RADIATION LABORATORY
UNIVERSITY OF NOTRE DAME

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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. EY-76-C-02-0038. 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 DOE's Division of Environmental Research and Development and the Office of Standard Reference Data of the National Bureau of Standards.

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Dr. Maria V. Encinas, Assistant Professor in the Department of Chemistry at the Technological University of Chile, joined the staff as a Research Associate on January 9 and will spend a period through the late summer with us. She is collaborating with Dr. Scaiano on problems involving the reactions of organic biradicals produced photochemically.

Dr. Robert McNeil of the University of Tennessee joined the Laboratory on February 15. He holds an appointment in the Chemistry Department as an American Petroleum Institute Fellow. He is working with Dr. Thomas on studies of intermediates in micellar systems.

Mr. V. Bhagat, on leave from Tata Institute in Bombay, joined the staff on February 17. He is assisting Drs. Fessenden and Venkataraman in the development of a pulsed ESR spectrometer for carrying out relaxation measurements and for examining the time dependence of ESR signals.

Miss Debbie Jefferson (1-19-78) and Mrs. Dolores Nelson (3-27-78) joined the staff of the Radiation Chemistry Data Center as secretarial assistants.

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Professor A. Henglein of the Technical University of Berlin and the Hahn-Meitner Institute in Berlin has accepted an invitation to spend a sabbatical year with us and will join the Laboratory's staff on August 1. While with us Professor Henglein will also serve as a Visiting Professor in the Department of Chemistry.

Professor F. Wilkinson of the University of East Anglia, England, will spend August and September with the Radiation Chemistry Data Center to assist in the development of programs for compiling photochemical data.

Professor H. Levanon of The Hebrew University, Israel, will return to spend August and September with us in a continuation of the researches begun here during his sabbatical stay last year.

Professor G. Tripathi, currently at Miami University, has accepted an appointment as Assistant Professional Specialist and will join the staff on August 1. He is on leave from Gorakhpur University and expects to extend his spectroscopic interests.

Dr. P. K. Das of the University of Houston has accepted an appointment as Research Associate and will join our staff on September 1. His interests include spectroscopic studies of energy transmission in polyenes.

Dr. T. Nakayama of the University of Nagoya has accepted an appointment to our staff as Research Associate and will join the chemical physics program on September 1.

Mr. James Brummer, who is currently completing the requirements for the M.S. degree at the University of Montana, has accepted an appointment as Staff Professional Specialist and will join the staff of the Radiation Chemistry Data Center on July 1.

This year the Laboratory's summer student research program will be intensified with appointments being made available to 8-10 qualified undergraduate and graduate students from a number of universities in this country and abroad. To date appointments as Summer Research Assistants have been made to A. Scherz and U. Eliav (Hebrew University, Israel) R. Aker (Purdue), T. Paino (St. Louis) and D. Maurice (ESPCI, Paris). It is expected that 3-5 additional appointments will be made for this coming summer.

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Dr. H. Paul returned on February 21 to his appointment as chief assistant at the University of Zurich.

Mrs. M. MacMillan (1-31-78), Mrs. M. Latimer (3-3-78) and Mr. C. Boston (3-21-78) left the staff to assume other duties.

Mr. M. Chandra, a graduate student in Electrical Engineering, resigned from the Laboratory January 15 in order to carry out his thesis studies directly in the Department of Electrical Engineering.

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LABORATORY EQUIPMENT

The Laboratory has recently acquired a Cary 219 Recording Spectrometer and a Perkin-Elmer DSC-2 Differential Scanning Calorimeter and a

Tachisto Excimer Laser. The first instrument has a sensitivity of ~ 0.0003 (noise level at RC ~ 10 sec) and covers the wave length range of 200-900 nm. It will be interfaced with the Laboratory's PDP 11/55 computer and used to establish disc files of spectra taken in the Laboratory. The calorimeter is equipped with accessories to enable thermal data to be taken down to liquid nitrogen temperature and is expected to be useful in programs designed to examine the storage of energy in irradiated systems. The Tachisto laser, presently equipped to operate with krypton-fluorine mixtures to give an intense pulse (~ 0.1 joules) at 248 nm will be extremely useful in the development of our photochemical programs.

Publications:

K. Kalyanasundaram and J.K. Thomas

Radiation-induced processes in nonionic micelles

Micellization, Solubilization and Microemulsions, Vol. 2, Ed. K.L.

Mittal, Plenum Publishing, p. 569 (1977) [NDRL-1048]

M.A. Motara and K.S. Rai

Chromosomal differentiation in two species of aedes and their hybrids revealed by giemsa c-banding

Chromosoma (Berl.) 64, 125 (1977) [NDRL-1722]*

J.C. Scaiano

Photochemistry of phenyl alkyl ketones in the presence of organophosphorus (V) compounds

J. Organic Chem. 43, 568 (1978) [NDRL-1742]

G. Ferraudi and L. Patterson

Spectroscopic evidence for non-planarity in nickel (III) complexes of macrocyclic ligands. Pulse radiolysis and electron spin resonance studies in aqueous solution

J. Chem. Soc., Chem. Comm. 755 (1977) [NDRL-1755]

D. Razem, W.H. Hamill and K. Funabashi

Localization of the dry electron by OH and OD groups in alcoholic and in aqueous systems

Chem. Phys. Letters 53, 84 (1978) [NDRL-1759]

H.-K. Hong and C.W. Jacobsen

Resonant Raman studies of pyrazine with tunable UV lasers: An analysis based on the generalized vibronic theory of Raman intensity

J. Chem. Phys. 68, 1170 (1978) [NDRL-1768]

P. Neta and H. Levanon

Spectrophotometric study of the radicals produced by the reduction of syn- and anti-azobenzene

J. Phys. Chem. 81, 2288 (1977) [NDRL-1773]

M. Isildar and R.H. Schuler

On the precursor of fragment radicals in the radiolysis of normal alkanes

Radiat. Phys. Chem. 11, 11 (1978) [NDRL-1779]

W.H. Hamill and K. Funabashi

Kinetics of electron trapping reactions in amorphous solids; a non-Gaussian diffusion model

Physical Review B, 16, 5523 (1977) [NDRL-1782]

H. Levanon, P. Neta and A.M. Trozzolo

Correlation of singlet energies of aromatic hydrocarbons with the rates of protonation of their anion radicals

Chem. Phys. Letters 54, 181 (1978) [NDRL-1789]

H.-K. Hong

Theory of resonant Raman scattering. III. Toward the total synthesis of molecular spectra and Raman excitation profiles within the generalized vibronic theory and from an exciton-in-molecule viewpoint

J. Chem. Phys. 68, 1253 (1978) [NDRL-1791]

D. Razem, W.H. Hamill and K. Funabashi

Inverse isotope effect for electron transfer reactions in ethanol

J. Chem. Phys. 67, 5404 (1977) [NDRL-1792]

V. Madhavan, R.H. Schuler and R.W. Fessenden

Absolute rate constants for reactions of phenyl radicals

J. Am. Chem. Soc. 100, 888 (1978) [NDRL-1798]

R.D. Small, Jr. and J.C. Scaiano

Absolute rates of hydrogen abstraction by tert-butoxy radicals

J. Am. Chem. Soc. 100, 296 (1978) [NDRL-1801]

M. Tachiya and H. Sano

Energy loss of electrons in random motion. Analytical result

J. Chem. Phys. 67, 5111 (1977) [NDRL-1814]

* Supported by the Division of Biomedical and Environmental Research.

I. (NDRL-1848) RESONANCE ENERGY TRANSFER IN DIPHENYLMETHYLENE AND FLUORESCEIN AT 77°K¹ (K.C. Wu and A.M. Trozzolo)

ABSTRACT: A resonance energy transfer process has been found between the excited triplet state of diphenylmethylen and fluorescein in a rigid alkaline glass at 77°K. By measuring the effect of fluorescein on the life-time of excited diphenylmethylen, the critical transfer distance R_0 and the rate of energy transfer were found to be 61 Å and $3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively. This compares favorably with the theoretical value of 50 Å calculated by the Forster-weak-interaction dipole treatment.

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

II. (NDRL-1849) ACTIVATED AND ACTIVATIONLESS LOCALIZATION AND IMPURITY TRAPPING OF THE DRY ELECTRON IN METHANOL AND PROPANOL: RATE CONSTANTS FOR SOLVATED ELECTRONS¹ (D. Razem and W.H. Hamill)

ABSTRACT: Dry-electron trapping by impurity competes with localization by the medium. Observations in the range 80-300 K for methanol and 1-propanol provide evidence that each of these processes has activated and activationless components, most clearly shown for methanol. The activationless processes dominate below ~150 K. They are considered to resemble electron resonances in the gas phase, the energy being supplied by the electron, as for benzene. The disordered medium converts potential energy of electronic polarization to kinetic energy by scattering. The rate constants for scavenging solvated electrons do not correlate with dry-electron scavenging efficiencies over the range $\sim 5 \times 10^6 - 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and only correlate poorly with the enthalpy of activation. For each scavenger the rate constants change systematically from solvent to solvent.

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

III. (NDRL-1850) PROMOTION OF PHOTOCHEMICAL REACTIONS BY MICELLAR SYSTEMS¹ (J.K. Thomas)

ABSTRACT: Aqueous solutions of micelles provide an ideal medium for promoting photo-induced electron transfer reactions and photo-ionization. Both processes are possible avenues for conversion of light energy into either chemical or electrical energy. The talk will concern itself with two prime factors in the above process that are emphasized in micellar solution. The first effect is the lowering of the photo-ionization potential of a solution in micellar solution compared to that in the gas phase or in liquid alkanes. This effect tends to bring the photo-ionization threshold of molecules into the visible region, and will be explained in terms of the V_o of the medium and the polarization energy of the solute cation. The tunneling mechanism for electron transfer will also be discussed. The second effect is efficient separation of the charges, produced in the primary photochemical event, by the micellar surface, thus enabling utilization of the ionic species in subsequent reactions.

(1) Submitted for presentation at 52nd Colloid and Surface Science Symposium, Knoxville, Tennessee, June 12-14, 1978.

IV. (NDRL-1852) THE OPTICAL WINDOW AND WHAT WE CAN DO WITH BOROSILICATE, QUARTZ AND SAPPHIRE¹ (D. Blessing)

ABSTRACT: This paper deals with four window sealing techniques. It will be broken down under four headings each explaining the preparation, preheating, sealing and annealing operations necessary. The first will be the lathe sealing method used with both borosilicate and quartz when a vacuum type graphite fixture is available. The second is a technique suitable when constructing optical cells or optical dewars where window distortion is of great concern. The third is a seal used for very thin windows in a quartz optical cell. The fourth is a simple bench sealing procedure for joining Sapphire windows to glass including the graded seal needed for joining to borosilicate glass.

(1) Presented at American Scientific Glassblowers Society Symposium held at Boston, Massachusetts, June 19-23, 1977. To be published in the Proceedings.

V. (NDRL-1853) EFFECT OF MOLECULAR GEOMETRY ON THE ELECTRON AFFINITY
of $\text{H}_2\text{O}^{\cdot -}$ ¹ (D.M. Chipman)

ABSTRACT: Using self-consistent-field molecular orbital methods with inclusion of diffuse atomic orbitals in the basis set, the potential energy surfaces of H_2O and $\text{H}_2\text{O}^{\cdot -}$ gas phase monomers have been studied as the HOH bond angle varies from 30° to 180° and as one OH bond length is stretched from its equilibrium value by up to $0.3 \text{ \AA}$. The potential surface of $\text{H}_2\text{O}^{\cdot -}$ was found to be very close to that of H_2O at all points studied. In particular, the $\text{H}_2\text{O}^{\cdot -}$ surface showed no local minima other than the absolute minimum which occurs at the same geometry as the minimum of the H_2O surface. $\text{H}_2\text{O}^{\cdot -}$ is calculated to be slightly stable with respect to vertical electron detachment at geometries with an HOH bond angle of less than about 95° or at any angle if one OH bond length is stretched sufficiently. However, the calculated binding energy of the excess electron is so small in the Franck-Condon region (a maximum of about 10^{-4} eV) that calculations not invoking the Born-Oppenheimer approximation would be required to determine whether $\text{H}_2\text{O}^{\cdot -}$ is truly a stable species.

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

VI. (NDRL-1854) QUALITATIVE ASPECTS OF ELECTRON LOCALIZATION IN
POLAR MEDIA¹ (K. Funabashi and W.H. Hamill)

ABSTRACT: Localization of dry electrons (quasi-free electrons) has been examined in the light of multi-phonon non-radiative transition theory. Special emphasis is placed on the role of vibronic coupling between the electron and intra-molecular vibrations and also on the effect of the disordered structure for the clarification of the temperature dependence of the initial yield and of the meaning of the "pre-existing trap." As a working theoretical model of the solvated electron, we propose that the center of the localized charge distribution is the deformed negative ion rather than a cavity or void.

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

VII. (NDRL-1855) RATE CONSTANTS AND MECHANISM OF REACTION OF VARIOUS OXIDIZING RADICALS¹ (P. Neta, P. Maruthamuthu and K. Hasegawa)

ABSTRACT: Oxidizing radicals such as $\dot{\text{S}}\text{O}_4^-$, $\dot{\text{P}}\text{O}_4^{2-}$ and its protonated forms, and Cl_2^- were produced in irradiated aqueous solutions and their reactivities were studied by kinetic spectrophotometry. Rate constants for reaction with a variety of organic and inorganic compounds were determined. The mechanism of reaction was further studied by ESR observation of the intermediate radicals and by product analysis. In general, these radicals react by hydrogen abstraction, addition, or electron transfer oxidation. Most saturated aliphatic and certain inorganic compounds (such as H_2O_2 , NH_2OH , H_2PO_3^-) undergo hydrogen abstraction. In these reactions the reactivities decrease in the order OH , $\dot{\text{S}}\text{O}_4^-$, $\text{H}_2\dot{\text{P}}\text{O}_4^-$, $\text{H}\dot{\text{P}}\text{O}_4^-$, $\dot{\text{P}}\text{O}_4^{2-}$, Cl_2^- , Br_2^- . However, in oxidation reactions the sulfate and phosphate radicals exhibit greater oxidizing capabilities than OH . They can oxidize aliphatic carboxylic acids to alkyl radicals and CO_2 . They also react with aromatic compounds by one-electron oxidation rather than addition and produce the cation radicals. These intermediates are sufficiently stable in certain cases to allow direct observation, but in most cases they undergo rapid deprotonation, decarboxylation, or hydroxylation. The Cl_2^- is a weaker oxidant than the sulfate and phosphate radicals. It can oxidize aromatic compounds which contain OH , NH_2 , OR as substituents but not the hydrocarbons or acids.

(1) Submitted for presentation at the 26th Annual Meeting of the Radiation Research Society, Toronto, Canada, May 1978.

VIII. (NDRL-1856) ASSIGNMENT OF STATES IN THE VALENCE PHOTOELECTRON SPECTRUM OF H_2S ¹ (D.M. Chipman)

ABSTRACT: In addition to the well known 10.5 eV $^2\text{B}_1$, 13.2 eV $^2\text{A}_1$, 15.3 eV $^2\text{B}_2$ and 22 eV $^2\text{A}_1$ valence peaks in the photoelectron spectrum of H_2S , a possible additional peak near 19 eV has been observed but not assigned in the X-ray spectrum. We present calculations based on a self-consistent field valence bond model together with the recently developed Extended Koopmans' Theorem which indicate that the 19 eV peak is due to a $^2\text{A}_1$ state of H_2S^+ . Both this state and the main 22 eV state arise from a strong mixing of two configurations in the H_2S^+ wavefunction.

(1) Submitted for publication in the Journal of Electron Spectroscopy.

IX. (NDRL-1857) SINGLE VIBRONIC LEVEL RESONANT RAMAN SCATTERING OF MOLECULAR IONS IN SOLID GLASS AT 77°K: PYROMELLITIC DIANHYDRIDE ANION AND NAPHTHALENE CATION¹ (S.-J. Sheng and G. Hug)

ABSTRACT: The resonant Raman spectra were obtained for the radical anion of pyromellitic dianhydride in MTHF glass and the radical cation of naphthalene in Freon glass at 77°K by using a pulsed tunable dye laser. The laser frequency is tuned to the individual vibrational levels of the absorption band. The resonant Raman thus obtained resembles hot fluorescence in appearance. Overtones and combinations of one specific vibrational mode prevails in the entire spectrum. All of the major Raman active modes are identified as the totally symmetric modes in the symmetry group of D_{2h} . The relative Raman intensity of various modes is calculated by using the dispersion relation of the polarizability theory and the Franck-Condon principle. The overlap integrals are evaluated in the framework of displaced harmonic oscillators. Agreement between experiment and theory is good.

(1) Submitted for presentation at the 33rd Annual Molecular Spectroscopy Symposium to be held June 12-16, 1978 at Columbus, Ohio.

- X. (NDRL-1858) PHOTOCHEMICAL REDOX REACTIVITY OF DIMERIC AND MONOMERIC COPPER (II) AND COBALT (II) PHTHALOCYANINES¹ (G. Ferraudi and E.V. Srisankar)

ABSTRACT: The dimeric copper (II) and cobalt (II) sulfophthalocyanines are dissociated in oxidized and reduced metastable species by ultraviolet photolyses. The intermediates, studied by flash photolysis, were characterized as copper (II)-ligand radical species and sulfophthalocyanines containing Co(I) and Co(III) metal centers. Stable products were not formed in the absence of appropriate scavengers.

Photochemical redox tendencies were observed also in photolyses of monomeric species in the presence of alcohols.

Quantum yields demonstrate that this reactivity arises from the population of an upper excited state. The possible nature of such a state is discussed.

(1) Submitted for publication in Inorganic Chemistry.

- XI. (NDRL-1859) OXIDATION OF HYDROQUINONE ANION BY β -OXOALKYL RADICALS¹ (S. Steenken)

ABSTRACT: β -Oxoalkyl radicals, $R_1\dot{C}(O)CR_2R_3$, react with hydroquinone anion by electron transfer to yield p-benzosemiquinone radical anion with rate constants between $\sim 5 \times 10^8$ and $2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, depending on the nature of R_1 , R_2 , and R_3 . The rate constants decrease in the series $(R_1=R_2=R_3=H) > (R_1,R_2,R_3=H, \text{hydroxyalkyl}) > (R_1,R_2,R_3=H, \text{alkyl})$. This effect is explained in terms of a reduction of the oxidizing power of the β -oxoalkyl radicals due to hyperconjugation of alkyl substituents.

The β -oxoalkyl radicals were produced by elimination of OH^- from ionized α,β -dihydroxyalkyl radicals and by elimination of alkoxide from ionized linear and cyclic α -hydroxy- β -alkoxyalkyl radicals. With cyclic radicals of this type elimination of alkoxide results in ring opening.

The rate constants for elimination of OH^- from ionized α, β -dihydroxy-alkyl radicals $\text{R}_1\dot{\text{C}}(\text{O}^-)\text{C}(\text{OH})\text{R}_2\text{R}_3$ were determined to be between $3 \times 10^6 \text{ s}^{-1}$ (for $\text{R}_1 = \text{R}_2 = \text{H}$ and $\text{R}_1, \text{R}_2, \text{R}_3 = \text{H}$, hydroxyalkyl) and $8 \times 10^6 \text{ s}^{-1}$ (for $\text{R}_1 = \text{R}_2 = \text{CH}_3$, $\text{R}_3 = \text{H}$), using a competition method involving N-methylisonicotinic acid. The rate constants for elimination of alkoxide from ionized α -hydroxy- β -alkoxy alkyl radicals are $> 10^6 \text{ s}^{-1}$.

The selective reaction of β -oxoalkyl radicals with hydroquinone anion provides a method for the determination of the yields of OH attack on the glycol or glycolmonoalkylether parts of complex molecules.

(1) Submitted for presentation at the 26th Annual Meeting of the Radiation Research Society to be held at Toronto, Canada, May 14-18, 1978.

XII. (NDRL-1860) RADIATION CHEMISTRY TODAY¹ (J.K. Thomas)

ABSTRACT: The "trinity" of radiation chemistry must surely be that the interaction of ionizing radiation with matter produces ions, excited states, and free radicals. The advances and specialization in this science over the past two decades have tended to obscure this simple statement and various groups emphasize strongly their interests which are often locked to available techniques. It is the purpose of this symposium to present a balanced if abridged view of radiation chemistry today in terms of the "trinity." The symposium will be of interest to radiation chemists who may challenge the concepts presented by the speakers, and also to the biologists who can gain immediate knowledge of just what radiation chemists have achieved over 30 years, and also how this information may aid them in a physico-chemical description of their own work.

(1) Submitted for presentation at the 26th Annual Meeting of the Radiation Research Society to be held at Toronto, Canada, May 14-18, 1978.

XIII. (NDRL-1861) PARTIALLY DIFFUSION-CONTROLLED REACTIONS¹

(A. Mozumder)

ABSTRACT: A theory is formulated which, within the framework of the diffusion model, takes into account a reaction probability $p(<1)$ at the encounter separation. For a pair of reactants in the liquid phase the time-dependent reaction rate is given mainly in terms of the first encounter probability. Other useful information, such as the ultimate escape probability, reaction with a uniformly distributed scavenger etc., can be obtained from the fundamental result, the last by using a Laplace transformation. Physical interpretation of p and application to photo- and radiation-chemistry are attempted.

(1) Submitted for presentation at the 26th Annual Meeting of the Radiation Research Society to be held at Toronto, Canada, May 14-18, 1978.

XIV. (NDRL-1862) BIRADICAL DOUBLE TRAPPING BY NITRIC OXIDE. AN ESR STUDY¹ (P. Maruthamuthu and J.C. Scaiano)

ABSTRACT: The biradicals produced in the Type I photocleavage of cycloalkanones in solution can be trapped by nitric oxide. The reaction results in the formation of relatively long lived cyclic nitroxide radicals which contain structural information on the nature of the two biradical ends. The reaction is likely to proceed in a stepwise manner. In the case of 2-methylcyclohexanone the radical produced is I, for which $g = 2.0066$, $a_N = 7.07$ G and $a_H = 1.91$ G.

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

- XV. (NDRL-1863) SINGLE VIBRONIC LEVEL RESONANT RAMAN SCATTERING OF MOLECULAR IONS IN SOLID GLASS: PMDA ANION AND NAPHTHALENE CATION¹
(S.J. Sheng and G. Hug)

ABSTRACT: Resonant Raman spectra were obtained for the radical anion of pyromellitic dianhydride (PMDA) in MTHF glass and the radical cation of naphthalene in alkyl halide glass at 77°K by using a pulsed tunable dye laser. The single vibronic level resonant Raman resembles hot fluorescence in appearance. Overtones and combinations of the excited vibrational mode prevail in the spectra.

(1) Submitted for publication in Chemical Physics Letters.

- XVI. (NDRL-1864) A BIBLIOGRAPHIC DATA BASE ON FAST REACTION KINETICS IN IRRADIATED SYSTEMS¹ (W.P. Helman and A.B. Ross)

ABSTRACT: A bibliographic data base has been developed by the Radiation Chemistry Data Center in support of its data compilation activities. Data flagging has been carried out through use of a controlled vocabulary. Retrospective searches are available covering about 40,000 references since 1966 and a biweekly current-awareness series is provided. The data base covers the kinetics of fast reactions initiated by light or ionizing radiation, thermodynamic and spectroscopic properties of reaction intermediates, radiation yields and quantum yields.

(1) Submitted for presentation at the 41st Annual Conference of the American Society for Information Science, November 13-17, 1978, New York, New York.

XVII. (NDRL-1865) RADICAL PROCESSES IN LIPIDS. RADIATION STUDIES
IN MODEL LIPID SYSTEMS¹ (L.K. Patterson)

ABSTRACT: Biological membranes are found to incorporate various cis-unsaturated fatty acid moieties into their lipid structures for control of microviscosity. However, the allylic hydrogen atoms associated with such moieties may be readily abstracted, introducing free radical sites and subsequent processes of peroxidative degradation into the lipid structure. Several sources of data imply that molecular organization plays a significant role in determining the vulnerability of these unsaturate sites to radical induced damage. Because the extent and character of their unsaturate content may be varied, fatty acid soap micellles provide good elementary model systems in which to study lipid degradation -- as well as associated free radical behavior -- as functions of unsaturate composition and microviscosity.

In pulse radiolysis studies an intense absorption band at 280 nm, associated with radicals formed at doubly allylic sites on the fatty acid hydrocarbon chain, has been used to monitor: (1) peroxy radical formation, (2) intermolecular radical transformation, (3) interaction among soap radicals. Non-specific OH attack on the hydrocarbon chain for various soap anions and subsequent intramolecular radical transfer to doubly allylic sites have also been investigated using this probe.

Using steady state radiolysis methods, the extend of radiation induced hydroperoxide formation in various soaps has been closely correlated with the extend of soap aggregation and the degree of micellar close-packing. Further, the antioxidant and prooxidant behavior of α -tocopherol (vitamin E) at very low concentrations has been characterized in soap micelles.

(1) Submitted for presentation at Processes on Organized Molecular Systems conference to be held at Deutsche Bunsengesellschaft fur Physikalische chemie, Munich, West Germany, April 10-12, 1978.

XVIII. (NDRL-1866) IMPORTANCE OF INTERMOLECULAR BIRADICAL REACTIONS IN POLYMER PHOTOCHEMISTRY. POLY (PHENYL VINYL KETONE)¹

(R.D. Small, Jr. and J.C. Scaiano)

ABSTRACT: The biradicals generated in the photochemistry of poly (phenyl vinyl ketone) are shown to undergo a number of intermolecular reactions. The substrates include oxygen, nitric oxide, di-tert-butylnitroxide radicals, sulfur dioxide, di-tert-butylselenoketone and methylnmethacrylate. It is suggested that biradical trapping in polymers could be a very common process; the detection, rather than the occurrence being the unusual phenomenon.

(1) Submitted for publication in Macromolecules.

XIX. (NDRL-1867) ELECTRON TRANSFER IN PHOTOGENERATED BIRADICALS¹
(J.C. Scaiano)

ABSTRACT: The Norrish Type II reaction involves the intermediacy of 1,4-biradicals, reaction 1.

The ketyl site in B is an excellent electron donor and will reduce acceptors like 2,5-dinitrobenzoic acid and paraquat (1,1'-dimethyl-4,4'-bipyridilium) dications (PQ^{++}), reaction 2.

These reactions are actually quite fast and in the example given above $k_2 = 3.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in methanol. A number of reactions of this type have been examined using nanosecond laser techniques, an approach which allows the measurement of both, k_2 and the biradical lifetime, τ_B .

If the γ -position in the molecule has no hydrogen atoms, but is a good electron donor, the triplet state decays via the formation of a biradical zwitterion, reaction 3.

This process is strongly pH dependent and the resulting biradicals can also be trapped using electron acceptors. The possibility of abstracting electrons from other donors using the amino radical-ion site has been considered, but the process seems to be rather inefficient.

Similar reactions can also take place in related systems, e.g. in the photoenolization of ortho-alkylsubstituted acetophenones. A number of reactions of this type, as well as their solvent and temperature dependence will be discussed.

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- (1) Submitted for presentation at the Department of Energy Solar Photochemistry Research Conference, Brookhaven National Laboratory, May 8-10, 1978.
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XX. (NDRL-1868) THE PHOTOCHEMISTRY OF THE SULFOPHTHALOCYANINES OF TRANSITION METAL IONS IN AQUEOUS SOLUTIONS¹ (G. Ferraudi)

ABSTRACT: The photochemistry of sulfophthalocyanine (PTS) complexes of transition metal ions has been investigated in homogeneous aqueous solutions by means of flash and continuous irradiations. The photochemical redox dissociation is a characteristic reaction mode of the dimeric complexes. Generation of oxidized and reduced Cu(II)-ligand radical intermediates,

and Co(I)-Co(III) species,

were observed by flash photolysis of Co(II) and Cu(II) sulfophthalocyanines. These processes seem to originate in an upper oxidation state which is a more powerful oxidant than the ground state. Indeed, redox reactions were also observed with monomeric species when they were excited in the presence of hydrogen donors.

The photochemical behavior of Cu(II) and Co(II) sulfophthalocyanines will be compared with that of the low spin d^6 , Co(III) and Fe(II) complexes of the same ligand. The photoredox reactivity in these systems present some of the features indicated above for Co(II) and Cu(II) and an intramolecular redox mode, in which an electron is transferred from the phthalocyanine ligand to the metal center, e.g.

Such a reaction can be perturbed using various axial ligands. The competition between reaction modes permitted some control of the photochemistry of these systems. Mixed dimers have been obtained between the phthalocyanine complexes and either $\text{Cr}(\text{bipy})_3^{3+}$ or $\text{Ru}(\text{bipy})_3^{2+}$. These species give characteristic photoinduced redox reactions by excitation of the incorporated sensitizer, $\text{Cr}(\text{bipy})_3^{3+}$ or $\text{Ru}(\text{bipy})_3^{2+}$.

Reaction mechanisms will be discussed. Further, photochemical reaction pathways with a potential application in the storage of solar energy will be analyzed according to the properties presented by these compounds.

(1) Submitted for presentation at the Department of Energy Solar Photochemistry Conference, Brookhaven National Laboratory, May 8-10, 1978.

XXI. (NDRL-1869) INFLUENCE OF MICELLES ON PHOTOCHEMICAL REACTIONS¹
(J.K. Thomas)

ABSTRACT: It has become increasingly apparent over the last seven years that micellar systems often have profound effects on radiation induced reactions. For the most part the micellar systems are composed of suitable surfactant molecules e.g. anionic sodium lauryl sulfate NaLS, cationic cetyl trimethyl ammonium bromide CTAB, or neutral ethylene oxide micelles, igepal, triton etc. The aggregates of micelles formed by these surfactants in water encapsulate or solubilize hydrophobic molecules, and present a barrier of negative charge NaLS, positive charge CTAB or lipid phase igepal to the aqueous phase. Photochemical reactions induced in these systems reflect on the nature of the micelle phase. For example, if two reactants are solubilized in the micellar phase their local concentrations may be some 10^4 that in the bulk or water phase. Any radiation induced reaction is catalyzed some 10^4 fold under these conditions. If one reactant is in the micelle phase and the other in water phase the reaction is retarded due to the barrier exposed by the micelle between the two reactants.

In particular two unique photochemical micellar effects are to be discussed. The first involves photo-ionization and the second photo-induced electron transfer across the lipid/water boundary. It was observed quite early that micelles markedly improve the photo-ionization yield of many molecules. For example, pyrene or phenothiazine are readily photo-ionized by 3471 Å light from a frequency doubled ruby laser. The cation ion of the solute remains with the micelle while the electron is ejected into the aqueous phase and appears as a hydrated electron e_{aq}^- . In NaLS micelles, the back reaction of the ion is prevented by the micelle surface charge. It is also observed that while the photo-ionization threshold for these processes in the gas phase is in excess of 6.0 or even 7.0 eV, nevertheless in NaLS micelles the energy required to produce e_{aq}^- is <3.0 eV. The extra energy required for photo-ionization is provided by the micelle surface and by the rapid or early (V_o) solvation energy of the electron. We have synthesized amino-perylene which in NaLS micelles photo-ionizes at $\lambda > 5300$ Å i.e. well into the visible spectrum.

Rather than eject the electron into the water phase, it may be transferred to an acceptor. Well known exciplex systems are ideal candidates for such experiments in micelles. For example an arene, e.g. pyrene for $\lambda \leq 3800 \text{ \AA}$ or tetracene $\lambda \leq 4800 \text{ \AA}$ is solubilized in a micelle interior and dimethyl aniline DMA, is solubilized in the micelle surface. Excitation leads to e^- transfer, $\text{DMA} + \text{Arene} \xrightarrow{h\nu} \text{Arene}^- + \text{DMA}^+$. With a CTAB micelle the positive micelle charge ejects the DMA^+ and back reaction which has a $\tau_{1/2} < 1 \mu\text{sec}$ in homogeneous solutions becomes 1 μsec or longer in micelles. This latter system provides an ideal method to efficiently photo-generate ions which "could" be used for storage of visible light energy.

(1) Submitted for presentation at Department of Energy Solar Photochemistry Research Conference, Brookhaven National Laboratory, May 8-10, 1978.

XXII. (NDRL-1870) A TIME-RESOLVED ESR STUDY OF THE OXIDATION OF ASCORBIC ACID BY HYDROXYL RADICAL¹ (R.W. Fessenden and N.C. Verma²)

ABSTRACT: Time-resolved ESR spectroscopy for the study of radicals produced by pulse radiolysis is illustrated by a study of the oxidation of ascorbic acid by OH radical in aqueous solution. In basic solution, the direct oxidation product, the ascorbate mono-anion radical, is formed within less than 2 μsec of the radiolysis pulse. In acid solutions (pH 3-4.5, N_2O saturated) three radicals are initially formed, the ascorbate mono-anion radical, an OH adduct seen also in steady-state ESR experiments, and an OH adduct at C2 with the main spin density at C3 of the ring. The first OH adduct decays with an initial half life of about 100 μsec , probably by bimolecular reaction. The second OH adduct, which shows one hyperfine splitting with $a^H = 24.4 \pm 0.36$ and $g = 2.0031 \pm 0.0002$, decays with a half life of about 10 μsec . On this same

time scale the concentration of the ascorbate radical approximately doubles. It is concluded that the adduct at C2, but not the other adduct, loses water rapidly to form the ascorbate radical.

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- (1) Submitted for presentation at the Biophysical Discussion of Fast Reactions to be held at Airlie, Virginia, April 3-5, 1978.
 (2) Bhabha Atomic Research Centre, Bombay, India.
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XXIII. (NDRL-1871) THE TIME DEPENDENCE OF ESR SIGNALS OF RADIOLYTICALLY PRODUCED RADICALS¹ (R.W. Fessenden)

ABSTRACT: The types of behavior observed for the ESR signals of radicals produced by pulse radiolysis are discussed. Methods for analysis of these time dependent curves by means of modified Bloch equations are described. Several examples of polarization produced by the radical pair mechanism are given. The use of ESR signal growth to determine T_1 is illustrated. Examples are described showing the effect of magnetization of reactant upon the ESR signal of a product radical. In several instances the same radical has been produced with initial spin populations corresponding to both zero and Boltzman population differences. The transfer of polarization built up by the radical pair mechanism is also demonstrated. The observed effects are discussed in relation to radical formation in radiation chemical "spurs." Several calculated curves showing possible ESR response for photochemically generated radicals are also given.

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- (1) Submitted for presentation at the workshop on Chemically Induced Magnetic Polarization, Queen's University, Kingston, Ontario, Canada, June 7-10, 1978.
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- XXIV. (NDRL-1873) RADIATIONLESS DEACTIVATION OF BENZOPHENONE TRIPLETS IN AROMATIC SOLVENTS. CHARACTERIZATION OF TRANSIENTS INTERMEDIATES IN THE PRESENCE OF DIPHENYL ETHER¹. (R.D. Small, Jr. and J.C. Scaiano)

ABSTRACT: Triplet benzophenone has a lifetime of 160^{+20} ns in neat diphenyl ether at room temperature. The fast decay is the result of the formation of an adduct, which we have detected directly using laser flash photolysis techniques. The adduct shows a band with $\lambda_{\text{max}} \approx 440$ nm and decays with first order kinetics and $k = 7.5 \times 10^4 \text{ s}^{-1}$.

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

- XXV. (NDRL-1874) EXCITED STATE REDOX CHEMISTRY OF POLYPYRIDYL CHROMIUM (III) COMPLEXES. A DETERMINATION OF THE CHROMIUM (III) - (II) SELF-EXCHANGE RATE¹ (G.J. Ferraudi and J.F. Endicott²)

ABSTRACT: The photochemistry of transition metal polypyridyl (PP) complexes has been rich and varied, owing largely to the relatively long excited state lifetimes and to the redox lability of these systems. Such complexes have been the focus of recent interest because the lowest thermally equilibrated excited states are often 1-2 eV more powerful as oxidizing and/or reducing agents than the respective ground states. Thus the lowest energy excited states of $M(PP)_3^{n+}$ complexes have been used to oxidize or reduce a variety of organic and inorganic substrates, generally with a view of studying highly exergonic reactions or with attempting to make use of the chemical energy contained in displaced redox equilibria.

In the course of our studies of $\text{Cr}(\text{PP})_3^{3+}$ complexes we have found that some of the redox behavior implicates solvent species. Thermal and photochemical oxidations of solvent species by polypyridyl and related complexes are often mechanistically complex, but reasonably commonplace. On this note we report our investigations of this behavior and explore some of its implications.

(1) Submitted for publication in Inorganic Chemistry.

(2) Wayne State University, Detroit, Michigan.

XXVI. (NDRL-1875) THE FLUORESCENCE OF 4-METHYLUMBELLIFERONE IN AQUEOUS AND NON-AQUEOUS SOLUTIONS¹ (K.C. Wu and A.M. Trozzolo)

ABSTRACT: The relative fluorescence yield of 4-methylumbelliferone (4MU) in different solvents has been measured. The emission yield of 4MU is very small in a non-hydroxylic solvent and it is concluded that 4MU forms a molecular aggregate in the non-hydroxylic solvents. The emission at 485 nm i.e., the (X^*) emission, from 4MU solutions also has been investigated, and it is shown that (X^*) can exist in non-aqueous solutions. Its stability is not too dependent on the polarity of solvent. The emission maximum of (X^*) is relatively independent on the nature of solvent. It is also shown that acid is much more efficient in increasing the yield of (X^*) in solution than water alone. The nature of (X^*) is discussed.

(1) Submitted for publication in the Journal of Luminescence.

XXVII. (NDRL-1876) PHOTON-INDUCED ELECTRON TRANSFER TRANSITIONS OF THE SOLVATED ELECTRONS¹ (K. Funabashi, I. Carmichael and W.H. Hamill)

ABSTRACT: The role of electron transfer transitions in the absorption spectrum of the solvated electron in liquid water is studied in terms of the generalized line shape function. When the density of trapping sites is greater than one third of the density of solvent molecules, the transition-dipole moment for photon-induced electron transfers was found to be greater than that of the single-site $1s \rightarrow 2p$ transition. The solvated electron is assumed to be coupled with low-frequency solvent modes and a high-frequency molecular mode. The latter mode is responsible for a small isotope shift in the peak energy. The spectrum consists of contributions from short-distance transfers ("bound-bound") and long-distance ("bound-free") transfers, the latter being the minor component of the total spectrum.

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

XXVIII. (NDRL-1878) DETECTION OF REACTIVE RHODIUM CONTAINING INTERMEDIATES FOLLOWING FLASH PHOTOLYSIS OF TRIS (β -DIKETONATE) RHODIUM (III) COMPLEX¹ (G. Ferraudi, Paul A. Grutsch² and C. Kutal²)

ABSTRACT: Flash photolysis trans-tris(trifluoroacetylacetonate)-Rhodium(II), trans-Rh(tfa)₃, investigated in various alcoholic media, shows two distinct intermediates. A short lived transient, $\lambda_{\max} \sim 360\text{nm}$ and $t_{1/2} \sim 200\text{ns}$, has been assigned as a Rh(II) β -diketonate complex. The decay of the long lived species, assigned as an hydride complex, is accelerated by hydrogen ions. The mechanisms for the photoredox transformation of trans-Rh(tfa)₃ is discussed.

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

(2) Department of Chemistry, University of Georgia, Athens, Georgia.

XXIX. (SR-43) NONLINEAR PROBLEMS IN THE THEORY OF PHASE TRANSITIONS¹

(J.J. Kozak)

ABSTRACT: In recent years there has been a renaissance of interest in examining the underlying nonlinear structure of statistical-mechanical theories of phase transitions. The motivation behind these studies has classical overtones: Given that modern formulations of the phase transition problem often lead to nonlinear equations, and given that such equations can exhibit multiple solutions in certain situations, what thermodynamic significance (if any) can be attributed to the possible bifurcating branches of solutions to these equations? And further, given that branching is possible, what is the relationship between the point of bifurcation and the position of the actual thermodynamic singularity? It is to these questions that the present review is addressed.

(1) Submitted for publication as a chapter in Advances in Chemical Physics.

XXX. (SR-44) RATE CONSTANTS FOR REACTION OF INORGANIC RADICALS IN AQUEOUS SOLUTION¹ (A.B. Ross and P. Neta)

ABSTRACT: Rate constants have been compiled for reactions of various transient inorganic radicals produced by radiolysis or photolysis in aqueous solution. Data are included for the carbonate radical, sulfate radical, phosphate radical, nitrate radical and other nitrogen-, sulfur- and selenium-containing radicals, and the halide and pseudo-halide radicals Cl_2^- , Br_2^- , I_2^- and $(\text{SCN})_2^-$. The radicals react with other inorganic ions, as well as aliphatic, aromatic and heterocyclic compounds.

(1) Submitted for publication to the National Standard Reference Data Service, National Bureau of Standards.

XXXI. VAPOR PHASE STRUCTURES OF INORGANIC SALTS (M.E. Schwartz and H.F. Baney)

Monomeric salts occur in the vapor phase at high temperatures, and are of some importance in magnitohydrodynamic and corrosion studies, among others. There has been considerable speculation in both the U.S. and U.S.S.R. that such salts have "polytopic" structures -- that is, the metal ion may be essentially free to move about the complex anion over a potential surface which has no deep wells and in which several sites are energetically nearly equivalent. We have studied extensively the structures of NaNO_3 and NaBO_2 via our valence-only model potential electronic structure theory. Both molecules show deep wells in their surfaces which should produce a definite molecular structure with negligible cation mobility. For example, NaNO_3 has the planar structure.

lying about 0.5 eV below the metastable planar structure

which is in turn about 0.5 eV below the non-planar structure

(These three were said previously to be "consistent" with both electron diffraction and photoelectron spectra.)

The electron binding energies as measured by the molecular orbital energies showed little correlation with experimental photoelectron spectra. This indicates substantial rearrangement associated with ionization, and mitigates against the usual Koopmans' Theorem approach to interpretation of the photoelectron spectra. This is readily understood, since the valence ionizations correspond to the unusual case in which ionization occurs in one part of a molecule, and leaves (at least initially) the positive hole in another part of the molecule:

Further studies on the ionic states are planned, to help unravel the photoelectron spectra.

XXXII. SOLVATED ELECTRONS (I. Carmichael and K. Funabashi)

A new class of transitions contributory to the optical absorption spectrum of solvated electrons has been identified. Following a preliminary study which, rather arbitrarily, divided these charge-transfer transitions into a short- and a long-range component, more rigorous calculations including properly weighted transfers to all possible sites have been performed. Choosing the wave function of the excess electron to be hydrogenic indicates that around five quanta of the single intramolecular mode (0.1 eV) invoked are necessary to reproduce the absorption peak in water. Representing the charge distribution by a Gaussian form requires as many as ten quanta. In both cases the computed width is also in substantial agreement with experiment but the high energy asymmetry is inadequately predicted. This difficulty may be resolved by adopting an alternative description of the variation of the rearrangement energy with distance from the initial site.

XXXIII. EXCHANGE PERTURBATION THEORY FOR MANY-ELECTRON INTERACTIONS(J.O. Hirschfelder^{*} and D.M. Chipman)

A new formalism is proposed for treatment of the effects of electron exchange on intermolecular forces. The procedure is based on a modification of the Van Vleck partitioning perturbation theory, which was originally developed to treat problems involving degeneracy or near degeneracy. Our method removes much of the arbitrariness found in previous approaches that arises from the ambiguous definition of "perturbation order." The expansion is expected to show rapid convergence and is simple to use even for many-electron interactions. It is expected that this method will be useful in extending the long-range theory of intermolecular forces in order to determine the wave functions and potential energy surfaces which occur in molecular interactions and van der Waals' molecular complexes.

^{*}University of Wisconsin, Madison.

XXXIV. ON THE CONCEPT OF ORBITAL FOLLOWING (D.M. Chipman, B. Kirtman^{*} and W.E. Palke^{*})

Bonding orbitals in H₂O and H₂S obtained from highly optimized localized molecular orbital and perfect-pairing valence bond wavefunctions have been examined as the bond angle changes. This provides rigorous tests of the concept of orbital following in saturated compounds from the standpoint of different orbital models, both with and without orthogonality constraints, and with polar and relatively nonpolar bonds. Somewhat surprisingly, it is found in all the cases studied that the bonding orbitals associated with the central atom move only slightly or not at all as the hydrogen nuclei sweep through an arc of 30° or more, although significant hybridization changes do occur. We tentatively conclude that the traditional concept of orbital following is not supported by ab initio calculations. Similar studies are in progress on CH₄ and NH₃ for comparison.

^{*}University of California, Santa Barbara.

XXXV. CALCULATION OF VIBRATIONAL FORM FACTORS IN ELECTRON IMPACT
EXCITATION (W.M. Huo)

The direct evaluation of vibrational form factors using harmonic oscillator functions is investigated. This is an alternative to the approach of Itikawa and Takayanagi using an unshielded long range dipole potential and a short range potential consisting of the sum of individual atomic potentials. The use of harmonic oscillator function provides a more realistic representation of the interaction since molecular binding effects are included in the short range part of the potential. The contribution from the interaction between the incoming electron and nuclear vibration is expressible in terms of Whittahus' functions, and the effect of ee interactions on vibrational excitation is being studied. The form factor so obtained shows the glory undulation recently observed by Krutein and Linden in the vibrational excitation of CO. The calculated form factors will be used in the study of vibrational energy transfer.

XXXVI. THE LIMITING BEHAVIOR OF MOLECULE-MOLECULE INELASTIC COLLISION
AMPLITUDE AT ZERO MOMENTUM TRANSFER (W.M. Huo)

Assuming that the Born series converges, it is shown that the collision amplitude of inelastic molecule-molecule collisions is bounded at the limits of zero momentum transfer but diverges for T-E, V, R transfer in ion-molecule collisions. In the latter case, the limiting value of the collision amplitude multiplied by momentum transfer K as $K \rightarrow 0$ is proportional to the molecular transition dipole moment, a situation reminiscent of that found by Lassettre in electron-molecule collisions.

XXXVII. PARTIALLY DIFFUSION-CONTROLLED REACTIONS OF ISOLATED PAIR IN
CONDENSED MEDIA (A. Mozumder)

The theory of partially diffusioncontrolled reactions of isolated pairs in condensed media has been completed in terms of the probability of first encounter and the probability of successful reaction at an encounter. The last quantity is explained in terms of the enthalpy and entropy of homogeneous reaction. Application of theoretical results to experiments require the systematic elimination of diffusion effects from observed reaction rates. When that correction is effected the evaluated activation entropy is often quite different from earlier reported values although the activation energy remains about the same. Time-dependent reactivity appropriate to the problem is evaluated and discussed.

XXXVIII. FIELD-DEPENDENT MOBILITIES (I. Carmichael and A. Mozumder)

The effect of introducing an initial distribution of separations on the probability of escaping geminate neutralization for an isolated ion-pair is being investigated. Cases in which the measured drift velocity is both sublinear (neopentane) and superlinear (n-hexane) in the applied field have been considered. By comparison with the observed free ion yields, it appears that the inclusion of such non-linearities tends to equalize otherwise disparate medium thermalization lengths.

XXXIX. T-R ENERGY TRANSFER BETWEEN ELECTRONICALLY EXCITED ARGON (Ar^*3P_2)
AND GROUND-STATE CO_2 (D.H. Winicur, J. Bentley and E.R. Manzanares)

The rotational excitation of CO_2 by collision with electronically excited argon atoms is being studied as a function of collision energy over the range from 0.05 eV to 0.20 eV. This range includes the thresholds for vibrational excitation of the lowest two CO_2 levels (0.082 eV, 0.172 eV).

The T-R energy transfer is peaked at large angles implying that the anisotropic part of the potential is dominant at small internuclear separations. These maxima become very broad and move to smaller angles as the collision energy decreases. The product of the peak angle and the collision energy is roughly constant implying that the T-R exchange is dominated by a single feature of the anisotropic potential. The threshold for the exchange occurs at the internuclear separations at which the potential becomes repulsive (similar to the quenching of Ar*).

The nature of the T-R transfer changes when a vibrational channel opens up. The maximum most probable energy transfer at our lowest collision energy (0.05 eV) is 60% of the available collision energy but decreases rapidly with increasing collision energy. The decrease is roughly proportional to $E^{-10/3}$ below the first vibrational threshold. Above this threshold, the decrease is less rapid, roughly proportional to $E^{-3/2}$. At energies above the second vibrational level the energy transfer again decreases rapidly becoming essentially zero at 0.184 eV.

This decrease of the transferred T-R energy is opposite to the observations of Loesch for ground-state Ar + CO₂ and Blair, Cross and Kwei for Ar + CS₂. It may reflect a difference in energy transfer mechanisms, e.g. the Ar* (which behaves like ground-state K) exchange may proceed via complex formation whereas ground-state Ar could proceed via a direct exchange.

XL. DOSE AND DOSE-RATE EFFECTS IN THE RADIOLYSIS OF LIQUIDS

(A. Mozumder)

Recent experiment of Trumbone et al. of the effect of dose on the time-dependent decay of the hydrated electron yield is analyzed using the spur theory. The use of homogeneous energy deposition in the discussion of dose effect is criticized. It is replaced by a statistical theory of charged particle penetration consistent with the delivered dose and stopping power of the medium. Some earlier work using steady irradiation is being reassessed for dose-rate effect.

XLI. CIDEP (I. Carmichael)

The effect of solvent-modulated indirect exchange has been incorporated into a program to calculate the spin polarization chemically induced by spin-selective radical recombination liquids. This is operational on the IBM 370 of the Computing Center. A more restricted computation of this type is possible on the Laboratory's PDP/11. This version is based on a program kindly supplied by Prof. J.H. Freed and is limited to direct exchange interactions which are spherically symmetric to normal diffusive trajectories. Using these tools, an investigation of the solvent dependence of the anomalous spin polarizations in photochemically produced t-butyl radicals is continuing.

XLII. COULOMBICALLY CORRELATED CHARGE-PAIR DISTRIBUTION AND RECOMBINATION: THE ROLE OF NON-GAUSSIAN DIFFUSION (W.H. Hamill and K. Funabashi)

The decay of a population of n correlated charge pairs is a transform of the original radial distribution $n(R)$ of holes and electrons, given by [1]: $d \ln n / d \ln t = -(d \ln n / d \ln R)(d \ln R / d \ln t)$ [1]. From the essentially empirical Deby-Edwards law for decay of isothermal recombination luminescence intensity (ITL), $I \propto t^{-m}$ and $m \geq 1$ [2], $n(t) = \int I dt$ from t to ∞ , or $n(t) \propto t^{1-m}$ [3]. This relation has a general validity as eq [2] and has been successfully applied to systems ranging from liquid alkanes to aqueous glasses, from 4 to 300 K, and from 10^{-8} to $> 10^3$ s. The validity of [3] is not limited to systems which exhibit ITL. Consequently $d \ln n / d \ln t = 1-m$ [4]. For ion-ion recombination in liquids, $t \propto R^3$ and $d \ln R / d \ln t = -1/3$. For ion-electron recombination the mobility is time dependent, $\mu \propto t^{-\alpha}$, with $0 < \alpha < 1$ (Scher-Montroll) and $d \ln R / d \ln t = -\alpha/3$ [5], the general case. Combining [1], [4] and [5] gives $d \ln n / d \ln R = 3(1-m)/\alpha$, empirically, for various media. In methylcyclohexane the parameters are the same at 4 and 77 K. Both activated and activationless trapped electron diffusion require further theoretical examination.

XLIII. STUDY OF NON-BONDED INTERACTIONS (J. Bentley)

In order to develop a model for the general study of non-bonded interactions, we have examined the collision-induced electron density distortions of pairs of rare gas atoms. We have determined localized atomic distortions by the generalized scattering factor method, and have used the resulting density functions to calculate local electric fields, dipole moments, etc. The local properties are only weakly dependent on the collision partner, indicating that the collision densities themselves may be transferable. A theory is being developed to describe collisional interactions by additively combining atomic fragments.

XLIV. PULSE RADIOLYSIS STUDIES ON HYDROCARBON RADICAL SCAVENGING PROCESSES (G. Foldiák and R.H. Schuler)

By signal averaging of pulse radiolytic data on 100 nsec time scale it was found that the reactions of iodine with both cyclopentyl (CP) and cyclohexyl (CH) radicals are certainly very near to being diffusion controlled. The rate constant of CH with iodine has been found to be $1.1 \pm 0.1 \times 10^{10}$, and that with galvinoxyl (GO) $9.1 \pm 1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, the former proved to be about 50% higher than a previous crude estimate in literature. The analogous reactions of CP are some twice as fast. The ratio of absolute rate constants for reaction of cyclohexyl radical with CH and GO is similar to that found many years ago with methyl radicals by one of the authors in competitive experiments. Reaction with galvinoxyl is sufficiently slow that radical combination can be studied in competition with the scavenging process. By varying the dose by scavenging with GO, preliminary estimates show that the rate constant of the recombination of CH radicals is about $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

XLV. OXIDATION OF METHOXYHYDROXYCYCLOHEXADIENYL RADICALS BY QUINONES

(S. Steenken)

2- and 4-methoxyhydroxycyclohexadienyl radical, formed by addition of OH to methoxybenzene, react with para-benzoquinone to yield para-benzosemiquinone ($k \sim 4 \times 10^8$ and $\sim 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively). An improved differentiation between 2- and 4-methoxyhydroxycyclohexadienyl radical can be obtained by oxidation using 2,5- or 2,6-dimethyl-para-benzoquinone. In this case the ratio of the rate constants for oxidation, $k_{\text{para}}/k_{\text{ortho}}$, is ~ 20 ($k_{\text{para}} \sim 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). From the fact that the total yield of electron transfer from the OH adducts of methoxybenzene to quinone is $\leq 90\%$ it is concluded that the rate constant for oxidation of 3-methoxyhydroxycyclohexadienyl radical is $< 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Pulse radiolysis studies involving conductivity detection show that the lifetimes of any carbonium ions formed by oxidation of the 2- and 4-methoxyhydroxycyclohexadienyl radicals are $< 10^6 \text{ s}$.

As in the case of mono-methoxyhydroxycyclohexadienyl radicals, the rate constants for oxidation of di- or trimethoxyhydroxycyclohexadienyl radicals depend on the positions of the methoxyl groups relative to the hydroxymethylene group: if CHOH and CH_3O are para to one another the rate constants are larger than if CHOH and CH_3O are ortho to each other. A methoxyl group meta to CHOH seems to have a deactivating effect on the rate of electron transfer. In the case of 2,4-di- or 2,4,6-trimethoxyhydroxycyclohexadienyl radicals the rate constants for electron transfer to benzoquinones approach $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. 2,4,6-trimethoxyhydroxycyclohexadienyl radical is able to reduce anthraquinone-2-sulfonate ($k \sim 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).

XLVI. DETERMINATION OF TRACE ISOMERIC HYDROXY PHENOLS AND BENZOIC ACIDS
IN AQUEOUS SOLUTION BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY
 (N.V. Raghavan)

In order to investigate the radiation induced oxidation products of phenol, it was necessary to develop a sensitive method for the quantitative determination of hydroxy phenols in aqueous solution. The ortho, para, and meta hydroxy phenols were separated under reverse phase conditions using μC_{18} bondapak column with 4% dioxane - 1% ethylene glycol - water mixture as the mobile phase. Quantitative determination of the three isomers ($>2\mu\text{M}$) from phenol (10^{-2}M) and the oxidants (10^{-3}M), $\text{Fe}(\text{CN})_6^{3-}$, quinone, and anthraquinone-2-sulfonate was made using the above stationary and mobile phases. The effect of dioxane composition on the retention times is being investigated. Separation of aniline from phenol, and benzene was also achieved. Moreover, using acetonitrile-water mixtures as the mobile phase, separation of the isomeric hydroxy and amino benzoic acids were carried out. A comparison of the separation of the latter components on an anion-exchange column show that the peaks are much broader than that obtained from the present investigations.

XLVII. REACTION OF OH RADICAL WITH PHENOL (N.V. Raghavan and S. Steenken)

The products of the radiation induced hydroxylation of phenol have been investigated using high pressure liquid chromatography methods. The 3 isomeric dihydroxycyclohexadienyl radicals formed by OH addition to phenol can be oxidized by $\text{Fe}(\text{CN})_6^{3-}$ to yield catechol, resorcinol, and hydroquinone. The yield of resorcinol was found to be $\sim 10\%$ of $\text{G}(\text{OH})$. However, the yields of catechol and hydroquinone cannot be determined quantitatively in the presence of $\text{Fe}(\text{CN})_6^{3-}$, due to relatively fast thermal oxidation of catechol and hydroquinone by $\text{Fe}(\text{CN})_6^{3-}$. To cir-

cumvent this difficulty, a search for milder oxidants was made and it was found that, e.g., para-benzoquinone and anthraquinone-2-sulfonate are able to oxidize ortho- or para-dihydroxycyclohexadienyl radical ($\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$) but not meta-dihydroxycyclohexadienyl radical ($< 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Using this method, the yields of catechol and hydroquinone from reaction of OH with phenol were found to be ~ 50 and $\sim 40\%$, respectively, of $G(\text{OH})$. This result shows that the reaction of the electrophilic OH radical with phenol proceeds by preferential addition to the activated ortho and para positions.

XLVIII. ELECTRON TRANSFER REACTIONS BETWEEN PHENOXYL RADICALS OR SEMIQUINONES AND IONIZED DI- OR TRIHYDROXYBENZENES
(S. Steenken and P. Neta)

Electron exchange reactions between phenoxyl or semiquinone anion radicals and ionized di- and trihydroxybenzenes were studied at pH 13-14 using pulse radiolysis with optical detection. The rate constants for reaction of phenoxyl radical with 1,2- and 1,4-dihydroxybenzene are of the order 10^8 - $10^9 \text{ M}^{-1} \text{ s}^{-1}$ and electron transfer is complete, whereas in the reaction between e.g., ortho-benzosemiquinone anion radicals with ionized hydroquinones electron transfer is reversible, which makes possible the determination of equilibrium constants. These measurements show that, in general, the free enthalpy for formation of para-benzosemiquinones is larger than that for formation of ortho-benzosemiquinones and much larger than that for production of meta-benzosemiquinones. The effect of substituents on electron transfer equilibria corresponds to that expected on the basis of their Hammett σ values: electron withdrawing (donating) substituents increase (decrease) the oxidizing power of a semiquinone radical.

XLIX. STUDIES OF THE OXIDATION OF Cu(II) AMINO COMPLEXES BY PULSE
RADIOLYTICALLY GENERATED RADICALS (P. Maruthamuthu, G. Ferraudi
and L.K. Patterson)

Although a number of Cu(III) complexes have been reported by various authors, not all of these species have been fully characterized. The difference between Cu(III) complexes and other possible metastable species has not been established.

Our previous studies on the oxidation of Ni(II) macrocyclic complexes, suggest that the tendency of $\cdot\text{OH}$, Br_2^- , Cl_2^- to oxidize ligands in Cu(II) complexes should be equal to or larger than in Ni(II) analogs. This has been investigated using $\text{Cu}(\text{en})_2^{2+}$; $\text{Cu}(\text{teta})^{2+}$ and $\text{Cu}[\text{Me}_6(14)\text{dieneN}_4]^{2+}$. The reactions of $\cdot\text{OH}$; Cl_2^- , $\cdot\text{HPO}_4$ and Br_2^- have been studied using pulse radiolytic optical and conductivity detection under a wide range of conditions. The reaction scheme, indicated by equations (1) and (2), is suggested by pulse radiolysis observations and the product analyses of γ -irradiated samples. We have found that the metal center oxidation a less favorable reaction pathway with these compounds than in the case of Ni(II) complexes.

L. β -CAROTENE. A MOLECULAR CONDUCTOR OF ELECTRONS AND HOLES THROUGH
BIMOLECULAR LIPID MEMBRANES? (M. Almgren and J.K. Thomas)

It has been suggested that molecules like β -carotene may function as conductors of electrons and/or holes through photosynthetic membranes, enabling the reduction and oxidation to take place on opposite sides of the membrane. In order to find out if such a process really takes place we have begun pulse radiolytic and laser experiments, starting by studying β -carotene as an electron acceptor and donor in micellar solutions.

LI. THE EQUILIBRIUM DYNAMICS OF AROMATIC MOLECULES SOLUBILIZED IN AQUEOUS MICELLAR SOLUTIONS (F. Grieser, M. Almgren and J.K. Thomas)

We have measured both the association rate ($0.7-1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$) and dissociation rate ($2 \times 10^4 \text{ sec}^{-1}$) constants of Br-Naphthalene with NaLS micelles. The results have been obtained assuming a 2 phase system in which the Br-Naphthalene is partitioned. It has been shown that this assumption is a good approximation to the physical situation.

The results from this system have been useful in understanding the factors which actually control the exit rate from a micellar phase. It appears that the most important parameter governing the exit rate is the solubility of the arene in the aqueous phase. The higher the solubility the faster the exit rate.

The micelle head group can also affect the exit rate if there is some interaction with the solubilized compound. This has been observed in the case of naphthalene and CTAB micelles. Here the exit rate is somewhat slower than the exit of naphthalene from NaLS where no interaction occurs.

The influence of counter ions on the exit rate from NaLS micelles has also been studied. The results indicate that there is little if any change in exit rate if the counter ion is altered.

LII. SYNTHETIC BILAYERS STUDIES (R. McNeil and J.K. Thomas)

Didodecyldimethylammonium bromide, which is reported to form bilayers in water, is being characterized by several types of studies. Fluorescence polarization experiments using 1,6-diphenylhexatriene show that the microviscosity in the interior of the bilayers is 0.6 p, the same as observed in micelles of cetyltrimethyl ammonium bromide (CTAB). Variation of polarization with temperature shows that the vesicles are more stable than CTAB micelles but less stable than phospholipid vesicles. Ligand scintillation studies show that the vesicles are not rigid units but are permeable, allowing slow equilibration between the solution trapped inside and that outside.

LIII. A COMPUTERIZED LASER PHOTOLYSIS FACILITY FOR MEASUREMENTS IN THE NANOSECOND REGION (J. Scaiano and L.K. Patterson)

Facilities for automated data gathering from laser photolysis kinetic measurements have been developed employing the Tektronix 7912 transient recorder and PDP 11/55 computer. Software has been implemented which provides computer control of data gathering, reduction and storage, but which is essentially transparent to other users of the RSX 11-M operating system. Associated graphics routines -- using a Tektronix 4010 terminal -- display the raw kinetics data, results from data smoothing and calculated kinetics superimposed on measured values. The time response of the system is ca. 1-2 ns, and it can at favorable wavelengths, generate signal-to-noise ratios of 500 to 1 for single measurements. Repetitive measurements and averaging may be used for further enhancement of signal to noise. A single kinetics measurement followed by data reduction and storage, along with associated graphics monitoring, consumes about 2 seconds.

LIV. PHOTOCHEMISTRY OF β -(DIMETHYLAMINO)-PROPIOPHENONE (M.V. Encinas and J.C. Scaiano)

Photoexcitation of β -(dimethylamino)-propiophenone leads to intramolecular electron abstraction from the triplet manifold. The product of the reaction can be best described as a biradical zwitterion (I), $\text{Ph}\dot{\text{C}}(\text{O}^-)\text{CH}_2\text{CH}_2\text{NMe}_2^+$. In the absence of electron donor-acceptor interactions I decays via reverse electron transfer leading to the ground state of the parent ketone. In the presence of electron acceptors (A) I will transfer an electron to give A^- and an aminoketone radical-cation; quite frequently their fate is ultimately controlled by radical-ion disproportionations. Typical electron acceptors include bipyridylium dications and 2,5-dinitrobenzoic acid. These reactions, as well as the multiple acid-free equilibria involved in the process are currently under study.

LV. SOLVENT EFFECTS ON THE LIFETIMES OF PHOTOGENERATED BIRADICALS

(R.D. Small, Jr. and J.C. Scaiano)

The lifetimes of biradicals of the type $\text{Ph}\dot{\text{C}}(\text{OH})\text{CH}_2\text{CH}_2\dot{\text{C}}\text{R}_2$ are controlled by triplet-singlet intersystem crossing. The rates for this process are dependent on the hydrogen bonding properties of the solvent and on the presence of heavy atoms. For example for $\text{R}=\text{Me}$ the lifetimes are 101ns in ethanol, 69ns in γ -chloroethanol, 30ns in cyclohexane and benzene and 16ns in dibromomethane. Examination of a variety of substrates leads to a linear correlation between $\ln \tau$ and the ΔH for hydrogen bonding with standard compounds (e.g. phenol).

LVI. OXIDATION OF AMINES BY TRIPLET DUROQUINONE (J.C. Scaiano and P. Neta)

Triplet duroquinone was produced by laser photolysis of 2 mM duroquinone in aqueous-methanolic (4:1) solutions. Rate constants for reaction of this species with solutes were determined by following the decay of its absorption at 490 nm. As expected, the rate constant for reaction with aniline was found to be very large, $3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at pH 6-8. The reaction with the anilinium ion at pH 0 was about an order of magnitude slower, $2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Measurements at intermediate pH values showed that the change in rate constants is totally ascribable to the acid-base equilibrium of aniline. The reaction with CH_3NH_3^+ at pH 0 was found to be surprisingly as rapid as that with CH_6NH_3^+ . However, when the measurement of the rate constant for CH_3NH_2 in alkaline solution was attempted, the decay of duroquinone triplet was found to be very rapid at high pH. Measurements at pH 11-12 indicated a rate constant of $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for reaction with OH^- but the mechanism is still under study.

IVII. GENERATION AND DECAY OF AROMATIC ALKOXYPHOSPHORANYL RADICALS

(D. Griller,* K.U. Ingold,* L.K. Patterson, J.C. Scaiano
and R.D. Small, Jr.)

The radical Bu^tOPh_3 (I) has been generated by photodecomposition of di-tert-butylperoxide in the presence of Ph_3P . The alkoxy radicals react with the phosphine with $k \sim 2.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ to produce I, which has an absorption maximum at 430nm and decays with $k \sim 4000 \text{ s}^{-1}$ at room temperature and 0.03 s^{-1} at -79° . The ESR spectra of I shows an unusually low a_p coupling constant. A similar radical, MeOPh_3 (II) can be produced by radiolysis of methanolic solutions of triphenylphosphine. In this case we find that the reaction of the alkoxy radical with the phosphine occurs with $k \sim 5.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and the resulting radical (II) is considerably longer lived than I, probably reflecting the dependence of the β -scission reaction of the stability of the alkyl radical produced.

* National Research Council, Ottawa, Canada.

LVIII. PHOTOCHROMIC AZIRIDINES: DIFFERENTIATION AND CHARACTERIZATION OF YLID INTERMEDIATES (R.D. Small, Jr., T.M. Leslie and A.M. Trozzolo)

The photochemical formation of ylid (1) and its isomerization to ylid (2) have been examined using laser flash and standard flash photolysis techniques.

We have measured the difference in ylid reactivities toward dipolarophiles and the interaction of ylid (2) with oxygen.

Previous reports of dipolarophile trapping of ylid (1) have been demonstrated to be invalid.

LIX. THE PHOTOCHEMISTRY OF TRANSITION METAL PHTHALOCYANINES IN AQUEOUS MEDIA (G. Ferraudi)

The photochemistry of phthalocyanines with various metal ions, M(PTS) with M: Cu(II); Co(II); Co(III) and Fe(II) has been investigated by flash and steady photolysis. The photoredox dissociation in ligand radicals, eq. 1, or in species with metal centers in different oxidation states, eq. 2, is the most general reaction mode observed with dimeric species.

Other photochemical reactions have been observed using monomeric complexes. One reaction mode has been associated with a ligand centered excited state which is a more powerful oxidant than ground state. Reactions of such a state with alcohols have been observed with Cu(II) and Co(II) phthalocyanines. However, the ability of Co(III) phthalocyanine for axial coordination opens a new photochemical channel characterized as a photochemical oxidation of the axially coordinated ligand, eq. 3.

Such a reaction has been studied for various ligands ($\text{X}^- = \text{Cl}^-$, Br^- , N_3^- , I^-). The study of various d^6 (Ru^{II} and Fe^{II}) phthalocyanines is in progress. Sensitized redox reactions of the Cu(II); Co(II) and Co(III) complexes have been observed as a sequence of redox reversible reactions. The determination of the various rate constants for all these processes is actually being carried out.

LX. THE PHOTOCHEMISTRY OF THE METASTABLE OXIDATION STATES OF MACRO-CYCLIC COMPLEXES (G. Ferraudi, S. Sheng and L.K. Patterson)

The photochemistry of various Co(II) and Ni(I) complexes with macrocyclic ligands ($\text{Me}_6[14]\text{dienoN}_4$ and tet-a) has been investigated. A combination of pulse radiolysis and laser flash photolysis was used for the production and subsequent study of the Ni(I) complexes. Steady and conventional flash photolysis were used for the study of the Co(II) compounds. The results obtained with both, Ni(I) and Co(II), show that they undergo photochemical transformations. Moreover such processes can not be related with a dissociation into solvated electrons and seem to be largely related with some sort of ligand degradation.

LXI. PRODUCTION OF SINGLET OXYGEN FROM EXCITED STATES OF ALIPHATIC KETONES (K.C. Wu and A.M. Trozzolo)

It has been well-established that some dye-sensitised photooxidation reactions involve the production of singlet oxygen. Usually, the singlet oxygen is the product from the quenching of the triplet excited state of the sensitiser, as shown in the following reaction scheme:

The production of singlet oxygen from ketone impurities has been postulated as a mechanism for the photo-oxidation of polyolefins though the production of singlet oxygen from excited aliphatic ketones has not been reported. In this experiment the quantum yield of production of singlet oxygen from excited aliphatic ketones will be measured. This can provide information of the contribution of ketones in the photooxidation of polymers.

LXII. OZONE DEGRADATION OF FATTY ACID MONOLAYERS (E.V. Srisankar and L.K. Patterson)

It has been observed that ozone in the parts per hundred million range is capable of rapid and efficient degradation of spread oleic and linoleic acid monolayers on a Langmuir trough. Both acids spread on a phthalate buffer substrate were found to be stable to pure O_2 over periods of four hours. Introduction of small increments of O_3 (10^{16} molecules each time) in a 40 liter volume containing the trough resulted in fractional contraction of the monolayer over a 3 minute period. The efficiency of the reaction was about 20 percent. The quantities of ozone introduced were standardized with KI analysis. The contraction rates were nearly equivalent in N_2 and O_2 atmospheres indicating that the ozone reaction with the fatty acid does not result in extensive chain peroxidation to produce soluble products. Details of the reactions involved are being pursued via liquid chromatographic procedures.

LXIII. ACTIVATION ENERGY OF THE INITIAL ELECTRON CAPTURE OF N_2O IN THE GAS-PHASE (H. Shimamori and R.W. Fessenden)

The thermal electron attachment in N_2O -neopentane mixtures has been studied at different temperatures ($-10^\circ C$ to $62^\circ C$) by the microwave conductivity method. At each temperature the attachment rate shows a clear saturation behavior with increase of neopentane pressure. The limit of this saturation is considered to be the rate constant (k_a) for the initial electron capture of N_2O in the two-step three-body process,

The activation energy for k_a has been determined to be 0.25 eV. This value is nearly half of the previously obtained activation energy (0.44 eV) for the reaction,

At present we can not clearly explain this discrepancy, but it might suggest that the possible intermediate N_2O^{-*} in (B) is different from N_2O^{-*} in (A).

LXIV. MEASUREMENT OF ELECTRON SPIN-LATTICE RELAXATION TIMES

(B. Venkataraman and R.W. Fessenden)

Measurements of electron spin-lattice relaxation time (T_1) by the saturation recovery method has been completed and the programs for data acquisition and transfer to the PDP 11/55 tested. Data are taken for two phases of the saturating power to allow both the saturation recovery and the free induction decay to be separated. At present, data can be obtained from as close as 1 μ sec to the end of the saturating pulse.

The entire system has been tested with 2,5 ditertiarybutyl-p-benzosemiquinone ion. The saturation recovery signal is found to fit a single exponential function. Preliminary results at 20°C agree with values reported earlier for this radical (6.6 μ sec). The three main hyperfine components show the same value of T_1 to within about 2%. The use of signal averaging enables measurements to be made to as low as $10^{-5}M$ so that many reactive radicals produced in steady-state photolysis and radiolysis experiments can be studied by this method.

LXV. DEVELOPMENT OF RJE SOFTWARE PACKAGE TO COMMUNICATE WITH
IBM 370 (S. Bose and E. Henry)

The overall logic for the Package incorporating Bisync protocol has been developed to interface the Laboratory's PDP 11/55 and the University's IBM 370-168 computers. Some of the basic modules for the programme are written and tested. Work on writing the rest of the modules is in progress.

LXVI. RADIATION CHEMISTRY OF 4-TERT-BUTYL-CATECHOL* (H.W. Richter)

A pulse radiolysis study of the radicals resulting from the reaction of OH-radicals and solvated electrons with TBC and with 4-tert-butyl-o-quinone in aqueous solution by optical absorption has been completed. The pH range from 3.0 to 10.5 was investigated. A paper describing the results is being prepared for submission to the Journal of Physical Chemistry. Rate constants of radical reactions and spectra of transients are presented. Reaction mechanisms are discussed.

* Joint research with Dept. of Chemistry, Carnegie-Mellon University.

LXVII. REACTIONS OF SUPEROXIDE RADICALS ($\cdot\text{O}_2^-$) AND MONO-OXYGENASES
(H. Richter)

A new project has been initiated in which the general nature of $\cdot\text{O}_2^-$ reactions will be examined and the possible involvement of this radical in aromatic hydroxylation reactions catalyzed by the group of enzymes called mono-oxygenases will be investigated. The project includes the development of a stopped-flow flash photolysis system for the measurement of rates of reactions of $\cdot\text{O}_2^-$ by kinetic spectroscopy. A special low pressure Hg-vapor/rare gas flash lamp system is being constructed for generation of $\cdot\text{O}_2^-$.