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RADIATION LABORATORY
UNIVERSITY OF NOTRE DAME

QUARTERLY REPORT

July 1, 1977 - September 30, 1977

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ISSUED

October 13, 1977

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The Notre Dame Radiation Laboratory is a facility of the U. S. Energy Research and Development Administration operated for ERDA 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 Division of Basic Energy Sciences of ERDA and unless otherwise noted in the following support can be attributed to the Division of Basic Energy Sciences. Certain additional programs, so indicated, are supported by ERDA's Division of Biomedical and Environmental Research. The Radiation Chemistry Data Center, a center for radiation chemical information services operated by the Laboratory, is jointly sponsored by the Office of Standard Reference Data of the National Bureau of Standards and the Division of Basic Energy Sciences of the Energy Research and Development Administration.

* * * * *

Dr. Winfred Huo began her appointment with us on August 1. Dr. Huo received her Ph.D. from the University of Chicago in 1964 and has since held appointments at Harvard, Rutgers and Carnegie-Mellon. She will be carrying out theoretical studies, particularly studies related to energy transfer processes.

Dr. Elapulli V. Srisankar of the University of Calcutta joined the staff as a Research Associate on September 1. While with us he expects to extend his doctoral studies on the radiation chemistry and photochemistry of inorganic complexes.

Dr. Gabor Foldiak, Director of the Hungarian Institute of Isotopes and also of the Institute of Graduate Studies of the Technical University

of Budapest began a year's stay in the United States as a guest of the National Academy of Science on September 15. He will spend this year with us as a Guest Professor of Chemistry.

Mr. Christian Segaud, a graduate student at Ecole Superiore de Physique et Chimie Industrielles in Paris, spent the period July 5 - September 16 with us. He assisted Dr. H. Paul in computational problems related to determining the second order rate constants of radical reactions from ESR data.

Miss Martha Mount joined the staff on September 19 as a technical assistant.

Mr. Mark Spence, a Notre Dame undergraduate, joined the staff on September 27 to assist with building operations.

Mr. Mahesh Chandra and Mrs. Sudesh Bose, both graduate students in the Department of Electrical Engineering, have been appointed as Graduate Research Assistants. Mr. Chandra is working with Drs. Berry and Hamill on the electrical properties of thin films and Mrs. Bose with Dr. Henry on software problems.

Dr. S. Steenken of the Max-Planck Institute at Mulheim has accepted an appointment as Assistant Professional Specialist and will join our staff on November 1.

Dr. Neervalur V. Raghavan of Ohio State University has accepted an appointment as Assistant Professional Specialist and will join our staff on December 15.

* * * * *

The following members of our research staff have completed appointments with us and left our staff: V. Madhavan (8/31/77), Arvind Sarpotdar

(8/31/77), John Jischke (8/31/77), Naohikb Mikami (8/31/77), Maureen Wong (8/31/77), Gilbert H-K. Hong (8/31/77), Francis J. Johnston (8/31/77), Clayton W. Jacobsen (9/15/77), Kaoru Iguchi (9/21/77), Dusan Razem (9/28/77), and Hitoshi Taniguchi (9/30/77).

The following members of the supporting staff have left their positions with us: Brian Kiel (8/26/77), Dale W. Schutt (8/31/77), Christopher Havlik (9/16/77), Branka Razem (9/21/77), and Hedva Levanon (9/27/77).

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Professor Nicholas Turro of Columbia University will spend the week of October 9 at Notre Dame as a guest of the Laboratory.

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Publications

- M. E. Schwartz
Electron Spectroscopy.
Methods of Electronic Structure Theory, Plenum Publishing Corporation,
pp. 357-380 (1977) [NDRL 988]
- D. A. N. Morris and J. K. Thomas
The Effect of Lysoplasmalogen on Some Physical Properties of Dipalmitoyl-
lecithin Bilayers: A Fluorescent Probe Study.
Micellization, Solubilization, and Microemulsions, Plenum Press, pp.
913-926 (1977) [NDRL 1050]*
- M. Wong and J. K. Thomas
Some Kinetic Studies in the Reversed Micellar System-Aerosol OT
(Diisooctyl Sulfosuccinate)/H₂O/Heptane Solution.
Micellization, Solubilization, and Microemulsions, Plenum Press, pp.
647-664 (1977) [NDRL 1054]
- B. P. Rao, R. L. Bush, and K. Funabashi
Field-Dependent Electron Mobility in Methane-Ethane Liquid Mixtures.
Can. J. Chem. 55 (11), 1952-1960 (1977) [NDRL 1055]
- R. J. Field and R. M. Noyes
Mechanisms of Chemical Oscillators: Conceptual Bases.
Accounts of Chemical Research 10, 214 (1977) [NDRL 1661, RRL 561]
- J. L. Magee
Electron Energy Loss Processes at Subelectronic Excitation Energies in
Liquids.
Can. J. Chem. 55 (11), 1847-1859 (1977) [NDRL 1706]
- M. Wong, J. K. Thomas, and T. Nowak
Structure and State of H₂O in Reversed Micelles.
J. Amer. Chem. Soc. 99, 4730-4736 (1977) [NDRL 1732]
- H. K. Hong
Theory of Resonant Raman Scattering in the Strong Vibronic Coupling
Limit-A Green's Function Approach.
J. Chem. Phys. 67 (2), 801-812 (1977) [NDRL 1735]
- W. P. Helman and K. Funabashi
Continuous-Time-Random-Walk in Three Dimensions as a Model for Electron
Scavenging and Ion Recombination in Liquids.
J. Chem. Phys. 66 (12), 5790-5797 (1977) [NDRL 1736]
- H. Levanon and P. Neta
Electron Transfer, Equilibrium, and Protonation in the System of Cis-
and Trans-Stilbene in 2-Propanol.
Chem. Phys. Letts. 48 (2), 345-349 (1977) [NDRL 1737]
- J. A. Labinger and S. Madhavan
Photoreactions of $[(\eta^5\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ with Potential Hydrogen Donors.
Journal of Organometallic Chemistry 134, 381-389 (1977) [NDRL 1739]

R. D. Small, Jr., and J. C. Scaiano
Interaction of Oxygen with Transient Biradicals Photogenerated from
 γ -Methyl Valerophenone.
Chem. Phys. Letts. 48 (2), 354-357 (1977) [NDRL 1740]

D. Razem and W. H. Hamill
Electron Scavenging in Ethanol and in Water.
J. Phys. Chem. 81, 1625-1631 (1977) [NDRL 1745]

P. Maruthamuthu and P. Neta
Reactions of Phosphate Radicals with Organic Compounds.
J. Phys. Chem. 81, 1622-1625 (1977) [NDRL 1741]

H. K. Hong
Theory of Resonant Raman Scattering. II. Overtones and Hot Bands.
J. Chem. Phys. 67 (2), 813-823 (1977) [NDRL 1750]

*Supported by the Division of Biomedical and Environmental Research.

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

I. (NDRL-1786) T-R ENERGY TRANSFER BETWEEN ELECTRONICALLY-EXCITED ATOMS AND TRIATOMIC MOLECULES¹ (E. Manzanares, J. Bentley and D.H. Winicur)

ABSTRACT: We report here thermal-energy studies of the translational to rotational (T-R) energy exchange between electronically-excited, metastable atoms (Ne^* and Ar^*) and both linear (CO_2) and non-linear (H_2O) triatomic molecules. Our crossed-beam apparatus provides both differential cross sections and time-of-flight (TOF) product velocity analysis.

In all cases studied so far, the T-R transfer is very efficient: up to 80 percent of the available translational energy is transferred to the rotation of the molecule. The energy exchange occurs over a narrow range of angles; the maximum in both H_2O systems is at about 104 deg (center of mass) and at about 70 deg (c.m.) for $\text{Ar}^* + \text{CO}_2$. In both $\text{Ne}^* + \text{H}_2\text{O}$ and $\text{Ar}^* + \text{H}_2\text{O}$ the maximum energy transfer coincides with a pronounced peak in the differential cross section but this is not observed in $\text{Ar}^* + \text{CO}_2$.

We observe no significant difference in the T-R exchange to a linear or a non-linear molecule. Comparison of our results with previously published studies of T-R transfer between ground-state atoms and linear triatomics indicates that T-R exchange is enhanced by the presence of the electronic excitation.

(1) Submitted for presentation at Gordon Research Conference on Molecular Energy Transfer, Wolfeboro, NH, July 10-15, 1977.

II. (NDRL-1787) ELECTRON DENSITY DEFORMATIONS IN COLLIDING ATOMS¹

(J. Bentley)

ABSTRACT: The wavefunctions of Gilbert and Wahl for He₂, and Ar₂ have been analyzed in terms of charge density expansions about each atom. Atomic dipole and quadrupole moments, produced by Pauli exclusion forces due to the overlapping atomic charge clouds, have been obtained as a function of internuclear distance. These atomic moments vary exponentially with internuclear distance, and (except for He₂) indicate atomic shell structure. The dipole moments can be combined according to the rules given by F.T. Smith [Phys. Rev. A5, 1708 (1972)] to give molecular dipole moments for the unlike pairs HeNe, HeAr, NeAr.

(1) Submitted for presentation at Gordon Research Conference on Molecular Energy Transfer, Wolfeboro, NH, July 10-15, 1977.

III. (NDRL-1789) CORRELATION OF SINGLET ENERGIES OF AROMATIC HYDROCARBONS WITH THE RATES OF PROTONATION OF THEIR ANION RADICALS¹

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

ABSTRACT: The reaction of solvated electrons with an aromatic hydrocarbon in alcoholic solution produces the anion radical. This radical protonates according to $\text{Ar}^{\cdot-} + \text{ROH} \rightarrow \text{ArH} + \text{RO}^-$. Protonation rate constants for a series of compounds in 2-propanol were determined by kinetic spectrophotometric pulse radiolysis. The protonation rate constants were found to correlate with the $S_0 \rightarrow S_1$ transition energies of the aromatic hydrocarbon and with their ionization potentials. As the energy gap, $\Delta E_{S_0 \rightarrow S_1}$ between the ground and the first excited singlet increases the rate of proton transfer becomes faster. The rate constants vary from $4 \times 10^2 \text{ s}^{-1}$ for perylene ($\Delta E_{S_0 \rightarrow S_1} = 23,000 \text{ cm}^{-1}$) to $5.7 \times 10^5 \text{ s}^{-1}$ for naphthalene ($\Delta E_{S_0 \rightarrow S_1} = 32,200 \text{ cm}^{-1}$).

(1) Submitted as a Communication to the Journal of the American Chemical Society.

IV. (NDRL-1790) ACTIVATED AND ACTIVATIONLESS LOCALIZATION AND IMPURITY TRAPPING OF THE ELECTRON IN C_2H_5OH and C_2H_5OD ¹ (D. Razem and W.H. Hamill)

ABSTRACT: Dry electron localization by solvent and trapping by impurity has been examined for several molecules in C_2H_5OH and in C_2H_5OD from 150 to 300K. Each process involves two channels, one activated, the other activationless. For impurity the former is solvent dependent, the latter resembles the gas phase resonance. The compound negative ion of the solvent molecule is considered to be stabilized in the condensed phase. Below $\sim 150K$, activationless processes dominate and may correspond to those in low-temperature amorphous solids. Both are dependent upon the zero-point kinetic energy of strongly scattered electrons in disordered materials. Yields of solvated electrons in ice below $\sim 273K$ appear to depend almost entirely on activated localization but electron attachment by the near-resonant process may occur for hot electrons with small yields.

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

V. (NDRL-1791) THEORY OF RESONANT RAMAN SCATTERING. III. TOWARD THE TOTAL SYNTHESIS MOLECULAR SPECTRA AND RAMAN EXCITATION PROFILES WITHIN THE GENERALIZED VIBRONIC THEORY AND FROM AN EXCITON-IN-MOLECULE VIEWPOINT¹ (H.-K. Hong)

ABSTRACT: Applications of the Green's function method to the interpretation of molecular electronic spectra and Raman excitation spectra are further elaborated here. In particular, basic concepts in the generalized vibronic theory of Raman intensity are introduced as well as the concept of vibrational lattices and the exciton analogy. It is pointed out that Raman process can be considered from the solid state viewpoint as energy transfer (exciton migration) processes. Therefore, vibronic problems for a polyatomic molecule having M normal modes is analogous to an exciton in M-dimensional space. It is further shown

that most problems in one-dimensional space (one mode problem) can be exactly treated with the Green's function technique in the framework of the generalized vibronic theory. This allows us to handle specifically: (1) Franck-Condon effect with both changes in equilibrium positions and force constants upon electronic excitation, (2) Nonadiabatic Herzberg-Teller couplings with force constant changes in excited states and (3) mixed harmonic-quartic oscillators, etc. More complicated vibronic schemes can be dealt with in a similar fashion. For example, vibrational combinations and the Duschinsky effect in electronic and Raman spectroscopy can be treated as a pseudo one-dimensional problem. Green's functions for multiple mode problems with simple vibronic coupling schemes are given. Some recipes are also provided toward the total synthesis of molecular spectra and Raman excitation spectra.

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

VI. (NDRL-1792) INVERSE ISOTOPE EFFECT FOR ELECTRON TRANSFER REACTIONS IN ETHANOL¹ (D. Razem, W.H. Hamill and K. Funabashi)

ABSTRACT: The rate constants of solvated electrons reacting with scavengers in C_2H_5OD have been found to be larger than those in C_2H_5OH , particularly for those scavengers whose rate constants are much smaller than the value corresponding to the diffusion-controlled reaction. The observed effect is in accord with the theory of electron transfer reactions of Ulstrup and Jortner, who predicted that deuteration gives rise to both normal and inverse isotope effects. The present work implies that the electron is strongly coupled with the OH bond and deforms the intramolecular configuration of the alcohol molecule when it is "solvated."

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

VII. (NDRL-1793) THE EFFECT OF MICELLAR PHASE ON THE STATE AND DYNAMICS OF SOME EXCITED STATE CHARGE TRANSFER COMPLEXES¹

(B. Katusin-Razem, M. Wong and J.K. Thomas)

ABSTRACT: The effect of micellar phase on kinetic processes of electron transfer reactions of exciplexes formed by pyrene (P) and N,N dimethyl aniline (DMA) has been studied. Transitory species are produced by a 10 nsec pulse of 347.1 nm light from a Q-switched ruby laser and detected by rapid spectrophotometric or conduction techniques. Singlet excited pyrene (P*) readily accepts an electron from DMA to form an ion pair (P⁻ and DMA⁺), and the fate of the ion pairs depends critically on the micellar environment. In the case of cationic micelles, DMA⁺ is quickly expelled from the micellar surface while P⁻ is retained, leading to a long anion lifetime (~500μs). On the other hand, an anionic micellar surface traps DMA⁺ ions and enhances the geminate ion recombination process with P⁻. Several pyrene derivatives such as pyrene butyric acid, pyrene sulfonic acid, pyrene tetrasulfonic acid, pyrene dodecanoic acid, pyrene carboxaldehyde which are solubilized at different sites in micelles are also selected as e⁻ acceptors to investigate the effect of separation between P* and DMA on the forward and back e⁻ transfer processes. Similar studies were carried out with the molecule P-(CH₂)₃-DMA which forms intramolecular exciplexes. Here neither ion can escape from the exciplex due to the restraint of the propyl chain. The physical and chemical properties of excited states of this molecule-micellar system are dramatically different from those of intermolecular complexes. Micellar systems suggest a convenient method to efficiently separate and keep apart the constituent ions of exciplexes. This has implications for conversion of light energy into ionic fragments which can be subsequently utilized.

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

VIII. (NDRL-1794) RADIATION INDUCED REACTIONS IN MICELLAR SYSTEMS¹

(J.K. Thomas)

ABSTRACT: The unique properties of micelles in inhibiting or catalyzing photo-induced reactions will be discussed. As a preliminary the shape and structure of micelles will be illustrated, and the general techniques used to investigate the nature and position of probe molecules in micelles. For example N.M.R., Laser Raman, and fluorescence fine structure will give information on the location and environment of pyrene in a micelle.

The effects of micellar structure on the following photo-induced reactions will then be discussed:

- (a) Quenching of excited states
- (b) Excimer formation
- (c) Exciplex formation and electron transfer
- (d) Photo-ionization and lowering of ionization thresholds
- (e) Phosphorescence.

The unique effects of micellar surface polarity in these reactions will be discussed.

(1) Submitted for presentation at Gordon Research Conference on Photochemistry, Proctor Academy, Andover, NH, July 25-29, 1977.

IX. (NDRL-1796) IONIZATION POTENTIALS OF H₂O FROM VALENCE BOND AND MOLECULAR ORBITAL WAVE FUNCTIONS¹ (D.M. Chipman)

ABSTRACT: A comparison is presented of the H₂O ionization potentials calculated from molecular orbital wavefunctions using Koopmans' Theorem with those calculated from valence bond wavefunctions using the Extended Koopmans' Theorem. It is found that the two methods give closely comparable results for the main peaks in the photoelectron spectrum. In addition, the valence bond calculation predicts two additional weak, closely spaced, shake-up states which may correspond to a previously unassigned feature near 48 eV in the experimental photo-ionization spectrum.

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

X. (NDRL-1797) PHOTOREACTIONS OF METAL-METAL BONDED CARBONYLS WITH POTENTIAL HYDROGEN DONORS¹ (J.A. Labinger and S. Madhavan)

ABSTRACT: Photochemistry of several dimeric metal carbonyls containing metal-metal bonds in the presence of potential hydrogen atom donors has been examined, because of possible relevance to metal-catalyzed photogeneration of hydrogen. Irradiation of a solution of $[\text{CpFe}(\text{CO})_2]_2$ ($\text{Cp}=\eta^5\text{-C}_5\text{H}_5$) and benzaldehyde leads to formation of $\text{CpFe}(\text{CO})_2\text{Ph}$ in good yield. The quantum yield of this reaction (350 nm) is approximately .01. A number of other aldehydes gave no reaction under similar conditions. Photolysis of $\text{Mn}_2(\text{CO})_{10}$ with a variety of aldehydes gives a highly colored species (absorption maximum at ca. 500 nm) which disappears over a period of minutes upon cessation of irradiation. Only with benzaldehyde was a stable product obtained; in contrast to the above iron system, this appears to be a non-organometallic, carbonyl-free complex of Mn(II). Other classes of hydrogen donor show no photoreactivity with either metal dimer. Mechanistic interpretations of these results will be discussed.

(1) Submitted for presentation at meeting of American Chemical Society, Argonne National Lab., Argonne, Illinois, August 20 - September 2, 1977.

XI. (NDRL-1798) THE ABSOLUTE RATE CONSTANTS FOR REACTIONS OF PHENYL RADICALS¹ (V. Madhavan, R.H. Schuler and R.W. Fessenden)

ABSTRACT: The absolute rate constant for the addition of p-carboxyphenyl radical to p-bromobenzoate anion in aqueous solution at zero ionic strength has been determined by optical pulse radiolysis and time-resolved ESR experiments to be $7.6 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$. The rate constants for addition of phenyl radicals to most aromatic systems should be of this same magnitude. Addition of p-carboxyphenyl radical to benzene occurs with a similar rate constant and results in the formation of a substituted cyclohexadienyl radical that can be quantitatively oxidized to biphenyl-4-carboxylic acid. Abstraction from hydrogen donors results in the quantitative formation of benzoic acid. By reference to the absolute rate for addition to p-bromobenzoate the rate constant for H abstraction

from isopropyl alcohol has been determined from competitive measurements of benzoic acid formation to be $5.2 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$. Measurements by optical pulse radiolysis and time resolved ESR methods give comparable rate constants. H atom abstraction from other alcohols is found to be only modestly slower. It is clear from these measurements that the lifetime of phenyl radicals in the presence of most organic materials will usually be very low so that reactions second order in phenyl radicals will not normally be important. In most cases, therefore, synthetic processes which involve phenyl radicals will be controlled entirely by the relative rates for the various possible addition and abstraction reactions. The unpaired electron of the phenyl radical is known from ESR observations to reside in an orbital with $\sim 10\%$ s contribution. The relatively high reactivity of phenyl radicals noted here, at least four orders of magnitude greater than that for equivalent reactions of alkyl radicals, presumably reflects this σ character of the phenyl radical.

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

XII. (NDRL-1799) H₂O RELATED CENTERS IN POTASSIUM CHLORIDE¹ (G.C. Kuczynski[†] and P.E. Dietz,[†] W.H. Hamill, and J.H. Jischke)

ABSTRACT: Vacuum annealing of crystals of KCl at 600°C produces stable defect centers which trap electrons during u.v. or γ irradiation as well as during additive coloration. When vacuum annealed crystals are exposed to 2 atm H₂O at 200°C prior to γ irradiation coloration is suppressed, including the F band. This may be due to displacement of an electron from F by interstitial H₂O which occupies V_{Cl}⁻. When previously untreated crystals are exposed to 0.25 atm of HCl at 200°C and γ irradiated, only one of the color centers previously mentioned was observed. The same center was produced in crystals grown from aqueous KCl containing HCl. The center is attributed H₃O⁺F. Precursor H₃O⁺ (and OH⁻) is produced by heating in vacuum at 600°C. Additional chemical reactions are required to account for the other bands.

(1) Submitted for publication in Physica Status Solidi.

[†] Dept. of Metallurgical Engineering, University of Notre Dame.

XIII. (NDRL-1800) EXCITED STATE PROTONATION OF 6-ACETYL-2-NAPHTHOL¹

(A. Sarpotdar and A.M. Trozzolo)

ABSTRACT: Fluorescence spectra of 6-acetyl-2-naphthol in aqueous solutions had emission peaks at 444 (pH < 5), 496 (pH > 9) and 523 (HClO₄, 1.1 M) nm; which were assigned to the excited states of neutral molecule of the anion and of a new species formed by the excited state protonation of the neutral molecule respectively. Kinetic fluorescence quenching due to excited state protonation was studied at a variety of HClO₄ concentrations and a linear Stern-Volmer type plot of ϕ_f^0/ϕ_f vs [H⁺] was obtained. Fluorescence decay time τ at pH, 3 was measured using 1.5 ns Cerenkov radiation pulses (Van de Graaff accelerator). The value of τ so obtained was 2.23×10^{-9} sec. Using this value and the slope of the Stern-Volmer plot K_h , the rate constant for the excited state protonation was estimated to be equal to 8.69×10^{10} sec⁻¹.

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

XIV. (NDRL-1801) ABSOLUTE RATES OF HYDROGEN ABSTRACTION BY TERT-BUTOXY RADICALS¹ (R.D. Small, Jr. and J.C. Scaiano)

ABSTRACT: Absolute rate constants for hydrogen abstraction reactions of tert-butoxy radicals have been determined for the first time using nanosecond laser flash photolysis techniques. The values for diphenylmethanol and cumene are 6.9×10^6 and 8.7×10^5 M⁻¹s⁻¹ respectively at room temperature in 1:2 benzene:di-tert-butylperoxide. The values reported are considerably higher than previous estimates.

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

- XV. (NDRL-1802) EFFECT OF FIELD-DEPENDENT MOBILITY ON THE ESCAPE PROBABILITY. I. ELECTRONS PHOTOINJECTED IN NEOPENTANE¹ (A. Mozumder and I. Carmichael)

ABSTRACT: A general procedure is described for calculating the escape probability of an electron against neutralization in the presence of an external field after it has been ejected into a dielectric liquid from a planar surface. The present paper utilizes the field-dependent electron mobility measurement in neopentane by Bakale et al. The calculated escape probability, upon averaging over the initial distribution, is compared with the current efficiency measurement of Holroyd et al. The median thermalization length, inferred from this comparison, depends in general upon the assumed form of initial distribution. It is less than the value obtained when the field-dependence of the mobility is ignored but greater than that applicable to the high energy irradiation case. A plausible explanation is offered.

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

- XVI. (NDRL-1803) THE EFFECT OF SALT ON THE RADIATION SURVIVAL OF ESCHERICHIA COLI¹ (C.F. Kulpa[†] and J.K. Thomas)

ABSTRACT: The effect of various inorganic salts on the survival of Escherichia coli to Cobalt-60 irradiation was evaluated. It was found that certain salt concentrations in the range 0.1 - 0.20 M provided a radioprotective effect. These same salt concentrations were found to cause a change in the optical density of the cell suspension. This change was indicative of an osmotic effect resulting in cell shrinkage. These studies were conducted under normal atmospheric conditions. The radioprotective effect is also independent of the inorganic salt used since similar results were observed with NaCl, KCl, MgCl₂ and Na₂SO₄. This indicated that neither the Na⁺ nor the Cl⁻ were essential for this effect, rather it related to the osmotic environment created by the presence of the salt.

(1) Submitted for publication in Radiation Research.

* Supported by the Division of Biomedical and Environmental Research.

† Dept. of Microbiology, University of Notre Dame.

XVII. (NDRL-1804) REACTIONS OF RADICALS WITH LECITHIN BILAYERS¹ (D.J.W.

Barber and J.K. Thomas)

ABSTRACT: The kinetics of reaction of $\cdot\text{OH}$ and e_{aq}^- with lecithin bilayers have been measured. The rate for $\cdot\text{OH} + \text{lecithin}$ is $5.1 \pm 0.9 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ while the $e_{\text{aq}}^- + \text{lecithin}$ rate is very slow. When a solute such as pyrene is solubilized in the bilayer, $\cdot\text{OH}$ and e_{aq}^- may react with the solute; rates of $1.65 \pm 0.12 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ and $7 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ have been measured for reaction of $\cdot\text{OH}$ and e_{aq}^- respectively, with pyrene in lecithin. These rates are lower than those observed for similar reactions in homogeneous systems. This is explained in terms of a) the protective effect of the bilayer, this being especially true for e_{aq}^- which does not readily leave the aqueous phase, and b) in terms of the restricted diffusion imposed on the reactive species by the bilayer. The kinetics in these model systems are relevant to reactions of radicals with membranes.

Long-term alteration in the model membrane following $\cdot\text{OH}$ attack is manifested in terms of damage to the head-group, increasing water-penetration of the bilayer, and of cross-linking with the membrane, thereby restricting motion in the interior of the bilayer. Increased rigidity and "leakiness" of membranes is an expected consequence of radiation damage.

(1) Submitted for publication in Radiation Research.

* Supported by the Division of Biomedical and Environmental Research.

XVIII. (NDRL-1806) SPECTRAL MOMENTS OF SOLVATED ELECTRONS¹ (I. Carmichael)

ABSTRACT: A moment theory analysis is performed on the optical absorption spectra of surplus electrons localized in various media. The deduced attributes of the excess particle are compared with those obtained by a perturbation treatment of the exact ground state solution of a currently popular model potential for the species. Several frequency dependent observables are evaluated and a source of inadequacy in the current theory is revealed.

(1) Submitted to Chemical Physics Letters.

XIX. (NDRL-1807) THE INFLUENCE OF THE CONFORMATIONAL STATE OF POLYMETHACRYLIC ACID ON THE PHOTO-PHYSICAL PROPERTIES OF PYRENE IN AQUEOUS SOLUTIONS. A FLUORESCENT PROBE AND LASER PHOTOLYSIS STUDY¹ (T.S. Chen and J.K. Thomas)

ABSTRACT: The excited state of pyrene as observed via fluorescence and pulsed laser techniques is used to show that pyrene is solubilized in the polymer coil of aqueous solution of polymethacrylic acid, PMA at pH < 4-5. This leads to a decreased access of molecules such as I^- , Tl^+ , CH_3NO_2 and O_2 to excited pyrene in the polymer coil. The protection of the excited state by solubilization in the polymer is sufficient to enable 3-bromo-pyrene phosphorescence to be observed at room temperature in these systems. Increasing the pH of the system uncoils the polymer and leads to increased accessibility of excited pyrene to CH_3NO_2 , and eventually at pH > 5 the pyrene is ejected into the aqueous phase of the system. In the presence of micellar solutions of surfactants increasing pH transports the pyrene from the polymer to the micellar aggregates. These fluorescence techniques are used to investigate the kinetics of expansion of the polymer coil, and the system is suggested as a suitable model for the interaction of pyrene with biopolymers such as DNA.

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

XX. (NDRL-1808) PULSE RADIOLYSIS STUDIES IN MODEL LIPID SYSTEMS: FORMATION AND BEHAVIOR OF PEROXY RADICALS IN FATTY ACIDS¹ (K. Hasegawa and L.K. Patterson)

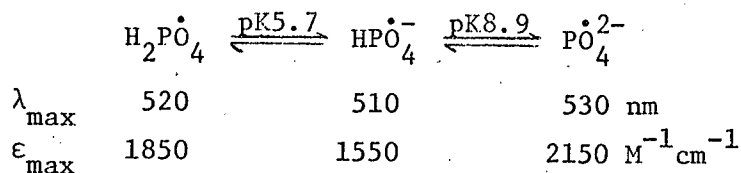
ABSTRACT: Radiolytic formation and peroxidation of fatty acid radicals have been investigated by pulse radiolysis techniques in oleate, linoleate, linolenate and arachidonate systems. The appearance of a strong absorption band at 280 nm associated with conjugated radicals, R_{conj}^\bullet , in polyunsaturated fatty acid moieties has been used as a probe for kinetic processes occurring at doubly allylic sites in the hydrocarbon chain. Formation of R_{conj}^\bullet by O^- has been found to be more efficient than the less selective $\bullet OH$ radical. Peroxidation of R_{conj}^\bullet is shown to be somewhat slower, ($k_{R^\bullet+O_2} = 3 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$), than O_2 reactions with

radicals in oleate ($k_{R+O_2} = 1 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$). Peroxy radicals disappear slowly by essentially second order processes ($2k_{RO_2} \sim 10^7 \text{ M}^{-1} \text{ sec}^{-1}$). Using formate solution at pH=11, O_2^- radicals showed little if any reactivity toward 10^{-2} M linolenate or arachidonate over periods of 20 seconds.

(1) Submitted for publication in Photochemistry and Photobiology.

XXI. (NDRL-1809) PHOSPHATE RADICALS: SPECTRA, ACID-BASE EQUILIBRIA, AND REACTIONS WITH INORGANIC COMPOUNDS¹ (P. Maruthamuthu and P. Neta)

ABSTRACT: The phosphate radicals were produced by the reaction of e_{aq}^- with peroxodiphosphate ions and their spectra and acid-base equilibria were determined:



The reaction of OH with phosphate ions was also examined and discrepancies in the literature are discussed. The rate constants for the reactions of the acid-base forms of the phosphate radical, as well as those of the sulfate radical, with several inorganic compounds were determined.

These reactions involve either hydrogen abstraction or one-electron oxidation. The radicals formed by H abstraction from H_2O_2 , HPO_3^{2-} , and $H_2PO_2^-$ can reduce peroxodisulfate and peroxodiphosphate efficiently and thus propagate a chain reaction. The rate constants for the abstraction reactions are similar for $\dot{S}O_4^-$ and $H_2\dot{P}O_4$ but slower for $H\dot{P}O_4^-$ and $P\dot{O}_4^{2-}$. The rate constants for oxidation differ considerably for the different radicals and substrates. From these rates it is concluded that the oxidation capabilities decrease in the order $\dot{S}O_4^- > H_2\dot{P}O_4 > H\dot{P}O_4^- > P\dot{O}_4^{2-}$.

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

XXII. (NDRL-1810) THE OXIDATION-REDUCTION OF METHYL RADICALS BY COPPER COMPLEXES. PHOTOCHEMICAL GENERAL OF METASTABLE METHYLCOPPER COMPLEXES¹ (G. Ferraudi)

ABSTRACT: The oxidation-reduction of the methyl radicals with copper complexes were investigated. Intermediates, assigned as methyl-copper species, were generated by flash photolysis. The large life time of the methyl copper (II) species ($k \approx (7.2 \pm 0.3) \times 10^2 \text{ sec}^{-1}$), compared with hydroxyalkyl copper (II) species, is discussed.

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

XXIII. (NDRL-1811) EFFECT OF OXYGEN ON BIRADICAL BEHAVIOUR¹ (R.D. Small and J.C. Scaiano)

ABSTRACT: The 1,4-biradicals produced in the Norrish Type II reaction of phenyl alkyl ketones interact with oxygen with rate constants of ca. $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The interaction leads to an intermediate complex $^x\text{BO}_2$ where the multiplicity 'x' is 1,3 or 5. The quintet state is dissociative, while the triplet and singlet states lead to molecular products in a 3:1 ratio, reflecting spin statistical factors.

The study of this type of processes is usually complicated by oxygen quenching of the precursor excited states. We have developed a technique involving the 'tuning' of the lifetime of the triplet state leading to the biradicals which allows the differentiation of excited state and biradical processes.

(1) Submitted for presentation at the 13th Informal Conference on Photochemistry, Jan. 4-6, 1978, University of South Florida, Tampa, Florida.

XXIV. (NDRL-1812) TEMPERATURE DEPENDENCE OF ELECTRON SCAVENGING IN ETHANOL-OH AND ETHANOL-OD¹ (D. Razem and W.H. Hamill)

ABSTRACT: Inefficient scavenging of solvated electrons (e_s^-) has been relatively neglected although it may provide understanding of details which are difficult to explore for nearly diffusion-controlled processes. Alcohols as solvents permit use of organic reagents, exhibit interesting dynamic solvation effects, and are particularly appropriate for dry-electron scavenging. Sixteen scavengers, with $k_{e_{aq}^-}$ in the range 10^7 - 10^9 $M^{-1}s^{-1}$, have been investigated in ethanol from 150 to 298 K. Values of E_{act} were higher for two efficient scavengers, ~ 4.5 Kcal/mole for CCl_4 and $HClO_4$, than ~ 3.8 Kcal/mole for inefficient scavengers such as toluene, with no evident pattern. Activation contributes little to differences in $k_{e_s^-}$. Many of the inefficient scavengers were moderately efficient as dry-electron (e^-) scavengers at 298 K. For toluene 63% of dry electrons were scavenged at 298 K by $C_{37} = 1.8$ M, but at 123 K by only $C_{37} = 0.43$ M. Temperature-dependent ionization $C_6H_5CH_3^- \rightarrow C_6H_5CH_3 + e_s^-$ is indicated. At 298 K and large combined concentrations of toluene ($k_{e_s^-} \approx 10^7$ $M^{-1}s^{-1}$) and biphenyl ($k_{e_s^-} \approx 10^9$ $M^{-1}s^{-1}$), toluene converts e_s^- to e^- .

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

XXV. (NDRL-1813) DIFFERENTIATION OF EXCITED STATE AND BIRADICAL PROCESSES. PHOTOCHEMISTRY OF PHENYL ALKYL KETONES IN THE PRESENCE OF OXYGEN¹

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

ABSTRACT: The photochemistry of butyrophenone, valerophenone, γ -methylvalerophenone and γ -phenylbutyrophenone has been examined in the presence of oxygen. The use of triplet quenchers to tune the triplet lifetime to a conveniently short value allows the differentiation of triplet state and biradical reactions. Typically oxygen quenches the triplet state with rate constants of ca. 4×10^9 $M^{-1}s^{-1}$ and interacts with the biradicals with $k_9 \sim 7 \times 10^9$ $M^{-1}s^{-1}$. The interaction results in the formation of an intermediate which has as its main decay path the

fragmentation to acetophenone, olefin and the regeneration of oxygen. About 75% of these intermediates decay giving Type II Products, while the other 25% yields a hydroperoxide. The ratio of products is probably controlled by spin statistical factors. Previous reports indicating that oxygen has no effect on the Norrish Type II reaction are incorrect.

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

XXVI. (NDRL-1814) ENERGY LOSS OF ELECTRONS IN RANDOM MOTION
ANALYTICAL RESULT¹ (M. Tachiya and H. Sano)

ABSTRACT: The average rate of energy loss of an electron moving in a dielectric medium can be expressed in terms of the power spectrum of the electric displacement generated by the electron. The power spectrum for an electron in random motion was analytically calculated from the autocorrelation function of the electric displacement by use of the Wiener-Khinchin theorem. Agreement between the present analytical results and numerical results of Magee and Helman (J. Chem. Phys. 66, 310 (1977)) is found to be good except at higher frequencies. It is also found that as far as the energy loss to dipolar relaxation is concerned, the random track has the same loss rate as the linear track.

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

XXVII. (SR-40) THE PHOTOEXCITED TRIPLET STATE AND PHOTOSYNTHESIS¹
 (H. Levanon and J.R. Norris[†])

ABSTRACT: This review presents the application of triplet state spectroscopy as a probe for studying structure and mechanism in the primary photosynthetic act.

We discuss the fundamental physical aspects of primary photosynthesis as revealed by optical and optical-magnetic resonance studies of photoexcited triplet states in model compounds and in vivo systems. Other than pertinent historical material, we emphasize the last five years literature, beginning with the direct observations of triplets in photosynthetic bacteria.

(1) Submitted for publication in Chemical Reviews.

[†] Chemistry Division, Argonne National Laboratory.

Other investigations in progress include:

XXVIII. EFFECT OF MOLECULAR GEOMETRY ON THE ELECTRON AFFINITY OF H₂O
 (D.M. Chipman)

Using self-consistent-field molecular orbital methods with inclusion of diffuse atomic orbitals in the basis set, the potential surfaces of H₂O and H₂O⁻ 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 Å. The potential surface of H₂O⁻ is found to be very close to that of H₂O at all points studied. In particular, the H₂O⁻ surface showed no local minima other than the absolute minimum occurring at essentially the same geometry as the minimum of H₂O surface. The electron affinity is calculated to be slightly positive, corresponding to an anion stable with respect to vertical electron detachment, at all geometries except those near linear. However, the calculated electron affinities are so small that observation of the stable species H₂O⁻ by conventional experimental techniques seems unlikely.

The electron affinity at the equilibrium geometry is calculated to be only about $+1 \times 10^{-4}$ eV. On varying the bond angle (with both bond lengths fixed at their equilibrium values) the calculated vertical electron affinity is found to attain a maximum value of $+6 \times 10^{-3}$ eV at $\theta(\text{HOH})=50^\circ$. This behavior correlates well with that of the dipole moment of H_2O , which also attains a maximum value in this vicinity. At all bond angles, the vertical electron affinity increases as one bond length is stretched from its equilibrium value of 0.96 \AA to 1.26 \AA . This effect is most marked at $\theta(\text{HOH})=50^\circ$, where the calculated vertical electron affinity rises to $+2 \times 10^{-2}$ eV at $R(\text{OH}_1)=.96 \text{ \AA}$, $R(\text{OH}_2)=1.26 \text{ \AA}$, although there is not a corresponding increase of the H_2O dipole moment in this case. As the bond is stretched further, the experimental vertical electron affinity should continue to increase (at any angle) up to a limiting value of 1.8 eV, corresponding to the well known electron affinity of $\text{OH}\cdot$ with an isolated $\text{H}\cdot$ atom at infinity.

Our molecular orbital calculations are expected to represent lower bounds to the experimental electron affinities since inclusion of electron correlation should stabilize H_2O^- relative to H_2O . Studies are being initiated to test this hypothesis by calculating the magnitude and sign of the correction due to electron correlation.

XXIX. EFFECT OF NON-SPHERICALLY SYMMETRIC EXCHANGE POTENTIAL IN ENERGY TRANSFER AND CIDEP (W. M. Huo)

The exchange potential between two molecules with p-type electrons is derived as a function of the intermolecular separation, its angle, and the relative orientation of the two molecules. This can be expressed in analytic form taking advantage of the fact that the exchange potential can be restated in terms of an integral over the Born-Oppenheimer exchange amplitude in electron-molecule collisions. The potential so derived is found to depend on the angle of the intermolecular vector up to the 4th order spherical harmonic. Thus in p-p type electron exchange, it is possible to induce rotational excitations simultaneously. This is

contrary to the conclusions drawn from a spherically symmetric exchange potential commonly used to interpret energy transfer data (Dexter model) and CIDEP (Freed and Pedersen). The model potential is being used to study the effect of non-spherical symmetry in these problems.

XXX. FRAGMENTATION PATTERNS IN THE RADIOLYSIS OF NORMAL ALKANES

(K. Funabashi and W. M. Huo)

A model calculation is being pursued on the fragmentation pattern of n-alkanes with the following assumptions: (1) The majority of the excited states generated by radiolysis decay via radiationless transitions to the lowest lying excited state. (2) Scission occurs as a result of radiationless transition from the lowest vibrational level of the first excited electronic state to a highly excited vibrational level of the ground electronic state. (3) Fragmentation pattern of the C-C bonds is related to the distribution of excitons in the first excited electronic state and the distribution of vibrational energy as a result of the radiationless transition. The computed fragmentation pattern will be compared with the experiment of Isildar and Schuler.

XXXI. PROPERTIES OF SOLVATED ELECTRONS (I. Carmichael)

The diffuse nature of the charge distribution of the solvated electron in condensed phases suggests that its momentum distribution will be quite sharply peaked. The appropriate transformations have been applied to wave-functions derived from a range of simple models for these species and the expected Compton profiles have been evaluated. It would seem that these will be resolvable.

XXXII. THE TEMPERATURE DEPENDENCE OF ELECTRON LOCALIZATION AND IMPURITY TRAPPING IN METHANOL AND PROPANOL (D. Razem, W.H. Hamill and K.P. Funabashi)

The lifetime τ of the dry electron e^- in a medium, relative to localization, and the competitive trapping of 63% of the initial e^- by [scavenger] = C_{37} , with rate constant k_{e^-} , are related by $C_{37} = k_{loc} [M] / k_{e^-}$ where $k_{loc} \equiv \tau^{-1}$ and $[M]$ is the concentration of localization sites, usually considered to be voids. However, for alcohols $[M]$ is proportional to $[ROH]$. Also, there is an isotope effect for C_2H_5OH and C_2H_5OD . Considering also a temperature dependence for C_{37} , which is roughly the same for most additives in one solvent, it has been concluded that localization involves activation of the C-O-H bending mode and formation of ROH^- . Measurements of C_{37} in methanol from 298 to 80 K for 12 additives, with k_{e^-} at 298 K in the range 10^9 to $<10^7$ $M^{-1}s^{-1}$, shows that C_{37} decreases to ~ 150 K, below which no further decrease can be detected. Each of the rate constants contains an activated and an activationless component, $k_{loc} = k_{loc,T} + k_{loc}^0$ and $k_{e^-} = k_{e^-,T} + k_{e^-}^0$. At low temperature $C_{37}^0 = k_{loc}^0 [M] / k_{e^-}^0$. Comparing methanol and propanol, $C_{37,MeOH}^0 / C_{37,PrOH}^0 \approx [MeOH] / [PrOH]$ is expected. The observed average ratio is 1.8 for 12 additives, compared to 1.84 for the concentrations of the solvents. The main experimental features of this work can be understood by applying the recent theories of non-radiative transitions to electron localization.

XXXIII. FIELD-DEPENDENT ELECTRON MOBILITY (I. Carmichael and A. Mozumder)

A general numerical procedure has been devised for evaluating the escape probability of electrons photoinjected from plates into dielectric liquids, even when the mobility is field dependent. Corroborative evidence for this treatment apparently only exists for neopentane; insufficient information is available in other systems. Indirect attempts to deduce this information from related observations are currently under way.

XXXIV. ALUMINUM CLUSTER AND ORGANOALUMINUM SYSTEMS (M.E. Schwartz and H.F. Baney)

In our work model chemisorption and catalysis, the molecular orbital studies of Al_n , Al_n+H , and Al_n+O are continuing. The $n=5$ investigations are nearly complete, and analyses/comparisons with experimental and other theoretical studies is underway. The Al-ethylene and Al-acetylene studies are also nearly complete. While Al-ethylene is basically a weak Π -complex (stability ~ 2 Kcal/mole), the Al-acetylene is more strongly bound (~ 8 Kcal/mole) and considerable distortion and bonding occurs here. These results are consistent with limited experimental data (on metal atom reactions under matrix conditions) and confirm the usefulness of the model calculation for such problems.

XXXV. COLLISION-INDUCED ATOMIC DIPOLE MOMENTS (J. Bentley)

Atomic dipole moments may be induced by distortion of the atomic electron density distributions during collisions. A number of such dipole moments have been calculated for various collision pairs involving rare gases as one of the atoms. Atomic dipole moments were calculated within the framework of the generalized scattering factor method [J. Chem. Phys. 63, 3786 (1975)] and analyzed with the reduced force coordinate of F.T. Smith [Phys. Rev. A5, 1708 (1972)]. These dipole moments can be used to predict molecular collisional dipole moments, which are required for the interpretation of collision-induced absorption spectra. The atomic moments are roughly proportional to atomic dipole polarizabilities.

XXXVI. T-R ENERGY TRANSFER BETWEEN ELECTRONICALLY EXCITED ATOMS AND GROUND STATE MOLECULES (D.H. Winicur, J. Bentley, E.R. Manzanares, and M. Butler)

The study of the translational-rotational (T-R) energy exchange between AR^* and CO_2 at thermal energies has been extended to a relative energy of 0.103 eV. The differential cross section is qualitatively similar to that at 40 meV but the rainbow peak is sharper. The time-of-flight distribution is qualitatively different from that at 50 meV. There is a gradual increase in the T-R exchange with scattering angle rather than a sharp increase at a preferred angle. The difference could be due to the accessibility of a vibrational channel which is not present at 50 meV. Experiments are continuing to probe the T-R exchange as a function of translational energy in the region of the vibrational channel threshold.

A study of the T-R exchange between He^* and H_2 was initiated in the hopes of observing exchange involving a single rotational quantum. At 50.5 meV, no T-R exchange is observed, the scattering being essentially elastic. This gives rise to the possibility of studying the exchange process in the threshold region as a function of translational energy.

XXXVII. CORRELATION BETWEEN THE ANISOTROPY OF POLARIZABILITY AND ELECTRON-DENSITY CONTOUR DIAGRAMS (D.H. Winicur)

The anisotropy in the molecular polarizability is of current interest because of its role in rotationally-inelastic molecular collisions. Experimental determination of the anisotropy factor κ is difficult and very few reliable measurements are available. Theoretical calculations of κ are available for a few molecules but these values can vary by as much as a factor of four. A correlation has been established for diatomic molecules between κ and the shape of the outer reaches of the molecular electron-density contour diagram, calculated in the Hartree-Fock limit. The 0.002 a.u. contour contains over 98% of the total electronic charge and defines a molecular size which correlates with van der Waals radii. The length to width ratio of the 0.002 a.u. contour is linearly related to measured values of κ if the width of the contour is taken as twice the largest non-bonded radius of the molecule.

XXXVIII. HIGH-FIELD CONDUCTION IN THIN-FILM ALKALI HALIDES (M. Pisanias and W.H. Hamill)

Anomalous high field electron conductivity of Al-MX-Al, $\sim 0.1 \text{ A/cm}^2$ at $\sim 10^5 \text{ V/cm}$, is preceded by drift of charged defects, probably anion vacancies in grain boundaries. They produce a compact positive space charge at the cathode followed by tunnel injection into the defect conduction band. Ion current, voltage, temperature and time (I,V,T,b) are empirically related by

$$I = AV \exp[(cV - E_a)/kT] t^{-b}$$

as a useful approximation, with A and c constant and b somewhat dependent on T and V. Ion drift is therefore field assisted and from the value of c for KCl the hopping distance is $\sim 35 \pm 10 \text{ \AA}$. Since tilt planes provide the required periodicity for defect conduction bands, are necessarily abundant in microcrystalline films, and have large repetition distances, the value obtained provides qualitative support for the model. The time dependence is under theoretical consideration by P.K. Funabashi.

XXXIX. CHEMICALLY INDUCED ELECTRON POLARIZATION OF t-BUTYL RADICALS IN SOLUTION (I. Carmichael and H. Paul)

Pursuing the source of anomalous polarizations observed in the esr spectrum of photo-produced t-butyl radicals, experimental evidence has been found that the polarization is produced in non reactive free radical encounters. Refined calculations of the intermolecular exchange interaction between two $2p_z$ -orbitals suggest a possible explanation in terms of the anisotropy of this interaction. A ' σ - π ' approach apparently favours a triplet ground state while the singlet is lower with a ' σ - σ ' alignment, at least for realistic values of the encounter distance. Introducing substantial hybridization into the orbitals may, however, alter this conclusion. The study is being continued to get a clearer picture of the actual mechanism(s) causing the unusual transient populations of the Zeeman levels.

XL. NONLINEAR RESPONSE OF RADICAL SYSTEMS TO MODULATED INITIATION

(C. Segaud and H. Paul)

The response to modulated initiation of systems containing two kinds of radicals which terminate in second order self-and cross-reactions and carry electron spin polarizations due to radical initiation and termination has been computed numerically for a wide range of rate constants and modulation frequencies. The results clearly demonstrate the limitations of the applicability of linear response theory to these systems. In addition they provide an exact basis for the evaluation of rate constants and electron spin polarizations from modulation esr experiments. With suitable scaling and interpolation procedures the numerical results are expected to allow an expansion of the modulation experiments to a wider frequency range.

XLI. MEASUREMENT OF ELECTRON SPIN-LATTICE RELAXATION TIMES

(B. Venkataraman and R.W. Fessenden)

The ESR spectrometer for time resolved experiments is being modified for measurement of electron T_1 by the saturation recovery method. Construction is well along and completion will follow soon after receipt of diode microwave switches. The first radical system to be studied will be that of H atoms in irradiated acid water. A more complete understanding of this relaxation time will aid in the interpretation of kinetic curves obtained for H atoms in pulse ESR experiments.

XLII. ELECTRON ATTACHMENT TO N_2O IN THE GAS PHASE (H. Shimamori and R.W. Fessenden)

The studies of thermal electron attachment in pure N_2O and N_2O -hydrocarbon mixtures have been continued. The effect of molecular structure on the efficiency of the hydrocarbon as a third body in the attachment process has been investigated by studies on 1-, cis-2-, trans-2-, and iso-butene and on the pair n-pentane and neopentane. The

branched compounds are more efficient with isobutene and neopentane having three-body rate constants roughly ten fold higher than the other compounds. The reason for this difference is unclear but may involve the ease of transfer of vibrational energy from N_2O^- to the hydrocarbon (N_2O is linear while N_2O^- is bent). Attempts are being made to correlate the differences in rate of electron reaction in the various mixtures with previously reported yields of N_2 observed from those same mixtures in γ radiolysis experiments.

XLIII. LASER FLUORESCENCE OF CYCLOHEXADIENYL RADICAL IN IRRADIATED BENZENE CRYSTALS (S.-J. Sheng)

Fluorescence of cyclohexadienyl radical at 4.2°K is observed by site selective laser excitation. The visible transition previously observed in absorption is confirmed to be the lowest doublet doublet transition. This is a weak but dipole allowed transition. The present emission and emission excitation studies of cyclohexadienyl and per-deuterated cyclohexadienyl radicals allow us to complete the vibrational analysis and to discuss the vibronic activity of this transition.

XLIV. KINETICS OF RADICAL EXCHANGE BETWEEN MICELLES AND WATER

(M. Almgren, F. Grieser, and J.K. Thomas)

Exit/entrance rates of molecules, including the monomers, from/into micelles may be measured by following the change with time, from an original non-equilibrium state, of some readily observable, environment-sensitive property of the molecules. Most components of ordinary micelles and micro emulsions - alkyl chain detergent molecules, long chain alcohols, hydrocarbons - lack such properties. NMR-methods are in general too slow. Labeling the molecules with spin or fluorescence labels changes their properties significantly. We are exploring the possibility of using radicals of the molecules as probes.

Radicals of micelle monomers (NaLS) are produced preferentially in the aqueous phase by reaction with $\text{OH}\cdot$ in pulse electron-beam experiments in the presence of N_2O . The competition between direct bleaching of $\text{Fe}(\text{CN})_6^{3-}$ in the aqueous phase and entrance followed by exit and bleaching is studied. In principle the method allows a determination of both entrance and exit rates.

XLV. THE DYNAMICS OF PROBE MOLECULES IN A MICELLAR ENVIRONMENT

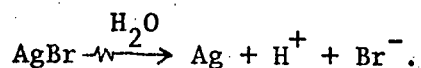
(F. Grieser and J.K. Thomas)

Stopped-flow experiments used to measure the exit time of pyrene in a micellar solution were continued. The exit times in non-ionic micelles (Triton X-100, Igepal 630 and Brig 35) were all found to be of the order of 2 msec, which is similar to that found in the ionic micelle, CTAB. These results indicate that there are no unusual probe-micelle interactions which effect either the equilibrium between the micelle and aqueous phase or the solubilization of the probe.

The aging effect briefly mentioned in the previous report was further investigated. In systems where (a) the probe was dissolved in a micelle solution close to the CMC or (b) the probe concentration was much greater (>5 times) than the micelle concentration, slow ($t_{1/2} \approx 20$ sec) solubilization (probe into micelle) kinetics were observed. The analysis of the results were interpreted as a dissolution of micro crystals of the probe that are suspended in solution, and not as a change in the micelle structure as was originally suspected.

XLVI. RADIOLYTIC REDUCTION OF COLLOIDAL SILVER BROMIDE (F. Johnston)

Colloidal silver bromide, when γ -irradiated in oxygen-free systems in the presence of 0.01-0.15 molar ethanol, isopropanol, acetone or benzene, is reduced to elemental silver and bromide ions



In the case of benzene, the organic oxidation product is phenol. The reaction has been followed conductometrically with suspensions of known average particle size and concentration. Average particle sizes were obtained by specific turbidity measurements at 436 and 546 nm. In two cases, comparisons were made of these sizes by electron microscopy. The agreement was very satisfactory. A typical colloid was comprised of 2×10^{10} particles per cc with an average apparent radius of 54 nm. These experiments were designed so that the amount of silver bromide on particle surfaces far exceeded that in the homogeneous phase. The experimental results indicate that the reaction occurs at the particle-solution interface and involves an attack at the surface by radicals formed from the organic additive. G values in these systems ranged from 0.65 for 4.0×10^{-4} M AgBr with 55 nm particles in 0.10 M acetone to 2.9 for 6.0×10^{-4} M AgBr with 51 nm particles in 0.10 M ethanol. Reaction rates varied with particle concentration to a power very close to one.

For the 51 nm particles reacting with a G value of 2.9, the rate corresponds to a reaction of 6100 surface molecules per second. On the basis of the model used, this corresponds to a minimum flux of reactant radicals at the surface of $1.9 \times 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$. These results suggest that the radicals involved are of very long mean life and that the silver bromide surface acts as an efficient oxidizing agent in reaction with these radicals.

With citrate ion as the additive, reduction is accompanied by the formation of colloidal silver and reaction in this system was followed by spectrophotometric measurements of the silver formed. G values in these systems were lower ($G(\text{Ag}) = 0.75$ for 2×10^{-4} M colloidal AgBr with $\bar{r} = 52$ nm and 10^{-3} M sodium citrate) and were somewhat less reproducible than in the system containing the other organic additives.

XLVII. CHARACTERIZATION OF STRUCTURE IN FATTY ACID AGGREGATE SYSTEMS:
MEASUREMENT OF MICROVISCOSITY (K. Hasegawa and L.K. Patterson)

Investigations of radical behavior in fatty acid systems have shown that various kinetic processes depend on the extent and character of molecular aggregation present. An important parameter in micelles is microviscosity, which reflects the nature of surfactant packing and associated mobility of species incorporated into the hydrocarbon core. Studies have been undertaken to characterize micellar fluidity in oleate, linoleate and linolenate systems using fluorescence depolarization of the probe, 1,6-diphenylhexatriene. The well studied surfactant, NaLS was used as a reference. The degree of polarization, P, was determined in each system. Fluorescence decays were measured using single photon counting techniques and were found to exhibit single exponential behavior in all cases. From application of both measurements to the well known Weber equation for microviscosity, we obtained values of 20, 14.7, 9.7 and 8.0 centipoise for NaLS, oleate, linoleate, and linolenate micelles respectively. These results show that, as in the complex membrane bilayer, the character of the micelle hydrocarbon core may be manipulated through inclusion of cis double bonds in the surfactant hydrocarbon chain.

XLVIII. PHOTOCHEMICAL REACTIONS OF Cu(II) COMPLEXES WITH MACROCYCLIC
LIGANDS (G. Ferraudi)

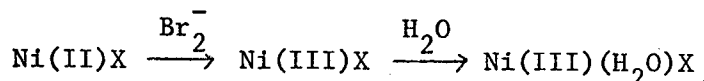
The photochemical decomposition of $\text{Cu}(\text{teta})^{2+}$ takes place through several intermediates. The shorter lived species was previously assigned as a Cu^{I} -cation ligand radical intermediate. Studies of the dependence of the product yields ($\text{Cu}_{\text{aq}}^{2+}$; $\text{Cu}_{\text{aq}}^{+}$ and CH_2O) on scavenger and acid concentration were carried out in order to clarify the nature of such species. These results strongly suggest that the already indicated transient transforms into a metastable Cu^{II} -alkyl species. Such a chemical reaction ($k > 4 \times 10^4 \text{ sec}^{-1}$), followed by acid hydrolysis of the Cu^{II} -alkyl intermediate ($5 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$), was observed in flash photolysis.

XLIX. STUDIES OF Ni(III) MACROCYCLIC COMPLEXES: PULSE RADIOLYSIS

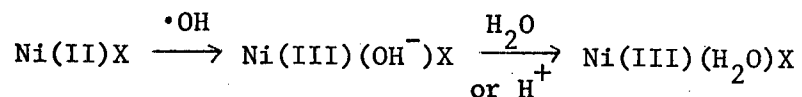
STUDIES WITH Br₂⁻ (P. Maruthamuthu, L.K. Patterson and G. Ferraudi)

From previous investigations of •OH reactions with the nickel macrocyclic complexes Ni(II)Me₆[14]anoN₄, Ni(II)Me₆[14]enoN₄, and Ni(II)Me₆[14]-1,4,8,11-tetraenoN₄, we have reported formation of Ni(III) transients in water with spectral properties differing markedly from those reported for Ni(III) species prepared electrolytically with these complexes in acetonitrile. Principally, it was found that in addition to charge transfer bands in the UV region, new long wavelength absorption appears in the region of 530-550 nm for •OH generated transients. These differences were assigned to formation of distorted ligand systems associated with the aqueous Ni(III) transients. Pulse radiolysis studies of Br₂⁻ reactions with these macrocyclics appear to provide the link between behavior of the electrolytically generated Ni(III) compounds and that observed via •OH attack. The bromide anion radical reacts rapidly with all the macrocyclics ($k_{\text{Br}_2^{\cdot-} + \text{Cpx}} \sim 10^8 - 10^9 \text{ M}^{-1} \text{ sec}^{-1}$) to give transient spectra with the same features as Ni(III) complexes in acetonitrile. Subsequently, these absorptions decay via first order processes ($t_{1/2} \sim 1-10$ msec) into the spectra observed with direct •OH attack.

This behavior is consistent with initial oxidation of the metal center via Br₂⁻, followed by relatively slow aquation at one of the axial positions:



In the case of •OH attack, the reaction may well occur through inner sphere attachment as has been suggested in the literature, followed by rapid protonation of the resulting hydroxyl group in short time to give the same species as that produced more slowly through Br₂⁻ oxidation.



L. RATE CONSTANT FOR OXIDATION OF HYDROXYCYCLOHEXADIENYL RADICAL BY FERRICYANIDE (V. Madhavan and R.H. Schuler)

Hydroxycyclohexadienyl radical is known to be oxidized quantitatively to phenol by ferricyanide even at concentrations $\sim 10^{-4}$ M of the latter. This fact implies a rate constant $> 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ for the electron transfer process. Absolute measurements on the latter have now been carried out by optical and conductometric pulse radiolysis methods and give a value of $2 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$. The optical studies show that inorganic reduction products other than ferricyanide are produced to a minor extent.

LI. ALKOXYL RADICAL REACTIONS WITH LIPIDS: A LASER PHOTOLYSIS STUDY (R.D. Small, J.C. Scaiano, and L.K. Patterson)

Alkoxy radical attack on fatty acid moieties is thought to play a role in the naturally occurring degradation of lipids. Such attack proceeds via hydrogen abstraction, hence some relation between reaction rate and the labile character of C-H bonds in the fatty acid moiety is to be expected. To investigate this relationship we have chosen as model systems reactions between the t-butoxy radical and fatty acids having differing numbers of cis double bonds incorporated into their hydrocarbon chains.

The oxy radicals were generated by photolytic decomposition of di-tert-butyl peroxide with a frequency doubled ruby laser, and competition between the reactant and benzhydrol was monitored using a technique recently developed. Data were gathered in seven acid systems: stearic, oleic, elaidic, linoleic, linolenic, linolaidic, and arachidonic. From the measured rate constants it is possible to write an equation correlating the number of secondary, allylic, and doubly allylic hydrogens present in the fatty acid molecule to the rate constant for reaction with the alkoxy radical.

$$k_{(\text{RO}\cdot + \text{FA})} = .072(\text{H}_{\text{sec}}) + .52(\text{H}_{\text{allyl}}) + 2.82(\text{H}_{\text{double allyl}}) \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$$

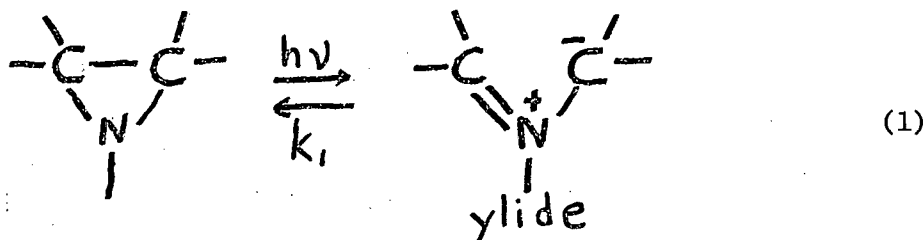
The coefficients in this equation provide a measure of the relative reactivity associated with each type of CH site, and may be useful in assessing the vulnerability of more complex lipids to alkoxy radical attack.

The fluorescence spectrum of I was measured under a variety of environmental conditions. The emission from (III) could be observed in some non-aqueous acidic solutions, and further, it was established that $[H^+]$ is at least 20 times more effective than water in bringing about the reaction $[I]^* \rightarrow [III]^*$. Therefore, the available evidence is still consistent with the phototautomer formulation of $[III]^*$.

LIV. PHOTOCHROMIC AZIRIDINES: RATE OF RING CLOSURE OF YLIDE (R.D.

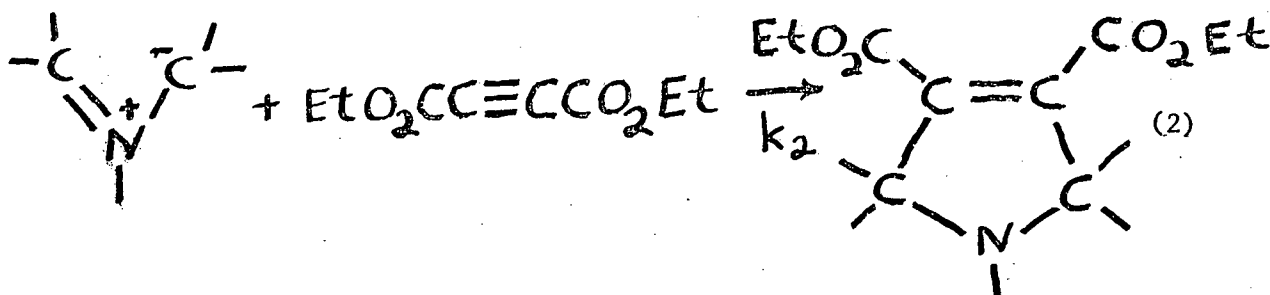
Small, Jr., T.M. Leslie and A.M. Trozzolo)

The rate of ring closure of the photogenerated ylide back to the parent compound (reaction 1) is being determined utilizing laser flash photolysis.



Three model aziridines are now being examined and their ylides have significantly different lifetimes (k_1 varies from $\sim 10^5$ to 10^7) which can be related to the structure of the parent aziridine.

We also plan to trap the various ylides with a series of depolarophiles (reaction 2) and determine k_2 for the cycloaddition reaction

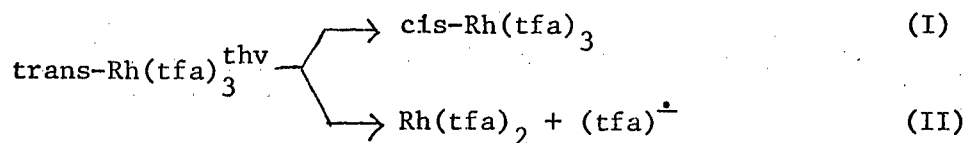


LV. PHOTOCHEMISTRY OF ACETYLACETONATE COMPLEXES OF d^6 METAL IONS

(G. Ferraudi and Ch. Kutal^{*})

Trans-cis isomerization (I) and redox decomposition(II) are the photochemical reaction modes observed with trans-Rh(tfa)₃. The efficiency of such processes depends on oxygen and alcohol concentrations. Transient absorptions ($\lambda_{\text{max}} \sim 360$ nm) were observed in flash photolyses of de aerated solutions containing large alcohol concentrations (Ethanol, $c > 2M$; 2-propanol, $c > 3M$). The dependence of the intermediates on acid concentration was also studied. The short lived species has been assigned as a Rh(II) complex which transforms into a metastable Rh(III) hydride complex with $t_{1/2} \sim 200$ μsec . The decay of the last species, Rh(tfa)₂(H⁻), takes place by a process with a first order dependence in hydrogen ion concentration ($k \approx 310^4 \text{ M}^{-1} \text{ sec}^{-1}$).

Studies will be carried out with cis-Rh(tfa)₃ and Co(tfa)₃ in order to obtain further information on the photochemical reactivity of these systems.



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