplace transform

relationship. Calculations show that this same relationship holds at elevated temperatures and so it provides a method for obtaining the experimental time dependent decay kinetics from available experimental scavenger data.

Further studies examining the chemistry of solutions of more than one scavenger, i.e., the cooperative effects of scavengers, are planned.

29. Cage Escape Probability of Neutral Radicals in Liquid Water Radiolysis

(A. Mozumder)

Track theories of energy loss in gaseous and liquid water (e.g. Kaplan *et al.*, Radiat. Phys. & Chem. 36, 493, 1990; Pimblott and Mozumder, J. Phys. Chem. 95, 7291, 1991) give good agreement with experiment for ionization yields and for the excitation yield in the gas phase. The calculated excitation yield in the liquid phase, however, is much greater than the experimental determination which has been attributed to cage recombination of $H + OH$ and for $H_2 + O$, amounting to from 50 to 75% for these neutral radicals depending on the model.

Formal application of the diffusion model to cage recombination is considered unsatisfactory both from the viewpoints of molecular dynamics simulation and of experiment on methylene iodide photodissociation which indicates single collision dominated geminate recombination (Schwartz *et al.*, Chem. Phys. Lett. 203, 503, 1993). For the $H + OH$ reaction, assuming a reaction radius of 0.27 nm, the initial separation varies only between 0.33 nm and 0.36 nm for the change in the recombination probability from 75 to 50%, calculated by the diffusion model. Such extreme sensitivity is of course undesirable.

On the basis of repeated arrival at the cage boundary we calculate the cage escape probability as

$$\omega_{\text{esc}} = P_1 \left[\rho_1 + \frac{q\rho(1-\rho_1)}{1-(1-\rho)q} \right]$$

where ρ is the probability of outward transmission at the cage boundary (ρ_1 for the first arrival), P_n is the probability of arrival at the boundary for the n^{th} time and q is the probability of arriving at the cage boundary for the next time after being reflected for the surface. In deriving the above equation we have treated the first arrival differently from the rest due to single, ballistic collision. If we take $P_1 \doteq 1$ by virtue of excess kinetic energy of the dissociation process we compute $\omega_{\text{esc}} = 0.5$ using $\rho_1 = 0.3$, $\rho = 0.4$ and $q = 0.5$. We are now considering physical mechanisms consistent with those values.

30. Free-Ion Yield in Liquid Argon Under Low-LET Irradiation

(A. Mozumder¹)

Currently available theoretical models for the free-ion yield in liquid argon (LAr) are inadequate. Models based on the Onsager theory imply an initial electron-ion separation of 120 nm at 87 K which is nearly the same as the inter-ion separation in the track at low LET (~ 125 nm), thus contradicting geminate recombination. Earlier attempts based on the Jaffé theory (Chem. Phys. Lett. 142, 381, 1987) imply $k_r/k_D < 0.01$, whereas the most recent experimental determination of this quantity is ~ 0.1. Here k_r is the electron-ion recombination rate and k_D is the Debye rate.

The present model is based on repeated encounters of the electron with the positive ions (Ar_2^+) on the track axis after an unsuccessful encounter. The probability of recombination is taken to be the experimental value of k_r/k_D , a concept which was used earlier in the LET-dependence of luminescence quenching in LAr at high LET (Phys. Rev. B46, 11463, 1972). The outer turning point of the electron is determined either by thermalization or by the potential field of the remaining ions. The final result for the escape probability P_{esc} is given by

$$P_{\text{esc}} = (1 - \kappa)^{m+1} + (\mu E / L_0) \left[\sum_{s=1}^m \tau_s (1 - \kappa)^s - (1 - \kappa)^{m+1} \sum_{s=1}^m \tau_s \right],$$

where $\kappa = k_r/k_D$, μ is the electron mobility, E is the external field, L_0 is the initial track length, τ_s is the return time for the s^{th} trip and m is the maximum number of trips determined by the transit time over the track length. An algorithm has been developed to compute τ_s and m .

Experimentally all available electrons are collected in LAr at $E \geq 22$ kV/cm for irradiation by ~ 1 MeV primary electrons. Our computed escape probabilities, normalized to that at $E = 22$ kV/cm, are 0.558, 0.616, 0.695, 0.784, 0.866, 0.911 respectively at $E = 100, 300, 10^3, 3 \times 10^3, 7 \times 10^3$ and 10^4 V/cm, which compare favorably with experimental determination. For these calculations we have used $\kappa = 0.1$, $\mu = 400 \text{ cm}^2/\text{V s}$ and $L_0 = 0.5 \text{ cm}$, that is, the experimental values where available.

(1) In collaboration with Professor T. Doke, Waseda University, Tokyo.

31. Radiolysis of Cyclooctane

(L. Wojnárovits and J.A. LaVerne)

We have begun to examine the radiolysis of liquid cyclooctane. These studies will elucidate the chemistry of the cyclooctyl radical which is mainly responsible for the formation of the major products cyclooctene and bicyclooctyl. We especially want to determine how its chemistry varies with the track structure of the irradiating particle. Using iodine scavenging techniques it is possible to determine the time scale on which the combination and disproportionation reactions of the cyclooctyl radical occur. In this procedure one observes the dependence of the yield of cyclooctyl iodide as a function of iodine concentration. This information can then be used to infer the temporal variation of the cyclooctyl radical in the neat liquid. In addition to the above mentioned products pentalane, a cross-bridged cyclooctane, is produced in the radiolysis of cyclooctane. It is produced by a unimolecular process and therefore can be used as a probe of the very early chemistry in particle tracks. These studies will utilize the gas chromatographic/ mass spectrometric techniques being developed in our laboratory which allow us to observe product yields with very low doses. This analytical technique requires extremely pure compounds and a number of purification techniques are being developed including the use of a spinning band distillation apparatus. Unfortunately, all of these procedures are extremely time-consuming.

Previous studies with cyclohexane would lead one to expect large differences in cyclooctyl radical yields with variation of particle type and stopping power. Experiments with gamma radiolysis at doses of 25 krad have determined that the yields of cyclooctene and bicyclooctyl are 3.2 and 1.9 molecules/100 eV, respectively, in neat cyclooctane. The addition of 0.1 mM iodine should scavenge only those cyclooctyl radicals which escape into the bulk and the yields of cyclooctene and bicyclooctyl are found to decrease to 2.3 and 0.6 molecules/100 eV, respectively. The change in these yields is the equivalent of the loss of 4.4 cyclooctyl radicals/100 eV and the measured yield of cyclooctyl iodide of 4.3 molecules/100 eV is in very good agreement. If one assumes that all of the cyclooctene and bicyclooctyl is produced via cyclooctyl radicals then about 43% of the chemistry of cyclooctyl radicals occurs in the bulk in gamma radiolysis. This value is similar to that found for cyclohexyl radicals in the radiolysis of cyclohexane, but it is a lower limit since a large fraction of cyclooctene is probably produced by unimolecular processes. Pentalane yields were found to be about 0.6 molecules/100 eV and reasonably independent of iodine concentration. Experiments with helium ions have been

performed and are currently being analyzed. The results will be compared to those found with gamma radiolysis.

32. Resonance Raman Study of Chemical Interactions in Riboflavin Semiquinone Radicals

(Y. Su and G. N. R. Tripathi)

The resonance Raman spectra of riboflavin semiquinone anion, neutral and cation radicals prepared by pulse radiolysis in aqueous solution are being used to investigate the effects of chemical interactions on the structure and bonding of the radicals. The vibrational assignment of the spectra indicate that the 1617 cm^{-1} frequency of the neutral radical should be sensitive to N_5H bonding, but not to N_3H bonding. As this frequency remains unchanged in the radical adsorbed on Ag electrodes, structural stabilization by N_3H -metal binding is indicated. In *Clostridium MP* flavodoxin, this frequency drops by $\sim 6\text{ cm}^{-1}$, indicating a N_5H -protein hydrogen bond interaction much stronger than that with water. In the flavin semiquinone anion radical, strong N_5H -protein bonding will increase the 1610 cm^{-1} frequency. Since this frequency decreases by $\sim 8\text{ cm}^{-1}$ in DAO, protein interaction at the N_5 site must be small or negligible, as compared to water interaction. The protein hydrogen bonding at N_1 , if stronger than in water, should increase the 1498 cm^{-1} frequency ($\text{C}_{4a}\text{C}_{10a}$ bond) and decrease the 1460 cm^{-1} (N_1C_2 bond) frequency of the anion radical. This is the case in DAO SQ anion where these frequency shifts are fairly large (18 and 12 cm^{-1} , respectively), indicating very strong protein interaction at the N_1 site. These examples illustrate that the semiquinone frequencies are much more sensitive to the site and strength of the protein interaction than those of the parent flavin.

33. Hydroxyl Radical Adduct at Sulfur in Methylated Derivatives of Methylthiomethyl Acetate

(K. Bobrowski, Ch. Schöneich¹ and R. Glass²)

We have recently shown (J.C.S. Chem. Commun. 1993) that the stability of an OH radical adduct at the sulfur atom in 2-(methylthio)methyl acetate is greatly enhanced resulting in a lifetime of $\tau_{1/2} = 12\text{ }\mu\text{s}$ (generally, such adducts convert into sulfur-centered radical cations with $\tau_{1/2} \leq 0.4\text{ }\mu\text{s}$). Stabilization of the OH adduct was rationalized in terms of formation of the internal hydrogen bond between the hydroxyl hydrogen and the adjacent carbonyl oxygen.

This hydrogen bonding was facilitated by the formation of a sterically favorable six-membered ring configuration. The rate of formation of such a cyclic transition structure should be affected by the rotational freedom of the S-C and C-C bonds. In order to check this, we have synthesized three methylated derivatives of 2-(methylthio)methyl acetate: $(\text{H}_3\text{C})_3\text{C-S-CH}_2\text{-COOCH}_3$ (1), $(\text{H}_3\text{C})_3\text{C-S-CH}(\text{CH}_3)\text{-COOCH}_3$ (2) AND $(\text{H}_3\text{C})_3\text{C-S-C}(\text{CH}_3)_2\text{-COOCH}_3$ (3). In all three esters we have observed the formation of a similar absorption spectrum with $\lambda_{\text{max}} = 340 \text{ nm}$, ascribed to the $>\text{S-OH}$ adduct. The lifetimes of such adducts, however, decrease with the number of the methyl groups and were found to be: 7.6 μs , 1.8 μs and 0.3 μs for (1), (2) and (3), respectively. Further experiments are under way.

(1) University of Kansas.

(2) University of Arizona.

34. 4-Carboxybenzophenone-Sensitized Photooxidation of Sulfur-Containing Aliphatic Alcohols in Aqueous Solutions

(K. Bobrowski, G. L. Hug and B. Marciniak)

The mechanism of photooxidation of sulfur-containing aliphatic alcohols (with variable relative location and number of terminal OH moieties with respect to the sulfur atom) sensitized by 4-carboxybenzophenone (CB) was examined using the nanosecond laser flash photolysis technique. Rate constants were determined for the quenching of the CB triplet state by five alcohols. 2-Methylthioethanol (2-MTE), 2,2'-thiodiethanol (2,2'-TDE), 3-methylthiopropanol (3-MTP), 3,3'-thiodipropanol (3,3'-TDP) and 4-methylthiobutanol (4-MTB) were found to quench with rates in the range $3.3\text{--}4.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Time-resolved transient spectra accompanying CB triplet quenching by high concentrations of alcohols were assigned to ketyl radical anion, and the ketyl radical of CB and to the $(\text{S} \cdots \text{S})^+$ dimeric radical cations derived from the alcohols. The formation of the intramolecularly $\text{S} \cdots \text{O}$ bonded radical was additionally observed in 3-MTP and 3,3'-TDP. The quantum yields of the transients, i.e., ketyl radicals, ketyl radical anions, $\text{S} \cdots \text{S}^+$ radical cations and $\text{S} \cdots \text{O}$ bonded radicals, have been determined and are in the ranges of 0.18-0.46, 0.08-0.26, 0.06-0.27, 0.39-0.52, respectively. A detailed mechanism for the CB-sensitized photooxidation of sulfur-containing aliphatic alcohols has been developed.

35. An in situ Radiolysis Time-Resolved ESR Study of Spin Trapping by Nitrones
(K. P. Madden)

Recent studies in these laboratories (Q-138) have characterized the effect inductive factors and steric interactions exert upon the spin trapping of carbon-centered radicals by the nitroso spin trap 2-methyl-2-nitrosopropane (MNP). It was found the dominant interaction controlling the rate of spin trapping was the reduction potential of the parent radical. We have started similar studies using the nitrone spin trap 5,5-dimethyl-pyrroline-N-oxide (DMPO). The rate constants measured by time-resolved ESR for methyl radical trapping and hydroxymethyl radical trapping by DMPO were 1.3×10^7 and $2.2 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$, respectively. The rate constants for methyl and hydroxymethyl trapping by MNP are 1.7×10^7 and 1.4×10^8 . The lower hydroxymethyl trapping rate of DMPO relative to MNP indicates that although the dominant canonical structure of DMPO is zwitterionic at the nitrone function, the site of parent radical attack (C-2) gains little positive charge from the adjacent N(+)-O(-) moiety. This contrasts with the situation in MNP, where parent radical reaction at the nitroso nitrogen is greatly enhanced by electron release into the polar N=O group.

36. Redox Reactions of Co(II) and Ni(II) with Azacyclophane Macrocyclic Ligands
(J. Vargas, J. Costamagna and G. Ferraudi)

The complexes $\text{Co}^{\text{II}}(\text{hexaazacyclophane})$ and $\text{Ni}^{\text{II}}(\text{hexaazacyclophane})$ catalyze the electrochemical reduction of CO_2 . The intermediates in such reactions are being investigated by pulse radiolysis of the complexes in water-methanol mixtures. Time-resolved spectra were recorded in the reduction of the complexes by CH_2OH . The products of the reactions with these complexes have similar spectral features and were assigned as complexes with a reduced ligand, i.e., a ligand-radical. The complexes with ligand-radicals undergo transformations that are distinctive of the coordinated metal. In the Cu(II) complex, acid accelerates the conversion of the ligand-radical transient into a new species assigned as $\text{Cu}^{\text{I}}(\text{hexaaza})^-$. The Co(II) ligand-radical complex did not undergo such an acid dependent process; spectral changes with $t_{1/2} \approx 60 \mu\text{s}$ were in accordance with an intramolecular electron transfer to form $\text{Co}^{\text{I}}(\text{hexaaza})^-$. Reduction of $\text{Co}^{\text{II}}(\text{hexaaza})$ and $\text{Cu}^{\text{II}}(\text{hexaaza})$ by the solvated electron respectively produces $\text{Co}^{\text{I}}(\text{hexaaza})^-$ and $\text{Cu}^{\text{I}}(\text{hexaaza})^-$ in large yields instead of the ligand-radical precursors. The reduction of the complexes by CH_2OH in solutions saturated with CO_2 generates the same

complexes with ligand-radicals described above. These species react with CO₂ to generate metastable products whose nature is being investigated.

37. Pressure/Solvent Effects of the β -Scission of Cumyloxyl Radical in Supercritical CO₂
(J. E. Chateauneuf)

The pressure effect on the unimolecular β -scission reaction of cumyloxyl radical to acetophenone and methyl radical (eq. 1) has been studied in supercritical CO₂ ($T_c = 31.0\text{ }^\circ\text{C}$; $P_c = 73.8\text{ bar}$) along the $35\text{ }^\circ\text{C}$ isotherm.

Cumyloxyl radical was generated by 266 nm laser flash photolysis (LFP) of dicumylperoxide ($\text{PhC(CH}_3)_2\text{O})_2$ and the rate constants for β -scission were obtained by monitoring the first-order decay of the cumyloxyl radical visible absorption band, $\lambda_{\text{max}} = 485\text{--}500\text{ nm}$ (Luszyk et al., J. Am. Chem. Soc. 1993, 115, 466). Rate constants were obtained from high to low pressure, 190–76 bar, and were found to increase from $8 \times 10^5\text{ s}^{-1}$ under high-pressure “liquid-like” conditions to $2 \times 10^6\text{ s}^{-1}$ in the low-pressure compressible region of the fluid. The change in rate constants observed over this pressure range corresponds to the change observed in normal liquids by changing the solvent polarity from acetonitrile to acetic acid. The change in rate constants can be attributed to the strength of solvation of the partially zwitterionic transition state for β -scission and ketone formation. This reaction is currently being studied in polar SCFs to determine the dynamic range of β -scission and to probe the cybotactic region of the solvent.

38. Kinetics of Heterogeneous Electron Transfer between an Excited Ru(II) Complex and Semiconductor Nanocrystallites

(R. W. Fessenden and P. V. Kamat)

Even though a variety of approaches have been considered in the past to probe the kinetics of charge injection from an excited sensitizer into the conduction band of a semiconductor, the kinetic information derived from these studies is rather limited. We have now employed two independent techniques, microwave absorption and luminescence measurements, to directly monitor the charge injection from excited Ru(II) bis(2,2'-bipyridine) (2,2'-bipyridine-4,4'-dicarboxylic acid) into SnO₂, ZnO, and TiO₂ nanocrystallites. The growth of

microwave absorption directly measures the rate of appearance of the charge carriers in the semiconductor while the decay of the luminescence measures the overall rate of decay of the excited states. The growth of microwave absorption should match the rate of one component of the luminescence decay. The rate constants for the charge injection were obtained by fitting the first-order microwave absorption growth with a calculation which included the laser pulse width (7 ns) and the apparatus time constant of 4.5 ns. The rate constants for the heterogeneous electron transfer for all the three semiconductors were similar ($\sim 1 \times 10^8 \text{ s}^{-1}$). The luminescence decay of these samples clearly showed two components and a similar analysis gave values near 10^8 s^{-1} for the faster of the two decay processes. This agreement strongly suggests that the same process is measured by the two techniques. In contrast to the behavior of the Ru(II) complexes, charge injection from an excited singlet (e.g., $^1\text{Chl } a^*$) was very fast and could not be resolved ($\tau < 2 \text{ ns}$). The slower kinetics observed in the case of the Ru(II)* system suggests that a relatively long-lived CT-excited state of Ru(II) ($t=0.5 \mu\text{s}$ in aqueous solution) interacts with the semiconductor in a different way than does the singlet excited organic dye.

39. Charge Injection from Excited Acridine Orange into SnO_2 Nanocrystallites

(S. Das, S. Hotchandani and P. V. Kamat)

The photosensitizing properties of acridine dyes are being investigated by using Acridine orange (AO) as a representative example. This dye has been found to complex with SnO_2 colloids. The absorption of this complex is broad ($\lambda_{\text{max}} \sim 480 \text{ nm}$) compared to the sharp absorption band of the acridine orange ($\lambda_{\text{max}} = 494 \text{ nm}$). The lower emission yield of the AO- SnO_2 complex indicates the deactivation of the excited state via a charge injection process. This charge injection from excited AO into SnO_2 has been probed further by monitoring the sensitized photocurrent generation at an AO-modified SnO_2 nanocrystalline film. Using these dye-modified electrodes an incident photon-to-photocurrent efficiency of $\sim 5\%$ at 500 nm has been achieved. Further characterization of AO-modified SnO_2 electrodes is currently in progress.

40. Electrochromic Effect in Nanocrystalline SnO_2 Films

(I. Bedja, S. Hotchandani and P. V. Kamat)

The electrochromic behavior of nanocrystalline SnO_2 semiconductor films deposited on optically transparent electrodes (OTE/ SnO_2) was investigated by carrying out *in situ* absorption

measurements during electrochemical biasing. With increasing negative potentials the SnO_2 film turned blue as the absorption in the visible and IR increased. After attaining a potential of -0.3 V, the electrode was discharged by reversing the potentials. The absorption spectra recorded during the charging cycle were easily reproduced in the discharge cycle. This dependence of the absorbance on the applied potential clearly highlights the reversibility of the electrochromic behavior of SnO_2 particulate films. The laser flash photolysis experiments of SnO_2 colloids also produced transient absorption spectrum similar to that observed in electrochemical experiments. The broad absorption in the red-infrared region indicates accumulation of electrons within the SnO_2 nanocrystallites. Metal ion sites such as Sn^{4+} are likely to act as trapping sites.

41. Photoinduced Electron Transfer in Organized Systems. Lipid-Functionalized Pyrene and Viologens in Spread Lipid Monolayers

(L. Li and L. K. Patterson)

Following previous measurements of electron transfer between singlet lipid-functionalized pyrene and methyl viologen, we have undertaken to determine the effects on transfer of adding hydrophobic groups to the electron acceptor. It has been found that addition of one hexadecyl chain to the viologen renders it soluble in lipid layers although not sufficiently hydrophobic to exhibit good monolayer properties by itself, i.e., very small surface areas were found by force-area measurements. Time-resolved quenching measurements, fit to Stern-Volmer plots, exhibited some deviation at low quencher concentrations, probably reflecting the partitioning of viologen in the layer and subphase. Calculations of diffusion coefficient by the method of Owen gave values of $1 \times 10^{-6} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$, a value approximately half that found previously through excimer formation. This too would indicate such partitioning. Laser flash photolysis studies in parallel vesicle systems confirm formation of pyrene cation and reduced viologen. Studies of the kinetics of the back reaction are in progress. Other acceptors of varying hydrophobicity are being prepared.

42. Effects of Molecular Organization on the Electronic Spectrum of Chlorophyll *a* in Lipid Monolayers at the Gas-Water Interface

(Yi-Ming Wang and L. K. Patterson)

Absorption spectra have been determined for pure and lipid diluted Chlorophyll *a* (Chl *a*) in spread monolayers at surface pressures <1 to 25 mN/m. The data have been analyzed

analyzed by a Gaussian curve-fitting procedure to obtain spectral components over the whole range of concentrations and pressures. It may be seen by comparison of these component that there is a continuous narrowing and blue shift of the Chl *a* Q-band from pure chlorophyll to the most dilute system. It may further be seen that the spectral band peaks shift as a function of Chl *a* surface concentration with little effect of surface pressure. The spectral range of the Q-band maximum is 667 nm ($1.50 \times 10^4 \text{ cm}^{-1}$) in the most dilute case to 681 nm ($1.47 \times 10^4 \text{ cm}^{-1}$) at the highest compression of pure chlorophyll. Plots of peak O.D. as a function of surface concentration *do* show some dependence on surface pressure, suggesting an expected compression effect on the average angle between porphyrin and the interface. The shift in spectrum appears dominated by Chl-Chl interaction which probably alters the nature of solvation as Chl concentration changes.

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