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QUARTERLY REPORT

January 1 - March 31, 1994

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Dr. Mohamed Sarakha of the Université Blaise Pascal, Clermont-Ferrand, France, arrived in January to spend a sabbatical year with us. His interest is in the photochemistry of inorganic compounds.

Ms. Genevieve Sauvé, a recent graduate of Concordia University in Montreal, will be doing research under the supervision of Dr. P.V. Kamat this summer. She arrived in March.

Lt. Roger Hilarides defended his Ph.D. thesis "Destruction of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin on Soil Using Cobalt-60 Gamma Radiation", based on work conducted in the Laboratory. Dr. Hilarides is now serving a tour of submarine duty.

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Visitors during the quarter included the following:

Prof. D.A. Armstrong of the University of Calgary spent part of March in the Laboratory, conducting radiolysis experiments in collaboration with Drs. Schuler and Tripathi.

Prof. H. Taniguchi of Yamaguchi University also visited in March. He collaborated with Dr. Madden in ESR experiments.

Publications

2

G. Ferraudi, T. Nyokong, M. Feliz, M. Perkovic and D.P. Rillema
Redox Reactions of an Mo(V) Tetrasulfophthalocyanine.
Inorganica Chimica Acta 215, 27 (1994) [NDRL 3329]

S.M. Pimblott and J.A. LaVerne
Models for the Radiation Chemistry of Aqueous Solutions.
Radiation Protection Dosimetry 52, 183 (1994) [NDRL 3454]

M.T.H. Liu and J.E. Chateauneuf
Self Quenching Reaction of (Phenoxymethyl)chlorocarbene with Diazirine.
Res. Chem. Intermed. 20, 195 (1994) [NDRL 3586]

J.E. Chateauneuf
Exploratory Laser Flash Photolysis Investigations of Diphenylcarbene
Reactivity in Supercritical Fluids.
Res. Chem. Intermed. 20, 159 (1994) [NDRL 3589]

R.D. Guthrie, M. Patwardhan and J.E. Chateauneuf
Cleavage Rates for Radiolysis-Produced Radical Anions of Naphthylmethyl
Phenyl Ethers and Naphthyl Benzyl Ethers.
J. Phys. Org. Chem. 7, 147 (1994) [NDRL 3591]

C. Mingotaud, J.-P. Chauvet and L.K. Patterson
The Behavior of Nitrobenz-2-oxa-1,3-diazol and Coumarin Dye Indicators in
Lipid Monolayers: A Study of Interfacial Effects on Polarity and pH.
Thin Solid Films 242, 243 (1994) [NDRL 3615]

J.A. LaVerne and R.H. Schuler
Track Effects in Water Radiolysis: Yields of the Fricke Dosimeter for
Carbon Ions with Energies up to 1700 MeV.
J. Phys. Chem. 98, 4043 (1994) [NDRL 3625]

B. Marciniak and G.L. Hug
Energy Transfer Processes in the Quenching of Triplet States of Organic
Compounds by 1,3-diketones of Lanthanides(III) and Magnesium(II) in
Acetonitrile Solution. Laser Flash Photolysis Studies.
J. Photochem. Photobiol. A: Chem. 78, 7 (1994) [NDRL 3628]

S. Das, J.S.D. Kumar, K.G. Thomas, K. Shivaramayya and M.V. George
Photocatalyzed Multiple Additions of Amines to α,β -Unsaturated Esters
and Nitriles.
J. Org. Chem. 59, 628 (1994) [NDRL 3629]

A. Ajayaghosh, S.C. George and M.V. George
Novel Phototransformation of o-Nitrobenzylic Polymers to Azopolymers.
J. Chem. Soc., Chem. Commun. p. 423 (1994) [NDRL 3630]

N.J.B. Green, S.H. Robertson and M.J. Pilling
Diffusion Equation Analysis of Energy Transfer.
J. Chem. Phys. 100, 5259 (1994) [NDRL 3634]

A. Hitachi, J.A. LaVerne, J.J. Kolata and T. Doke
Energy Resolution of Allene Doped Liquid Argon Detectors for Ions of
Energy 23-34 MeV/amu.
Nuclear Instruments and Methods in Physics Res. A 340,546 (1994) [NDRL 3637]

D.H. Baker, R.L. Champion, L.D. Doverspike and Y. Wang
Photon-stimulated Desorption of H^- from a BaO Surface.
Appl. Phys. Lett. 64, 1880 (1994) [NDRL 3659]

D.M. Chipman, R. Liu, X. Zhou and P. Pulay
Structure and Fundamental Vibrations of Phenoxyl Radical.
J. Chem. Phys. 100, 5023 (1994) [NDRL 3660]

I. Bedja, S. Hotchandani and P.V. Kamat
Preparation and Photoelectrochemical Characterization of Thin SnO_2 Nano-crystalline Semiconductor Films and Their Sensitization with Bis(2,2'-bipyridine-4,4'-dicarboxylic acid)ruthenium(II) Complex.
J. Phys. Chem. 98, 4133 (1994) [NDRL 3662]

C.E. Bolton, N.J.B. Green and S.M. Pimblott
Simulation of Geminate Ion Recombination Kinetics in Anisotropic Media.
Chem. Phys. Lett. 221, 175 (1994) [NDRL 3665]

J.E. Chateaufneuf
Picosecond Spectroscopic Investigations of Diphenylcarbene Protonation.
Res. Chem. Intermed. 20, 249 (1994) [NDRL 3685]

B. Marciniak, K. Bobrowski, G.L. Hug and J. Rozwadowski
Photoinduced Electron Transfer between Sulfur-Containing Carboxylic Acids and the 4-Carboxybenzophenone Triplet State in Aqueous Solution.
J. Phys. Chem. 98, 4854 (1994) [NDRL 3686]

External Talks and Presentations

Richard W. Fessenden, "Applications of ESR: Radical Structure and Reactions", Indiana State University, Terre Haute, IN, Feb. 8, 1994.

Keith P. Maddën, "In situ Radiolysis ESR Studies of Spin Trapping", Memphis State University, Memphis, TN, Feb. 18, 1994.

Guillermo Ferraudi, "Manipulation of Thermal and Photochemical Reactions with Double-Pulsed Irradiations of Reaction Intermediates and Excited States", University of LaPlata, Argentina, March 15; "Reactions of Radicals Coordinated to Transition Metal Ions", University of LaPlata, Argentina, March 18, Atomic Energy Commission, Argentina, March 22, and University of Santiago, Chile, April 16; and "Photochemical and Photophysical Reactions of Re(I) Complexes", University of Buenos Aires, Argentina, March 28.

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

1. **(NDRL-3675) Pulse Radiolysis and Laser Flash Photolysis Studies of Reactions in Supercritical Fluids¹**

(J. Zhang,² K. Connery,² J. E. Chateauneuf and J. F. Brennecke²)

Understanding the importance of local solvation effects on reactions in supercritical fluids is vital to determining the pressure effect on reaction rates. Previously we have shown that the increased local concentration of one reactant about another can be used to dramatically enhance kinetically controlled reactions of relatively nonpolar species in supercritical carbon dioxide. For those reactions the local solvation effects, which are prevalent over a wide range of density and not considered to be a critical phenomenon, dominate over the thermodynamic pressure effect on the rate constants predicted from transition state theory. The thermodynamic pressure effect is closely tied to partial molar volumes, which do reflect the proximity to the critical point. Conversely, we have shown that local solvation does not influence diffusion controlled reactions of neutral species in both nonpolar and polar supercritical fluids.

In this work, we extend our previous studies to the reactions of polar and ionic species in a wide variety of supercritical fluids. We are interested in studying ionic reactions because they are known to experience stronger solvent effects than the reactions of neutral species in liquids. Therefore, we will explore the relative contributions of critical (the thermodynamic pressure effect from transition state theory) and noncritical (local solvation) effects to the pressure effect on the rate constants. We have used pulse radiolysis and laser flash photolysis to produce both neutral radicals and carbocations, which then can react with ionic and non-ionic nucleophiles at kinetic control. We will also investigate whether there is any influence on diffusion controlled reactions of these species, which have stronger interactions with the solvent than those studied previously.

Supercritical fluids offer the possibility of tuning local and bulk solvent properties over a wide range by simple variation of temperature and pressure. This work is important because it explores a class of reactions that have not been studied previously and which have some of the greatest potential for being influenced by those changing solvent properties.

(1) Submitted for presentation at the Third International Symposium on Supercritical Fluids, Strasbourg, France, October 17-19, 1994.

(2) Department of Chemical Engineering, University of Notre Dame.

2. (NDRL-3676) Photocatalytic Oxidation of 4-Chlorophenol on Titanium Dioxide: A Comparison with γ -Radiolysis¹

(U. Stafford, K. A. Gray² and P. V. Kamat)

The photocatalytic degradation of 4-chlorophenol (4-CP) has been studied extensively. While many studies have addressed kinetic details of photocatalytic degradation of phenols, considerable doubt remains about the reaction mechanism by which halogenated aromatics are oxidized. It is not known whether the degradation of the reactants takes place on the surface of the catalyst, or away from the surface (i.e., in the aqueous phase), or both. Most of the mechanisms propose the hydroxyl free radical as the primary charge transfer intermediate in the mineralization of chlorophenols and other compounds, and consider the essential role of oxygen to be electron scavenging. Many different intermediate distributions have been seen during the photocatalytic destruction of 4-CP, indicating that the reaction mechanism may be more complex and more dependent upon catalyst surface conditions than can be explained by a simple hydroxyl radical mediated mechanism.

γ -Radiolysis results are shown in Table 1. By saturating 4-CP solutions with nitrous oxide, the effect of hydroxyl radical attack has been studied using γ -radiolysis. 4-CP is readily oxidized by hydroxyl radical attack via the dihydroxycyclohexadienyl radical (4-CDHCHD) following pathways presented in scheme 1. The major aromatic intermediates of the degradation are 4-chlorocatechol (4-CC) and hydroquinone (HQ). By estimating the rate of the subsequent oxidation of 4-CC and HQ, at pH 3, ~ 60% of the 4-CP is oxidized to 4-CC and ~12% to HQ as the initial step. This leaves a balance of ~ 28% that is degraded via other intermediates, possibly nonaromatic or unstable. At pH 6 the proportions are ~ 54% via 4-CC, ~8% via HQ and ~ 38% via unstable intermediates. At pH 9 the only significant reaction pathway is that via unstable intermediates. This indicates that there is a pH effect on the degradation intermediate concentrations most pronounced over the range pH 6-9. It is likely that the degradation rate of 4-CP at pH 9.1 is lower because the unstable intermediates are more readily oxidized than the 4-CP and use a larger number of the $\bullet$ OH radicals.

(1) Submitted for presentation at the Fourth Annual Symposium on Chemical Oxidation, Nashville, TN, February 16-18, 1994.

3. **(NDRL-3677) Naked and Surface-Modified Thin SnO₂ Semiconductor Colloid Films for the Photoelectrochemical Conversion of Light Energy¹**

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

The present study focuses on the method of preparation and characterization of nanocrystalline SnO₂ films for developing new electrode materials for photoelectrochemical cells. These electrodes are active in the UV region with incident photon-to-photocurrent conversion efficiency of 20% at 280 nm. Since these porous SnO₂ films have strong affinity for adsorption of organic molecules, they can be surface-modified with sensitizers such as chlorophyll derivatives. The sensitized 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. Results that compare the performance of SnO₂ colloid films with other oxide films such as ZnO and TiO₂ will be discussed.

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- (1) Submitted for presentation at the American Chemical Society Spring Meeting, San Diego, CA, March 13-18, 1994.
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4. **(NDRL-3678) Preparation and Photoelectrochemical Behavior of Nanocrystalline Semiconductor Films from Colloidal Suspensions¹**

(P. V. Kamat)

Colloidal suspensions of ZnO, TiO₂, SnO₂ and WO₃ (particle diameter 20-100 Å) have been employed to develop photoelectrochemically active transparent semiconductor films of thickness $\leq 1 \mu\text{m}$. These thin semiconductor films exhibit a variety of interesting properties which include extending the photoresponse of a large bandgap semiconductor material, electrochemical rectification, electrochemically assisted photocatalysis and electrochromic effects. Thin semiconductor films developed from colloidal semiconductor suspensions possess highly porous structure and can be easily surface-modified with sensitizers, redox couples and short-bandgap semiconductor particles. For example, SnO₂ films modified with a ruthenium complex, (Ru(bpy)₂(dcbpy)²⁺), exhibit excellent photoelectrochemical response in the visible with a power conversion efficiency of ~1%. Thin films of SnO₂ and WO₃ colloids also exhibit reversible electrochromic and photochromic effects. Such thin metal oxide films are potentially

useful in developing new electrode materials and designing electrooptic materials.

- (1) Submitted for presentation at the American Chemical Society Spring Meeting, San Diego, CA, March 13-18, 1994.
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5. (NDRL-3679) Thin Semiconductor Particulate Films as Novel Electrode Materials¹

(D. Liu, I. Bedja,² S. Hotchandani,² K. Vinodgopal³ 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. Moreover, by controlling the preparative conditions it is possible to tailor the properties of semiconductor particulate films. We have now employed metal oxide (TiO_2 , ZnO , WO_3) and metal chalcogenide (CdS and CdSe) semiconductor colloids for designing electrode materials with novel electrochemical properties. Both electrochemical and chemical deposition techniques have been employed to synthesize thin semitransparent films on conducting glass plates. These particulate films are highly porous and can easily be surface-modified with various sensitizers, redox couples and other semiconductor particles. Increased charge recombination has been found to be a major problem in attaining good photocurrent stability in thin semiconductor films such as CdSe . Coupling with thin TiO_2 particulate film improves the photocurrent stability as the electrons are quickly transferred to the lower-lying conduction band of TiO_2 . Electrochemical and spectroelectrochemical experiments that elucidate electrochemical rectification, photoelectrochemical, photocatalytic and electrochromic properties of these electrodes will be described.

- (1) Submitted for presentation at the Pittsburgh Conference, Chicago, IL, February 27-March 4, 1994.
 - (2) University of Quebec at Trois Rivières.
 - (3) Indiana University Northwest, Gary, IN.
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6. (NDRL-3680) In-Situ Reflectance FTIR Studies of Textile Dye Degradation on Semiconductor Surfaces¹

(K. Vinodgopal,² J. McNeil,² M. Soria² and P. V. Kamat)

This paper will discuss photosensitization methods on semiconductor (TiO_2) surfaces for degradation of colored organic pollutants, specifically large-volume, commercial, textile dyes such as Orange II and Chicago Sky Blue. The photosensitization technique involves preparing TiO_2 powder with the dye adsorbed on it and excitation of the dye with visible light. Charge injection from the excited state of the dye into the conduction band of the semiconductor results in an oxidized form of the dye which then undergoes degradation. The degradation of the dye is monitored by Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. Identification of the photoproducts resulting from such photosensitized degradation on surfaces has always been a difficult challenge. As a consequence of strong chemical bonding, these photoproducts are very difficult to strip from the TiO_2 surface using solvents, thereby rendering any subsequent analysis by conventional methods such as chromatography impossible. This technique was also used to identify the photoproducts that result from such photosensitized degradation. The Orange II dye readily undergoes photodegradation on the TiO_2 surface. The intermediates formed are most likely 1,2-naphthaquinone and 4-hydroxybenzenesulfonic acid which then undergoes further degradation on the TiO_2 surface to produce a carboxylic acid. This is the first time that the products resulting from photodegradation on a reactive surface such as TiO_2 have been identified. Photosensitized degradation of textile dyes using TiO_2 represents a significant new advance in the treatment of such colored water pollutants.

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- (1) Submitted for presentation at the Pittsburgh Conference, Chicago, IL, February 27-March 4, 1994.
- (2) Indiana University Northwest, Gary, IN.
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7. (NDRL-3681) Photoinduced Charge Transfer Between Carbon and Semiconductor Clusters. One-Electron Reduction of C_{60} in Colloidal TiO_2 Semiconductor Suspensions.¹

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

Fullerenes (C_{60} and C_{70}) possess interesting photophysical and photochemical properties. Their applications in photoelectrochemistry and non-linear optics have also been explored. One of the main focuses in recent months has been to carry out reduction of these carbon clusters in a controlled way using electrochemical, photochemical, radiolytic and potassium ion-reduction methods. Cyclic voltammetry has demonstrated that up to 6 reversible electron reductions of C_{60} can be carried out at 263 K. The reduction potentials for this are strongly dependent on the electrolyte and solvent medium. Although electrochemistry has provided a convenient way to prepare salts of C_{60} anions, reduction by photochemical and pulse radiolytic methods produces only short-lived transients. Back electron transfer and reaction with other radical species make these methods unsuitable for the production of fullerene anions. In our preliminary communication we demonstrated the ability of semiconductor clusters such as ZnO colloids to reduce C_{60} and C_{70} under UV excitation. Semiconductor clusters such as ZnO or TiO_2 are excellent choices to carry out reduction in a controlled way since the energy of their conduction bands ($E_{CB} = -0.5$ V vs. NHE at pH 7) thermodynamically favor only one-electron reduction ($C_{60}/C_{60}^- \approx -0.2$ V vs. NHE) and not higher reductions. But so far the mechanistic details of photocatalytic reduction of fullerenes have not been investigated in detail. The principle of a photoinduced charge transfer between a semiconductor colloid (TiO_2) and C_{60} is illustrated in Scheme 1.

Semiconductor colloids serve as an attractive medium for long-term storage of electrons. Both photoexcitation and electrochemical methods can be employed to trap electrons in these semiconductor nanocrystallites. These electrons stored at the surface traps can conveniently be used to reduce other substrates in the dark. The trapping of electrons in TiO_2 , ZnO and WO_3 colloids have been investigated in the past by means of laser flash photolysis and pulse radiolysis. The trapped electrons in these semiconductor colloids lead to the appearance of a broad absorption in the red-infrared region. The metal ion sites at the surface vacancies have been proposed to be the trapping sites for the photogenerated electrons. Recently, we reported electron storage effects in quantized WO_3 colloids and demonstrated the ability of stored electrons to reduce oxazine and thiazine dyes. We have now employed TiO_2 semiconductor colloids to carry out one-electron reduction of C_{60} . The steady-state and laser flash photolysis

results which describe interfacial electron transfer between semiconductor and carbon clusters are presented here.

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

8. (NDRL-3682) Photophysical Properties of Some Highly Fluorescent Derivatives of Vitamin B₁. Solvent Effect¹

(B. Marciniak, H. Kozubek,² J. Rozwadowski,² and G. L. Hug)

The influence of solvent on the photophysical properties of some highly fluorescent vitamin B₁ derivatives, the products of the reaction of N-methylated vitamin B₁ with cytidine (I), adenosine (II) and 2-amino-4-methylpyridine (III), was studied by means of absorption and fluorescence techniques (both steady-state and time-resolved). In the case of II and III, the photophysical properties did not change significantly in various solvents. For I, a large decrease of the fluorescence quantum yield and the lifetime of the singlet state was observed on changing solvent from acetonitrile to alcohol. These large changes in the photophysical parameters of I occurred in spite of small changes in the absorption spectra and the shape of the fluorescence spectra. No evidence for a specific solute-solvent interaction, i.e., a complex of I with alcohols, was found in pure (including deuterated) solvents or in mixed solvents. The measured values of the intersystem crossing quantum yields of I in acetonitrile and methanol (in the range of 10^{-2}) indicated that the ISC process was not responsible for the observed solvent effect. Possible explanations of the solvent's influence on the photophysical properties of I in its first excited singlet state are discussed.

(1) Submitted for publication in Photochemistry and Photobiology A.

(2) A. Mickiewicz University, Poznań, Poland.

9. (NDRL-3683) Local Solvation Effects on the Hydrogen Abstraction Reaction of Triplet-Benzophenone in Supercritical Fluids¹

(C. B. Roberts,² J. E. Chateaufneuf and J. F. Brennecke²)

We present laser flash photolysis investigations of the hydrogen abstraction reaction of triplet benzophenone (³BP) from 2-propanol and 1,4-cyclohexadiene in supercritical ethane and

fluoroform. Bimolecular rate constants based on bulk concentrations *decrease* with an *increase* in pressure along both isotherms studied. These results corroborate our previous studies in CO₂ that show increased reaction rates due to enhanced local compositions of cosolvent around the ³BP solute. Analysis of the results includes prediction of the thermodynamic pressure effect on the rate constant, which suggests an increase in the rate constant with pressure, as well as the effects of increased local cosolvent concentrations about ³BP. Spectroscopic measurements of the local composition of 2-propanol about a solute in supercritical CO₂ are presented and used to explain the apparent discrepancy between experiment and prediction, demonstrating the influence that the local environment has on kinetically controlled reactions in supercritical fluids.

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- (1) Submitted for publication in the American Institute of Chemical Engineering Journal.
 - (2) The Department of Chemical Engineering, University of Notre Dame.
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10. (NDRL-3684) Properties of the Narrow-Line ESR Signal of ³C₆₀¹

(R. W. Fessenden and A. V. Veselov)

A number of recent papers address the question of the origin of the narrow-line ESR signal observed from photoexcited C₆₀ in fluid solution. It seems that the line is clearly from the triplet, ³C₆₀, but the narrow width of this line is quite unique for a triplet in solution. It is important to show that this line behaves as a normal ESR line and represents the full concentration of the species and that, for example, the two triplet transitions contribute to its intensity. To this end and to further support the assignment to ³C₆₀, simultaneous time-resolved ESR and optical absorption measurements have been made on C₆₀ in benzene. The optical experiment measured the concentration of ³C₆₀ based on the known extinction coefficient while the ESR amplitude was compared with that of a stable radical, TEMPO. General agreement between these two measurements was found showing that the ESR line does behave as a normal ESR line with the appropriate statistical factor for a triplet state included in the calculation.

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- (1) Submitted for presented at 185th Meeting of the Electrochemical Society, San Francisco, CA, May 22-27, 1994.
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11. (NDRL-3685) Picosecond Spectroscopic Investigations of Diphenylcarbene Protonation¹

(J. E. Chateaufneuf)

The details of the picosecond kinetic investigation of diphenylcarbene ($\text{Ph}_2\text{C:}$) protonation with H_2O , MeOH , EtOH and 2-propanol by optical absorption technique are presented. The protonation reactions were monitored by detection of the diphenylcarbenium ion (Ph_2CH^+) product. Evidence of solvent induced alteration of the singlet-triplet energy level of $\text{Ph}_2\text{C:}$, and involvement of an excited carbene singlet state in the protonation of $\text{Ph}_2\text{C:}$ with H_2O are presented.

(1) Submitted for publication in Research on Chemical Intermediates.

12. (NDRL-3686) Photoinduced Electron Transfer Between Sulfur-Containing Carboxylic Acids and the 4-Carboxybenzophenone Triplet State in Aqueous Solution¹

(B. Marciniak,² K. Bobrowski, G. L. Hug and J. Rozwadowski²)

The mechanism of photoinduced electron transfer between sulfur-containing carboxylic acids and the 4-carboxybenzophenone (CB) triplet state in aqueous solution was investigated using laser flash photolysis and steady-state photolysis techniques. Bimolecular rate constants for quenching of the CB triplet state by six sulfur-containing acids, with varying numbers of COO^- groups and varying locations with respect to the sulfur atom, were found to be in the range $(0.3\text{--}2.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ depending on the charge of the acid molecule. The observation of ketyl radical anions and intermolecular ($\text{S}\cdots\text{S}$)-bonded radical cations of some of the acids was direct evidence for the participation of electron transfer in the mechanism of quenching. An additional absorption band at approximately 410 nm in the transient absorption spectra for some of the acids was assigned to an intramolecularly ($\text{S}\cdots\text{O}$)-bonded species (for acids where a five-member ring structure was sterically favorable). Quantum yields of formation of intermediates from flash photolysis experiments and quantum yields of CO_2 formation and CB disappearance from the steady-state measurements were determined. The values of these quantum yields clearly indicated that the diffusion apart (escape of the radical ions) of the charge-transfer complex, formed as a primary photochemical step, is the main photochemical pathway (contribution of $\sim 90\%$). Competing processes of proton transfer and back electron transfer within the CT complex gave only minor contributions to these yields. A detailed

mechanism of the CB-sensitized photooxidation of sulfur-containing carboxylic acids is proposed, discussed, and compared with that for sulfur-containing amino acids in aqueous solution.

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- (1) Submitted for presentation at the 18th DOE Solar Photochemistry Research Conference, Tahoe City, CA, June 5-9, 1994. Also submitted for publication in the Journal of Physical Chemistry.
 - (2) A. Mickiewicz University, Poznań, Poland.
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13. (NDRL-3687) Hyperfine Splitting in HOCO from *Ab Initio* Calculations¹

(I. Carmichael)

Results are reported from an *ab initio* molecular orbital study of the isotropic hyperfine coupling, a , in *trans*- and *cis*-HOCO. Equilibrium radical structures are obtained from large-basis-set second-order Møller-Plesset perturbation theory (UMP2) calculations. Vibrational frequencies are predicted for the analogous deuterated species from scale factors determined by comparison with the results of similar calculations on, and the known experimental vibrational spectra of, various isotopomers of formic acid. The isotropic splittings due to the possible magnetic nuclei, ^1H , ^{13}C , and ^{17}O , are then computed at these optimized geometries. An extensive investigation of the basis set dependence of the computed magnetic coupling constants is carried out at the unrestricted Hartree-Fock (UHF) and UMP2 levels of theory. Further electron correlation effects on the calculated splittings are determined from the results of coupled-cluster (UCCD) and the quadratic configuration interaction (UQCISD) treatments with moderately large basis sets. For the more readily observed couplings, $a(^1\text{H})$ and $a(^{13}\text{C})$ values of -4.7 MHz and 533 MHz are obtained for the *trans*-isomer. Experimentally $a(^1\text{H}) = \pm 6.8$ MHz is reported [Sears *et al.* J. Chem. Phys. (1993), 98, 6624]. Couplings in *cis*-HOCO are predicted to be 77 MHz at hydrogen and 608 MHz at carbon.

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- (1) Submitted for publication in the Journal of Physical Chemistry.
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14. (NDRL-3688) Temperature Effects on the Luminescence of Re(I) Complexes: On the Competitive Relaxations of Two Electronic States¹

(G. Ferraudi, M. Féliz, E. Wolcan,² I. Hsu,³ S. A. Moya² and J. Guerrero²)

The emission spectra and luminescence rates of $\text{Re}(\text{CO})_3\text{L}_2\text{X}$ (L_2 = pyridine or bisquinoline derivatives, X = halide) have been measured in various media at temperatures between 298 and 77 K. The emission in this series of complexes has been associated with the parallel relaxations of an intraligand and a metal to ligand charge transfer state. The rates of emissive relaxations exhibit a good correlation with the excited state - ground state energy gap. Mechanisms (Herzberg-Teller or pseudo-Jahn-Teller) mixing intraligand with charge transfer states are proposed as a means to explain the dependence of the emission rate on temperature.

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- (1) Submitted for publication in the Journal of Physical Chemistry.
 - (2) University of Santiago, Chile.
 - (3) Clemson University.
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15. (NDRL-3689) Time-Resolved Electron Spin Resonance Studies of Spin Trapping. Steric and Polar Effects Influencing Trapping by Nitrones¹

(K. P. Madden)

In situ radiolysis time-resolved ESR studies with nitroso spin traps have shown that carbon-centered radical trapping is considerably influenced by steric and electronic effects in the trap-radical encounter complex. Rapid spin trapping is observed with sterically unhindered straight-chain alkyl radicals, while bulky alkyl radicals such as 2-hydroxy-2-methylpropyl are sufficiently crowded about the radical center that second-order parent radical termination occurs in preference to radical trapping. Strongly reducing hydroxyalkyl radicals such as hydroxymethyl, hydroxyethyl and hydroxymethylethyl react quickly in spite of steric constraints, however, due to favorable electronic interactions between the radical and the polar $\text{N}=\text{O}$ moiety.

Preliminary time-resolved experiments with the nitrone spin trap DMPO show that although these steric and electronic effects are still operative, their influence in DMPO spin trapping reactions is diminished relative to nitroso traps. DMPO efficiently scavenges the 2-hydroxy-2-methylpropyl radical, in spite of the crowded steric environment near the parent radical SOMO. Polar effects tending to accelerate hydroxyalkyl radical trapping in nitroso traps

are less important with DMPO. The rate constant of the DMPO reaction with hydroxymethyl radical is similar to that of DMPO and methyl radical.

- (1) Submitted for presentation at the 42nd Meeting of Radiation Research Society, Nashville, TN, May 1-5, 1994.
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16. (NDRL-3690) Radiolysis of Cyclooctane with Gamma Rays and Helium Ions¹

(L. Wojnárovits and J. A. LaVerne)

Iodine scavenging techniques have been used to examine the role of the cyclooctyl radical in the radiolysis of cyclooctane with γ -rays and with 5 to 20 MeV helium ions. In γ -radiolysis about 70% of the total yield of cyclooctyl radicals are scavenged with 10^{-4} M iodine which agrees well with other studies on cycloalkanes that show most of the radicals produced in these systems react in the bulk medium at times longer than a microsecond. However, it is found that, out of a total yield of 6.6 cyclooctyl radicals/100 eV, 2.5 radicals/100 eV are produced by H atom precursors as compared to a value of 1.5 cyclohexyl radicals/100 eV in cyclohexane. With 10 MeV helium ions (average LET 106 eV/nm) half of the cyclooctyl radical reactions are complete within 30 nanoseconds and about 92% of all the radical reactions occur within a few microseconds due to the increased initial radical densities in the helium ion track. The cross-bridged product bicyclo[3.3.0]octane (pentalane) is believed to be formed only by unimolecular dehydrogenation of the singlet excited state of cyclooctane and no dependence of its yield on iodine concentration up to 0.03 M was found with both types of radiation. However, the pentalane yields with helium ions were approximately one third of that found in γ -radiolysis. The most likely reason for this result is the decreased yield of singlet state formation due to the enhanced probability of cross combination reactions of electron-cation pairs in the high density region of the helium ion track.

- (1) Submitted for publication in the Journal of Physical Chemistry.
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17. (NDRL-3691) A Dual Beam Spectrometer for Optical Studies of Spread Monolayers at the Air-Water Interface¹

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

An optical spectrometer for the study of low-level optical absorption and reflection of spread monolayers at the air-water interface is described. This spectrometer is suitable for measurements at wavelengths from approximately 350 to 800 nm and has a precision in the order of $\sim 2 \times 10^{-5}$ in terms of effective optical density. It employs a dual beam design utilizing fiber optic bundles to guide light and a multichannel photodiode array detection system. Instrumental control and data gathering are designed within Labwindows software. Representative spectral absorption data from chlorophyll *a* degradation kinetics are presented by way of illustration. Comparison of chlorophyll *a* reflection and absorption are also given.

(1) Submitted for publication in Review of Scientific Instruments.

18. (NDRL-3692) Slow Collisions of Na⁻ and K⁻ with Atomic Hydrogen¹

(J. A. Fedchak,² R. L. Champion,² L. D. Doverspike,² and Yicheng Wang)

Total cross sections for electron detachment and charge transfer have been measured for collisions of Na⁻ and K⁻ with atomic hydrogen for relative collision energies ranging from 2-20 eV. The cross sections for detachment are considerably larger than those for charge transfer and the experimental results for Na⁻ + H are analyzed with a model which employs available potential energy curves and an average width to describe the molecular anion in its unstable region. The charge transfer cross section for Na⁻ + H is compared to the results of a perturbed stationary state calculation which uses the average width inferred from the detachment results and a term of the form $H_{12} = \beta e^{-\gamma R}$ to describe the long-range coupling between the A²Σ and X²II states of NaH⁻. This latter calculation underestimates the observed low energy cross section for charge transfer.

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

(2) College of William and Mary, Williamsburg, VA.

19. (NDRL-3693) Reduction of Hexaazacyclophane Complexes of Co(II) and Cu(II) by CH_2OH and e_{sol}^- ; A Pulse Radiolysis Study¹

(J. Vargas, G. Ferraudi, J. Canale² and J. Costamagna²)

The reactions of CH_2OH and e_{sol}^- with hexaazacyclophane complexes of Co(II) and Cu(II) in methanol and or methanol-water mixed solvents were investigated by pulse radiolysis. The primary products from the reduction of the macrocyclic complexes were assigned a radical nature by comparing their optical spectra with those of related Co(I) and Cu(I) species. Such metal-ligand radical products undergo disproportionations with lifetimes equal to or longer than 10 μs . The product of the disproportionation was assigned as a Co(III) - hydride complex. Although a similar hydride could be produced in the disproportionation of the Cu(II)-ligand radical, the optical spectrum of the product is in accordance with the hydrogenation of a double bond in the ligand. Interception of the metal-ligand radical intermediates with CO_2 resulted in the formation of adducts.

(1) Submitted for publication in *Inorganica Chimica Acta*.

(2) Department of Chemistry, University of Santiago, Santiago, Chile.

20. (NDRL-3694) *In Situ* Radiolysis Electron Spin Resonance Studies of Spin Trapping¹

(H. Taniguchi and K. P. Madden)

In situ radiolysis time-resolved ESR studies of the reaction of 2-methyl-2-nitrosopropane (MNP) with carbon-centered radicals have shown that the trapping efficiency of this nitroso spin trap is considerably influenced by steric and electronic effects in the MNP-radical encounter complex. The ESR spectral intensity of a spin adduct is also strongly influenced by the adduct's second-order termination rate. We have examined spin adduct stability for a number of hydroxyalkyl and alkyl parent radicals reacting with MNP. Spin adducts are strongly stabilized by hydroxyalkyl substituents, while alkyl substituents are less effective. Bulky parent radicals stabilized the resulting spin adducts, but the dominant determinant of adduct stability was the substituent inductive effect. MNP-hydroxycyclohexyl radical adduct, in particular, is remarkably persistent.

Preliminary time-resolved experiments with the nitron spin trap DMPO show that although steric and electronic interactions between the trap and parent radical still influence trapping rates, their importance in DMPO spin trapping reactions is diminished relative to

MNP. DMPO efficiently scavenges the 2-hydroxy-2-methylpropyl radical, while the rate constant of the DMPO reaction with hydroxymethyl radical is one tenth that of hydroxymethyl and MNP.

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- (1) Submitted for presentation at the International Conference on Bioradicals Detected by ESR Spectroscopy, Yamagata, Japan, June 12-16, 1994.
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21. (NDRL-3695) On the Mechanism of Sensitized by N-(9-Methylpurin-6-yl)Pyridinium Cation Photooxidation of Sulfur-Containing Amino Acids in Aqueous Solution¹

(B. Marciniak,² J. Rozwadowski,² G. L. Hug and K. Bobrowski)

Sulfur-containing amino acids were oxidized via photosensitization by N-(9-methylpurin-6-yl) pyridinium chloride in neutral aqueous solutions. The mechanism of this reaction was investigated with laser flash and steady-state photolysis techniques. 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 $2.1 \times 10^8 - 7.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ 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 ($\lambda = 550 \text{ nm}$), the $(S\cdots S)^+$ radical cation for some of the amino acids ($\lambda = 480 \text{ nm}$), and the N-(9-methylpurin-6-yl)pyridinyl radical ($\lambda = 610 \text{ nm}$). 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. Quantum yields of pyridinyl radical formation from flash photolysis experiments were determined and compared with the quantum yields of CO_2 formation and pyridinium cation disappearance from the steady-state measurements. 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 the 12th Polish-Danish Symposium on Radiation Chemistry, Swidno, Poland, June 4-7, 1994.
- (2) A. Mickiewicz University, Poznań, Poland.
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22. (NDRL-3696) Photochemistry of Squaraine Dyes. 8. Photophysical Properties of Crown Ether Squaraine Fluoroionophores and their Metal Ion Complexes¹

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

The photophysical properties of a series of new bis[4-(monoaza-crown-ether)phenyl]squaraine fluoroionophores are reported. These dyes form aggregates in aqueous solutions. The aggregation is disrupted in β -cyclodextrin solutions as the dye forms a 1:1 complex with β -cyclodextrin. This complexation process is accompanied by a significant enhancement in the fluorescence yields of these dyes. Complexation of the fluoroionophores with alkali metal ions brings about drastic reductions in their fluorescence quantum yields as well as significant changes in their redox properties. These effects could be attributed to a cation-induced reduction in the electron donating ability of the azacrown-ether moiety.

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- (1) Submitted for publication in the Journal of Physical Chemistry.
- (2) Regional Research Laboratory, Trivandrum, India.
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23. (NDRL-3697) Stochastic Simulation of Transient Free-Radical Attack on DNA¹

(C. E. Bolton, N. J. B. Green 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 the 18th L. H. Gray Conference: Radiation Damage in DNA: Physics, Chemistry and Molecular Biology, Bath, England, April 10-14, 1994.
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24. (NDRL-3698) NDRL-NIST Solution Kinetics Database: Ver. 2.0 Diskette and User Guide¹

(A. B. Ross, W. G. Mallard,² W. P. Helman, G. V. Buxton,³ R. E. Huie² and P. Neta²)

Version 2.0 of the NDRL/NIST Solution Kinetics Database includes chemical kinetic data for free radical processes involving primary radicals from water, inorganic radicals and carbon-centered radicals in aqueous solution, and organic peroxy radicals in various solvents. Data from the literature through 1992 have been compiled and evaluated; recommended values of rate constants are designated for certain reactions. The user can find previously determined rate constants, and add data or append notes on specific reactions. Software enhancements in this version include searching by name fragments and optional retrieval of all ionic forms of the same species. The database includes 14,000 rate determinations for 10,800 reactions involving 7,800 chemical species for which there are data as reactants or products; 2,600 literature references are cited.

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- (1) National Institute of Standards and Technology, Gaithersburg, MD, Publisher.
 (2) Chemical Kinetics and Thermodynamics Div., NIST, Gaithersburg, MD.
 (3) University of Leeds, U. K.
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25. (NDRL-3699) Calculation of Electron Energy Loss Distributions in DNA¹

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

Experimentally derived optical constants and X-ray attenuation cross sections were used to construct the complete dipole oscillator strength distribution for solid, dry DNA. Monte Carlo simulations of the energy loss of electrons of initial energy 5 keV to 1 MeV in DNA were performed using cumulative inelastic cross sections obtained from a formulation incorporating the constructed dipole oscillator strength distribution. The energy loss distribution, the most

probable energy loss and the mean energy loss for electrons in DNA are compared to those for liquid water, gaseous water and gaseous hexane. For the most part, the calculations show electron energy loss in DNA is very similar to that in liquid water, however, it is quite different in both gaseous water and gaseous hexane. The mean energy losses for a 1 MeV incident electron in DNA, in liquid water, in gaseous water, and in gaseous hexane are 38.5, 37.7, 33.7, and 25.2 eV, respectively. The large differences found between the predictions for DNA and for the gaseous media bring into serious question calculations on radiation-induced damage in DNA which make use of cross sections for gaseous media. Stopping powers and csda ranges of the four media for electrons are also presented.

(1) Submitted for publication in Radiation Research.

26. (NDRL-3700) Magnetokinetic Effects in Reactions of Inorganic Compounds¹

(G. Ferraudi)

One goal of the present studies is to learn about the nature of magnetic interactions which influence the reactivity and spectroscopy of inorganic compounds. A second goal is to apply such knowledge to learn about spin-related effects in the mechanisms of electron and energy transfer reactions involving coordination complexes. In these regards the investigated reactions are either electron transfers, energy transfers or the relaxation of an excited state to the ground state. The basis for this selection is that they are tractable from a theoretical standpoint and because they provide different viewpoints for the examination of magnetokinetic effects in chemical reactions.

Magnetic field effects on the rates of ground- or excited-state reactions have been investigated at a constant field with intensities between 0 and 9 Tesla (90,000 Gauss). Flash photochemical and stopped-flow techniques were used for the measurements of the reaction rate and changes in the absorption and emission spectra under such fields. For example, in our initial work we explored effects on outer-sphere electron transfer between coordination complexes. These experimental observations are related to several contributions to the electronic matrix element. In a more recent development we have been studying field-induced changes in the inner-sphere reactions between a coordination complex and an inorganic radical, e.g., the reactions of Co(II) and Mn(II) complexes with Cl_2^- , Br_2^- and $\text{CO}_3\text{H}^\bullet$. We selected these reactions because they can be modeled in terms of the radical pair mechanism and because they

can be related to some of the reactions appearing in photochemical processes. The dependence of the rate with field can be related to simultaneous contributions from the suppression of HFC-induced transitions in the multiplet and to the Δg mechanism. Indeed, such combined contributions in reactions of high-spin Co(II) complexes result in an additional extremum in plots of k vs. B at fields of several tens of Teslas. The sense of the effect (increase or decrease with field) is in some reactions opposite to that in reactions between organic radicals. This is related to the symmetry of the orbitals involved in the electron transfer. In some reactions, magnetokinetic effects decrease monotonically with field at field intensities above 3 Tesla, i.e., where literature models predict quenching of the magnetokinetic effect by anisotropic terms in the Hamiltonian. Magnetic field dependencies of the rates for outer-sphere oxidations of complexes by radicals approach those of outer-sphere electron transfers between coordination complexes. Possible relationships between these two types of processes will be explored.

The experimental observations on electron transfer reactions have been extended to the interpretation of field effects on the charge transfer photochemistry of Co(III) complexes, e.g., $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ where X is halide. Quantum yields of radical photogeneration depend on the magnetic induction in a manner that is near the mirror image of the k vs. B curve for the fusion reaction of low-spin Co(II) with radicals. A large part of these magnetokinetic effects appears to be related to recombination processes of radical-ion pairs before spin relaxation in the metallo fragment.

Future Work: Magnetokinetic effects are to be studied in intramolecular electron transfer reactions of Co(III) complexes with ligand radicals, e.g., $[\text{Co}(\text{NH}_3)_5(\text{L}^{\cdot-})]^{2+}$ where $\text{L}^{\cdot-}$ = nitrophenyl radical. Similar studies will be carried out on outer-sphere electron transfer reactions between inorganic radicals and cryptate complexes of transition metal ions. Reaction kinetic studies will be complemented with time-resolved MCD spectroscopy of paramagnetic intermediates.

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- (1) Submitted for presentation at the 18th DOE Solar Photochemistry Research Conference, Tahoe City, CA, June 5-9, 1994.
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27. (NDRL-3701) Electron Transfer from Lipid-Functionalized Pyrene in Langmuir Films to Lipid Bound and Bulk Phase Acceptors¹

(L. Li and L. K. Patterson)

Kinetics of electron transfer between excited-state lipid-functionalized pyrene [1-(10-(6(8)-octadecylpyrenyl)decanoyl)-2-hexanoylphosphatidyl-choline, (OPyPC)] and alkyl viologens as well as related acceptors have been examined in spread lipid monolayers and corresponding vesicle systems. The lipids, zwitterionic dioleoylphosphatidylcholine (DOL) negatively charged dioleoylphosphatidylglycerol (DPG) and neutral dioleoylglycerol (DOG), have been used to determine the effects of headgroup on reaction rates. Using the treatment by Owen for two-dimensional diffusion, it is observed that quenching by 4-(N-hexadecylpyridinium-4-yl)pyridine chloride, (CB⁺) gives apparent diffusion coefficients similar to those obtained earlier by excimer formation. A parallel measurement in vesicles gives diffusion coefficients close to those found in monolayers, suggesting that some processes in the two systems may be compared. Electron transfer to methyl viologen in the subphase is highly dependent on the lipid headgroup. Surprisingly, in the presence of DOG with its neutral headgroup, dynamic transfer occurs much more rapidly than it does in DOL. Negatively charged DPG accelerates transfer to a bulk rate constant of $10^{13} \text{ M}^{-1}\text{s}^{-1}$ due to high surface potential, giving the most efficient transfer kinetics. Measurement of back reaction in vesicles shows that for lipid functionalized acceptors, the back reactions occur in accordance with two dimensional diffusion coefficients measured in forward reactions. However, because of monolayer viscosity, the ion pair lifetime will be long. Back reaction with subphase acceptor is even slower, by a factor > 2 . As expected, transfer by the triplet mechanism occurs two orders of magnitude more slowly than from singlet.

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- (1) Submitted for presentation at the 18th DOE Solar Photochemistry Research Conference, Tahoe City, CA, June 5-9, 1994.
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28. (NDRL-3702) Photoelectrochemical Behavior of Naked and Surface-Modified Nanocrystalline SnO₂ Semiconductor Films¹

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

Development of thin semiconductor films is of great interest because of their applications in electronics, electrooptics, imaging science, photoelectrochemical cells, and

photocatalysis. We have now succeeded in developing thin metal oxide semiconductor films of thickness 0.1 to 1 micron from colloidal suspensions of ZnO, SnO₂ and WO₃. Such methods provide a convenient way to tailor the semiconductor properties by controlling the preparative conditions of colloid precursors.

Thin, transparent films of nanocrystalline SnO₂ semiconductor have been prepared from 30 Å diameter colloids. The electron trapping process in SnO₂ particles has been investigated by both spectroelectrochemical and laser flash photolysis techniques. With increasing negative potentials (0.0 to -0.5 V vs. Ag/AgCl) an increase in the IR absorption band with an intense bleaching in the UV is observed. The absorption spectra recorded during the charging cycle are easily restored in the discharge cycle.

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 SnO₂ 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 (Ru(bpy)₂(dcbpy)²⁺), chlorophyll *a* and *b*, squaraine and oxazine dyes. SnO₂ films

modified with Ru(bpy)₂(dcbpy)²⁺ exhibit excellent photoelectrochemical response in the visible with a power conversion efficiency of ~1% at 470 nm.

Both microwave absorption and luminescence decay measurements have been carried out to obtain the rate constant for the charge injection process. The luminescence decay showed at least two components and the faster component gave rate constants ~10⁸ s⁻¹ which matched well with the rate constant obtained from the growth of the microwave absorption.

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- (1) Submitted for presentation at the 18th DOE Solar Photochemistry Research Conference, Tahoe City, CA, June 5-9, 1994.
 - (2) Centre de Recherche en Photobiophysique, Université du Québec à Trois Rivières, Trois Rivières, Québec, Canada.
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29. (NDRL-3703) Magnetic Field Effects on the Rate of Reactions with Coordination Complexes¹

(G. Ferraudi)

Magnetic field effects (MFE) on the rates of ligand photosubstitution, on the relaxation of excited states and on electron transfer reactions have been investigated at magnetic inductions between 0 and 9 Tesla. Flash photolysis and/or stop-flow techniques in conjunction with magnetic fields generated by a pulsed, air-cooled, magnet or a superconducting magnet were applied to kinetic studies. Examples about the photosubstitution in Rh(III) complexes and the excited state relaxation in Cr(III) complexes will be presented. The effect of the field on outer-sphere electron transfer reactions between diamagnetic reactants, e.g., $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$, will be compared with effects in related reactions between paramagnetic complexes. Significant magnetic field-induced changes in the rate of free radical, i.e., Cl_2^- , CO_3^- , oxidations of coordination complexes have also been investigated. They could provide a diagnostic tool when the reaction mechanism, namely inner-sphere *vs* outer-sphere, cannot be assessed by means of the reaction products. Applications of the MFE to the study of the mechanism of photoredox reactions in coordination complexes will be discussed.

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- (1) Submitted for presentation at the 4th Latin American Meeting on Photochemistry and Photobiology, Valparaiso, Chile, April 12-15, 1994.
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30. (NDRL-3704) Mechanism of the Oxidation of Benzoquinone by Radiolytically Produced OH Radicals¹

(Y. Liang and R. H. Schuler)

The present study examines the mechanism for attack of radiolytically produced OH radicals on 1,4-benzoquinone in neutral aqueous solution. HPLC analysis of the products from 100 μM solutions shows that the benzoquinone itself oxidizes the intermediate OH adduct radical to form 2-hydroxy-1,4-benzosemiquinone essentially quantitatively. The *p*-benzosemiquinone radical anions produced in this oxidation step undergo electronic disproportionation to form an equivalent yield of hydroquinone. Time resolved pulse radiolysis studies of the nano- and microsecond time scales show that oxidation results from electron transfer from the benzoquinone to the OH radical rather than by OH addition, as is usually the case with most aromatics. The initial radical cation then reacts with water on the

200 ns time scale to produce the adduct which is subsequently oxidized by electron transfer to benzoquinone to form 2-hydroxy-1,4-benzoquinone. For solutions 100 μM in benzoquinone these processes occur on the microsecond time scale. The rate constant for the initial attack is $\sim 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and that for the secondary transfer is $\sim 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

This study illustrates the power of pulse radiolysis methods in examining mechanistic details, particularly in resolving details of sequential pseudo-first order reactions which occur on similar time scales.

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- (1) Submitted for presentation at the 25th Reaction Mechanisms Conference, Notre Dame, IN, June 10-15, 1994.
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Other investigations in progress include:

31. Radiation Chemical Kinetics of Track Entities

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

While spurs account for over 90% of the energy loss events comprising a fast electron track, a significant fraction (about 25%) of the total energy of the incident electron is still transferred to larger entities, blobs and short tracks. Consequently, the radiation chemistry of these types of entities may have a significant effect on the observed kinetics in fast electron radiolysis. Previously, stochastic and deterministic modeling techniques have been used to investigate the diffusion and reaction in spurs. These methods are being developed to examine the chemistry of the more spatially extended track entities. The geometric modifications to the stochastic random flights and IRT treatments are straightforward. IRT simulations are in progress to elucidate the effects of the number density of the radiation-induced reactants and of spatial geometry on the observed kinetics. Preliminary results confirm that the chemistry of the larger track entities is very different from that of spurs. In particular there is a significant increase in the yields of reactions producing observable (molecular) products and a decrease in the yields of the recombination reactions. This difference will have direct consequences when considering experimental radiolysis data. The results also show that even small changes in the spatial arrangement of the reactive radicals and ions comprising an entity have a large effect upon the radical decay kinetics and upon the formation of the molecular products. The extension of the deterministic FACSIMILE method to model blobs and overlapping spurs

requires extensive changes to the methodology. These developments are in progress, however, convergence of the solution of the sets of coupled diffusion-reaction equations is problematic and has to be tested rigorously.

32. Theoretical Analysis of Dose and LET Effects on Radical Yield in Solid Films Induced by Ion-beam Irradiation

(A. Mozumder, H. Namba¹ and T. Taguchi¹)

Ion-beam irradiation (H^+ , He^{2+} , C^{5+} , etc.) of solid films produces radicals which are specific to the chemical nature of the film, e.g., deaminated radical in alanine, allyl radical in polyolefins, etc. However in every case the observed radical yield decreases with both LET and dose, presumably due to radical-radical reaction. We are developing a track theory for explaining these effects.

Under experimental conditions the radicals are trapped. Therefore, in the first phase, we only compute the overlap probability of spurs contained in the tracks. Specific rates of radical reaction will be introduced later to make the calculations complete. LET effect is expressed by intra-track overlap for which the probability is calculated to be $\pi(S) = 1 - \exp(-2a S/\epsilon)$ where S is the LET, a is the spur radius and ϵ is the spur energy. Therefore a LET effect is not expected below $S_0 = \epsilon/2a = 5 \text{ eV/nm}$, taking $\epsilon = 30 \text{ eV}$ and $a = 3 \text{ nm}$; this is consistent with experiment.

The dose-effect is expressible as intertrack overlap of spurs. Since there is no dose-rate effect in these experiments dose (D) and fluence (F) are simply related by $D = FS/\rho$, where ρ is the density. We calculate the probability of no intertrack overlap at fluence F as

$$1-\Gamma = \exp(-2a S/\epsilon) + (2a S/\epsilon) \exp(-4\pi a^2 F) \int_0^1 d\zeta \exp(4\pi a^2 \zeta^2 - 2a S\zeta/\epsilon). \quad (I)$$

Combining this with the LET effect the probability of either intra- or intertrack overlap is found to be $\pi = 1 - (1-\Gamma) \exp(-2a S/\epsilon)$ where Γ is to be obtained from eq. (I). These results show that: (1) at very low-LET ($S \sim 0.2 \text{ eV/nm}$) the overlap is essentially of intratrack type (purely dose effect) and (2) for He^+ -ions at 200 keV ($S \sim 100 \text{ eV/nm}$) and at very low dose, $\Gamma \approx 0$ but $\pi \approx 1$, implying nearly complete intra-track overlap. At an intermediate LET both dose and LET effects can be seen. Further research in progress includes secondary electron (penumbra) effect and effects arising from finite reaction rate and the distribution of spur size.

(1) Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Japan.

33. Energy Partition between the Core and the Penumbra in the Tracks of Au, La, Fe and Na Ions in Liquid Argon over the Energy Range 1-1000 MeV/amu

(A. Mozumder)

A recent theory of luminescence quenching in LAr [A. Hitachi et al., Phys. Rev. B46, 11463, 1992], based on a biexcitonic quenching mechanism, requires as input the partitioning of the deposited energy between the core and the penumbra of the heavy ions, because the process can only occur at high exciton density. In connection with recent experiments with Na, Fe, La and Au ions over a wide span of energy, performed in Professor Doke's lab at Waseda, we have calculated the energy partition for these particles in LAr utilizing the theories of electron transport developed in this laboratory.

In the relativistic regime (> 100 MeV/amu) Fermi's criterion determines the core size and all ions have the same energy partition, which levels off at 62% at high energies. At lower energies a "fission-fragment"-like effect is seen for very heavy ions, that is, there is a repulsive core expansion due to multiple ionization occurring at high LET. We see this effect at $\lesssim 30$ MeV/amu for Au, $\lesssim 10$ MeV/amu for La, $\lesssim 3$ MeV/amu for Fe and not at all for Na ions. The minimum core fraction for these ions occurs respectively at 30, 25, 20 and 20 MeV/amu with a value around $57.5 \pm 0.5\%$ in all cases. At relatively low energies (< 10 MeV/amu) the core fraction of the deposited energy increases again due to increased LET and scattering of the low-energy ejected electron. At 1 MeV/amu this percentage increases to 72% and 65% respectively for Au and La ions and to 57% for both Fe and Na ions.

34. Radiolysis of Cyclopentane

(L. Wojnárovits and J.A. LaVerne)

We have determined the yields of the major products formed in the γ -radiolysis of liquid cyclopentane. For doses of 50 krad the yields of cyclopentene, bicyclopentyl and 1-pentene in neat cyclopentane are 3.25, 1.23, and 0.9 molecules/100 eV, respectively. The yield of the cycloalkene is very similar to those observed in the γ -radiolysis of cyclohexane and cyclooctane, while the yield of the bicycloalkyl is about 70% of the values found with the other two cyclic hydrocarbons. The yields of all three products decrease with increasing iodine concentration. The decrease in the cyclopentene and bicyclopentyl yields from neat solution to 0.1 mM iodine solution gives a disproportionation to combination ratio of 0.97 for cyclopentyl radicals which is in good agreement with literature values. Above about 1 mM iodine the cyclopentene yield decreases much more rapidly with iodine concentration than does the bicyclopentyl yield.

Although the exact mechanism is not known, these results indicate that iodine can interfere with a nonradical precursor to cyclopentene. The production of 1-pentene which probably occurs by ring breakage and relaxation of the excited triplet state of cyclopentane also shows a decrease with increasing iodine concentration. A comparison of the mechanisms for product formation in the cyclic hydrocarbons is in progress. Studies on the LET dependences of the product yields in cyclopentane are also planned.

35. Chloride Atom Adducts to Diphenyl, and Dimethyl Sulfide in Carbon Tetrachloride (J. E. Chateaufneuf)

Recently, in a report describing the photochemistry of the diphenyl sulfide/chlorine atom adduct ($\text{Ph}_2\text{S}/\text{Cl}\cdot$) the complex was assigned to a π -molecular complex [Sumiyoshi et al., Bull. Chem. Soc. Jpn. (1993) 2510] due to similarities in the absorption spectrum with $\text{Cl}\cdot$ /arene π -complexes. However, there was no chemical evidence to support this assignment. The assignment is extremely intriguing in that the dimethyl sulfide/chlorine adduct ($\text{Me}_2\text{S}:\cdot\text{Cl}$) has been characterized in aqueous solution to be a sulfur-chlorine three electron bond adduct [Asmus et al., JACS (1984) 5988]. Therefore, the question arises as to whether $\text{Ph}_2\text{S}/\text{Cl}\cdot$ may demonstrate dual complexation, that is, π -interaction of $\text{Cl}\cdot$ with the aromatic rings and σ -bond formation with the sulfur center. This question may be addressed by measuring the apparent reactivity of the $\text{Ph}_2\text{S}/\text{Cl}\cdot$ adduct with 2,3-dimethylbutane (DMB) at low concentrations of complexing agent, and direct comparison with the reactivity of the known $\text{Cl}\cdot$ /benzene π -complex and the $\text{Cl}\cdot$ /pyridine σ -complex [Chateaufneuf, JACS (1993) 1915]. $\text{Ph}_2\text{S}/\text{Cl}\cdot$ was independently generated by both pulse radiolysis and 266 nm laser flash photolysis (LFP) of CCl_4 containing 1×10^{-3} M Ph_2S . Both absorption bands of $\text{Ph}_2\text{S}/\text{Cl}\cdot$ ($\lambda_{\text{max}} = 340$ nm; 500 nm) demonstrated identical kinetic behavior with little reactivity towards DMB, $< 1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$. This results in K_{eq} for formation of the adduct to be $> 3 \times 10^6 \text{ M}^{-1}$ according to: $K_{\text{Ph}_2\text{S}} = K_{\text{benzene}} \times k_{\text{DMB}}(\text{benzene})/k_{\text{DMB}}(\text{Ph}_2\text{S})$. For comparison, K_{eq} for formation of the $\text{Cl}\cdot$ /benzene π -complex is 200 M^{-1} and $k_{\text{DMB}}(\text{benzene}) = 1.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$; and K_{eq} for formation of the $\text{Cl}\cdot$ /pyridine σ -complex is $1.2 \times 10^5 \text{ M}^{-1}$ and $k_{\text{DMB}}(\text{pyridine}) = 2.6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$. The $\text{Me}_2\text{S}/\text{Cl}\cdot$ adduct ($\lambda_{\text{max}} = 365$ nm) was also generated by both pulse radiolysis and LFP of CCl_4 . $\text{Me}_2\text{S}/\text{Cl}\cdot$ also demonstrated little reactivity, $< 1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$, toward DMB even at $[\text{Me}_2\text{S}] = 5 \times 10^{-4}$ M. The above comparisons demonstrate that the reactivity of the $\text{Ph}_2\text{S}/\text{Cl}$ adduct is inconsistent with a loosely bound π -molecular complex, however, is nearly identical to the three-electron bond $\text{Me}_2\text{S}:\cdot\text{Cl}$ adduct. It is also interesting to note that in

aqueous solution K for neutral dissociation of $\text{MeS}\cdot\text{Cl} \rightarrow \text{MeS} + \text{Cl}\cdot$ is $<<10^{-10}$, however, ionic dissociation to $\text{MeS}^{\cdot+} + \text{Cl}^-$ is $K \approx 4$. In CCl_4 there was no evidence of $\text{Me}_2\text{S}^{\cdot+}$ formation, therefore the lack of solvating power of this solvent may prove useful in future characterizations of $\text{Me}_2\text{S}\cdot\text{Cl}$.

36. Free Radical and Triplet Reactivity with Molecular Oxygen in Supercritical Fluids

(J. E. Chateaufneuf, C. B. Roberts,¹ and J. F. Brennecke¹)

We have previously demonstrated [JACS (1992) 8455-8463] that dramatic enhancements of reaction rates in supercritical fluids may be obtained in reactions between dilute solutes and liquid cosolvents due to preferential solvation of the solutes by attractive cosolvents. Currently, the reactions of dilute solutes with a gaseous cosolvent, oxygen, is under investigation in order to determine the possibility of enhancement or exclusion of this cosolvent from the local environment around the solute. Specifically, the reactions of triplet benzophenone (^3BP) and benzyl radical ($\text{Ph}\dot{\text{C}}\text{H}_2$) with oxygen have been studied in SC CO_2 at temperatures above the critical point and at reduced pressures ranging from ~ 1.0 to 2.5 . Experimentally, k_{bi} for these reactions were obtained by two independent methods, by varying O_2 concentrations at constant molarity, and at constant mole fraction. The two methods yielded identical results for each reactant. The pressure effects on k_{bi} for both reactions were also essentially identical with the exception of absolute value. Both reactions demonstrated very little pressure effect and decreased only $\sim 25\%$ from high to low pressure. These results are in dramatic contrast to the 4- to 8-fold increase in k_{bi} observed for $^3\text{BP} + \text{liquid cosolvents}$. These results are an indication of the strength of the physical interaction between the dilute solute and cosolvent. With O_2 as cosolvent, ^3BP and $\text{Ph}\dot{\text{C}}\text{H}_2$ demonstrate no preference for O_2 over the supercritical CO_2 solvent. The small positive pressure effect on k_{bi} observed in these reactions is currently being analyzed in terms of the expected thermodynamic pressure effect on k_{bi} according to transition state theory. The reactions are also being investigated in other supercritical solvents of various polarities.

37. Nanocrystalline SnO_2 Films for Photocatalytic Degradation of Textile Azo Dyes

(K. Vinodgopal and P. V. Kamat)

In photocatalytic oxidation, scavenging of conduction band electrons by adsorbed oxygen (e.g., in TiO_2 particle suspensions) is considered to be an important step in promoting oxidation reactions involving valence band holes. Semiconductors such as SnO_2

have not been considered as suitable photocatalysts in the past because of their inability to reduce oxygen ($E_{CB} \sim 0.0$ V). Using our electrochemically assisted photocatalysis principle, we have succeeded in utilizing nanocrystalline SnO_2 films for the photocatalytic degradation of an azo dye, Orange-II. The externally applied bias enhances the charge separation within the nanocrystallites, thus promoting the oxidation at the semiconductor surface. The rate of degradation increases with increasing anodic bias potential. Further experiments are underway to establish the mechanism of oxidative degradation of azo dyes on SnO_2 nanocrystalline films.

38. Interaction of Dye Aggregates with SnO_2 Semiconductor Nanocrystallites

(D. Liu and P. V. Kamat)

Oxazine dyes (e.g., cresyl violet) form H-aggregates when adsorbed on nanocrystalline SnO_2 films. The aggregate of cresyl violet has a characteristic absorption at 520 nm which is blue-shifted compared to the absorption maximum of the monomeric dye (580 nm). These dye-modified semiconductor films are electrochemically active and undergo reversible reduction at -0.3 V vs. Ag/AgCl. Spectroelectrochemical experiments have been performed to probe the reduction of the dye aggregates adsorbed on SnO_2 thin films. The photocurrent response of the cresyl violet modified SnO_2 film confirms the participation of dye aggregates in the charge injection process. The maximum photon-to-photocurrent efficiency for this system is ~1%. An increase in the photocurrent generation efficiency was observed when an anodic bias was applied to the electrode. Both the charge injection mechanism and charge transport across semiconductor nanocrystallites are currently being investigated by laser flash photolysis and photoelectrochemical measurements.

39. Photochemistry of Squaraine Dyes

(G. Sauvé, P. V. Kamat, S. Das¹ and M. V. George¹)

The triplet excited properties of crown ether derivatives of squaraine dyes are currently being studied by laser flash photolysis. Triplet excited states of bis[4-(monoaza-crown-ether)phenyl]squaraine, SQ, were generated by a T-T sensitization technique using C_{60} as sensitizer. The rate constant for energy transfer was $2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in CHCl_3 . The dye triplet has an absorption maximum at 560 nm with a lifetime of 30 μs . The rate constant for the ground-state quenching of $^3\text{SQ}^*$ was determined to be $\sim 4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Further

experiments are under way to investigate the electron transfer reactions of the triplet excited state and utilize these dyes as sensitizers for large-bandgap semiconductor materials.

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