RADIATION LABORATORY
UNIVERSITY of NOTRE DAME

MASTER

Quarterly Report

DO NOT MICROFILM
COVER

October 1, 1980 — December 31, 1980

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

RADIATION LABORATORY
UNIVERSITY of NOTRE DAME

DOE/ER/00038--2210

DE81 013765

MASTER

Quarterly Report

October 1, 1980 — December 31, 1980

RADIATION LABORATORY
UNIVERSITY OF NOTRE DAME

QUARTERLY REPORT

October 1, 1980 - December 31, 1980

ISSUED

January 20, 1981

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS LIMITED
MGW

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

* * * * *

Dr. K. Tokumura, who is on leave from the faculty of Kanazawa University, joined the staff as a Research Associate on 10/6/80. While with us Dr. Tokumura will continue his interests on the photochemical reactions of organic systems.

Mrs. S. Baral joined the staff as a Research Specialist on 10/16/80 and is assisting Drs. P. Neta and P. Bays with the synthesis of nitro-aromatic compounds of interest in electron transfer studies.

Mrs. W. Rohn joined the staff of the Radiation Chemistry Data Center on 10/6/80 as a secretary.

Mr. K. Brennan, a physics undergraduate student, is assisting with software development (12/19/80 - 1/12/81).

* * * * *

Dr. P. Morliere returned to his appointment at the Laboratoire de Biophysique, University of Paris, on 12/24/80.

Dr. B-T. Ahn resigned from the staff on 12/29/80 to accept an appointment at Texas A & M University.

Dr. E. Janata returned to Hahn-Meitner Institute on 12/31/80.

Mr. R. Green left the supporting staff of the Laboratory on 10/20/80 to accept a position with the University maintenance department.

Mrs. L. Fitzpatrick resigned her position as secretary on 12/31/80.

* * * * *

Dr. M. V. George of the Indian Institute of Chemistry at Kanpur has accepted an appointment as Visiting Professor of Chemistry and will join the staff of the Laboratory in May. He expects to continue his studies on the photochemistry of organic systems.

Dr. H. Levanon of The Hebrew University of Jerusalem has accepted an appointment as Visiting Professor of Chemistry and will join the staff of the Laboratory in June. While with us he will extend his interests on the photo- and radiation chemistry of porphyrins.

Dr. Y. Inel of Bogazici University, Istanbul, Turkey, has accepted an appointment as an Assistant Professional Specialist. His interests lie largely in the chemical kinetics of radicals in gaseous systems.

Dr. P. R. Prasad of the University of Madras will join the staff of the Laboratory in January as a Research Associate.

Dr. T. Wismontski-Knittel of the Weizmann Institute, Israel, has accepted an appointment as a Research Associate and will join the staff in May to extend her photochemical studies.

Dr. G. Levey of Berea College will join the staff in September as a Visiting Research Associate while on leave from his position as Chairman of the Chemistry Department at Berea College.

* * * * *

Mr. V. Nagarajan, a graduate student in the Department of Chemistry, has begun his Ph.D. studies on laser induced photochemical reactions under the direction of Dr. R. W. Fessenden.

Mr. K. Morehouse, a graduate student in the Department of Chemistry, has begun his Ph.D. studies on the redox reactions of manganese porphyrins under the direction of Drs. R. H. Schuler and P. Neta.

* * * * *

Publications

S. Lahiri, V. Dabral, S. M. S. Chauhan, E. Chakachery, C. V. Kumar,
J. C. Scaiano and M. V. George
Photochemical Transformations of cis-1,2-Dibenzoylalkenes
J. of Organic Chem. 45, 3782 (1980) [NDRL-2042]

G. Ferraudi and C. Carrasco
Photochemistry of Low-Spin Iron(III) Complexes with Macrocyclic Ligands
Inorg. Chem. 19, 3466 (1980) [NDRL-2061]

C. Kutal, D. B. Yang and G. Ferraudi
Mechanistic Photochemistry of Transition-Metal β -Diketonate Complexes.
2. The Case of trans-Tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III)
Inorganic Chem. 19, 2907 (1980) [NDRL-2070]

P. K. Das and R. S. Becker
Spectroscopy of Polyenes--IV. Absorption and Emission Spectral Properties
of Polyene Alcohols Related to Retinol as Homologues
Photochem. and Photobiol. 32, 739 (1980) [NDRL-2076]

M. H. Dung and J. J. Kozak
Stability of Photochemical Mechanisms for Photogalvanic Cells
J. of Photochem. 14, 205 (1980) [NDRL-2078]

P. K. Das and R. S. Becker
Spectroscopy of Polyenes. 5. Absorption and Emission Spectral Properties
of Polyene Acids/Esters Related to Retinoic Acid/Ester as Homologues
J. Phys. Chem. 84, 2300 (1980) [NDRL-2081]

H. Paul and C. Segaud
Rate Constants for Self- and Cross Terminations of Transient Radicals in
Solution by Effect Modulated Electron Spin Resonance Spectroscopy
Internat'l J. of Chem. Kinetics XII, 637 (1980) [NDRL-2098]

A. Kumar and P. Neta
Complexation and Oxidation of Glycine and Related Compounds by Ag(II)
J. Am. Chem. Soc. 102, 7284 (1980) [NDRL-2100]

F. Grieser and J. K. Thomas
The Temperature Dependence of the Triplet Lifetimes of Some Aryl
Iodides and Bromides
J. Chem. Phys. 73, 2115 (1980) [NDRL-2106]

N. Selvarajan and N. V. Raghavan
Reaction of OH with Pyridine. Pulse-Radiolytic and Product-Analysis Studies
J. Phys. Chem. 84, 2548 (1980) [NDRL-2108]

R. D. Janz, D. J. Vanecek and R. J. Field
Composite Double Oscillation in a Modified Version of the Oregonator
Model of the Belousov-Zhabotinsky Reaction
J. Chem. Phys. 73, 3132 (1980) [NDRL-2112]

P. Natarajan

Direct Determination of the Rate Constant for the Reaction of Molecular Oxygen with a Cobalt(II) Ammine Complex
Inorg. Chimica Acta 45, L199 (1980) [NDRL-2121]

W. P. Helman and A. B. Ross

Radiation Chemistry Data Center: Information Services Produced from the Bibliographic Data Base
Radiat. Phys. Chem. 16, 425 (1980) [NDRL-2126]

G. N. R. Tripathi

Resonance Effect in the Ultraviolet Raman Spectra of Styrenes: Nature of the Photoreactive States
Chem. Phys. Letts. 74, 232 (1980) [NDRL-2127]

John Bentley

Effect of Potential Wells on Rotational Rainbow Structure
J. Chem. Phys. 73, 4708 (1980) [NDRL-2140]

D. M. Chipman and J. O. Hirschfelder

On Symmetry in the Polarization Expansion for Intermolecular Forces
J. Chm. Phys. 73, 5164 (1980) [NDRL-2150]

E. Janata and R. H. Schuler

Direct Observation of the Protonation of Acetone Ketyl Radical by Conductometric Pulse Radiolysis
J. phys. Chem. 84, 3351 (1980) [NDRL-2184]

V. Grebel

Porphyrins and Chlorophylls. I) Electron Transfer in Isotropic Solutions. II) Triplet State in Liquid Crystals
MS Thesis, Hebrew University, Jerusalem, Israel (1980) [SR-56]

External Talks and Presentations

R. W. Fessenden

"Measurement of the Dipole Moments of Photochemical Transients"
University of New Orleans, New Orleans, Louisiana
October 23, 1980

R. H. Schuler

"Interactive Computer Methods for Data Acquisition and Processing",
"Track Processes in Radiation Chemistry" and "Radiation Chemical Studies of the Oxidation and Reduction of Aromatic Systems"
The Hebrew University, Jerusalem, Israel
November 2, 19, 1980
"ESR Studies of Transient Radicals"
The Weizmann Institute, Rehovot, Israel
November 20, 1980

P. Neta

"Redox Properties of Free Radicals"
Catholic University of Puerto Rico, Ponce, Puerto Rico
December 22, 1980

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

I. (NDRL-2183) Transient Phenomena in the Pulse Radiolysis of Retinyl Polyenes. I. Radical Anions¹

(N.V. Raghavan and P.K. Das)

ABSTRACT: The spectra, and kinetics of formation and decay of radical anions of a number of retinyl polyenes have been studied in methanol at room temperature using pulse radiolysis and kinetic spectrophotometry. The bimolecular rate constants for the attachment of solvated electrons, e_{MeOH}^- , to the retinyl polyenes are in the diffusion-controlled limit ($8.6 \times 10^9 - 1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). The radical anions of retinol and retinol acetate have their spectral maxima at 370-390 nm, and undergo decay very slowly with second order kinetics. On the other hand, the radical anions of retinal, retinyl n-butylamine Schiff base and retinoic acid/ester have spectral maxima at 430-480 nm, and decay by first order kinetics with rate constants in the range $1.4 \times 10^4 - 1 \times 10^6 \text{ s}^{-1}$. The decay rate constant of retinal radical anion is decreased by a factor of thirty-five on going from methanol to less acidic alcohol, isopropanol, suggesting that protonation is the mode of its decay in protic media. In the case of retinyl Schiff base, an additional slow process with bimolecular rate constant, $1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, is observed for the formation of radical anion and is ascribed to the reaction with methanol radical, $\cdot\text{CH}_2\text{OH}$.

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

II. (NDRL-2184) Direct Observation of the Protonation of Acetone Ketyl Radical by Conductometric Pulse Radiolysis¹

(E. Janata and R.H. Schuler)

ABSTRACT: Improvements in conductometric pulse radiolysis methods allow direct observation of the protonation of the acetone ketyl radical anion on the 10 nsec time scale. The protonation period of 9.7 ± 0.5 nsec determined here is in good agreement with that estimated from the ESR line broadening studies of Laroff and Fessenden.

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

III. (NDRL-2185) Electron Spin Lattice Relaxation Times of Transient Free Radicals¹

(R.W. Fessenden, J.P. Hornak and B. Venkataraman)

ABSTRACT: The saturation recovery method has been used to measure the electron spin relaxation times of short-lived free radicals in solution. The radicals were produced by continuous in situ radiolysis with a 2.8 MeV electron beam (except for two cases where stable radicals were formed by air oxidation). The ESR spectrometer used broad-band amplification of the detected ESR signal (time constant, 100 ns) and signal averaging by means of a transient recorder and minicomputer. The magnetic field was stepped off the ESR line for alternate saturating pulses; the phase of the microwave saturating pulse could be changed by 180° to allow separation of the saturation recovery and free induction decay. The sensitivity was such that T_1 values greater than 1 μ s could be determined for samples of 10^{14} spins (i.e. 3×10^{-6} M radical in 50 μ l) if the ESR line width was 100 mG and transient curves from 40,000 saturating pulses were averaged. Somewhat smaller values of T_1 could be determined with higher radical concentrations. To achieve this sensitivity, it was necessary to use observing microwave powers which significantly perturbed the recovery signal so that an analysis in terms of an exponential decay of the ESR signal to the steady state value was not possible. Curve fitting of solutions to modified Bloch equations was used. Values of T_2 were determined from the damping of Torrey oscillations. Values of T_1 were determined for p-benzosemiquinone anion (2.0), the 2,5-di-tert-butyl analog (11.5), ascorbate anion radical (2.3), chelidonic acid trianion radical (5.0), 1,2-dicarboxylvinyl radical (9), and H atoms (12), all values in microseconds and accurate to about $\pm 10\%$. The radicals were produced in aqueous solution except for the semiquinones which were in ethanol. The values of T_2 were similar to the corresponding T_1 except for ascorbate radical and 2,5-di-tert-butyl-p-benzo-semiquinone anion where unresolved splittings made the apparent values smaller.

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

VI. (NDRL-2186) Temperature Dependence of Hopping Transport in Disordered Solids¹

(W.H. Hamill)

ABSTRACT: The time- and temperature-dependent drift mobility μ_d for transient photocurrents in disordered solids is $\mu_d(T, t) = L/Et_T$ in terms of distance L , field E and transit time t_T . Since current $I \propto t^{-(1-\alpha)}$ for $t < t_T$ and $0 < \alpha < 1$ by Scher-Montroll theory for hopping, among localized states, it can be shown that $\mu_d(T) = \alpha[\mu_d(T, t)]^\alpha (L/Et)^{1-\alpha}$ where $\tau \sim 10^{-3}$ s is estimated. Further $\mu_d(T) \propto \exp(-\Delta/T)$ and the activation energy Δ is time independent. On this basis Δ for the carbazole polymers is ca. zero, that for a-Se is ca. 0.05 eV, and that for a-As₂Se₃ is 0.35 eV rather than 0.5, 0.3 and 0.6 eV respectively on a phenomenological basis for $\mu_d(T, t)$.

(1) Submitted for publication in Applied Physics Letters

V. (NDRL-2187) The Critical Point Correlations of the Yvon-Born-Green Equation¹

(G.L. Jones², J.J. Kozak, E. Lee, S. Fishman³ and M.E. Fisher³)

ABSTRACT: The critical behavior of the Yvon-Born-Green integral equation for fluids is analyzed by a moment expansion which yields a nonlinear differential equation accurately describing the long-range correlations. Phase plane analysis show that for dimensions $d \leq 4$ a critical point is characterized by $\eta = 4-d$ with $g(r) - 1$ negative for large distances, r , in contrast to normal expectations. For $d > 4$ the differential equation allows $[g(r)-1] > 0$ and $\eta = 0$ or $4 - d$. The compressibility never diverges if $d = 1$.

(1) Submitted for publication in Physical Review Letters
 (2) Department of Physics, University of Notre Dame
 (3) Baker Laboratory, Cornell University

VI. (NDRL-2188) Optical Response of Excess Electrons in Dielectric Liquids¹

(K. Funabashi)

ABSTRACT: Excess electrons in polar liquids have been known to give rise to broad asymmetric absorption spectra in visible region. Since the pioneering work of Jortner, theoretical analyses of the absorption spectra have been based almost exclusively upon the use of total wavefunctions which have the product form of electronic and nuclear wavefunctions. Namely, the Born-Oppenheimer (B-O) separability has been imposed over the entire extended system.

The optical absorption spectra and DC mobility of excess electrons are related by the velocity-velocity correlation function in the Kubo formula. However, all the wavefunctions of B-O product form, regardless of how elaborate its derivation is, are not useful in calculations of DC mobilities; they all predict zero mobility regardless of temperature, even though the application of the Kubo formula with the same wavefunctions predicts an optical absorption spectrum. The current status of the theoretical predictions on the absorption spectra is critically examined. The main unsolved problem is to explain the line shape; width and asymmetry, rather than the peak transition energy.

The Kubo formula with small-polaron wavefunctions, which do not have the B-O product form, can be shown to result in a finite DC mobility, as well as a theoretical line shape, which is in an excellent agreement with experiment. Physical meaning of the absorption spectra is no longer given by the electronic resonance transition of (1s)→(2p) type, but becomes the vibronic non-resonant electron transfer transition. Additional UV transitions can also be predicted.

(1) Submitted for presentation at the Seventh International Conference on Conduction and Breakdown in Dielectric Liquids, Berlin, West Germany, July 27-31, 1981.

VII. (NDRL-2189) Transient Species in the Photochemical Decomposition of Cobalt(III)-Diketonate Complexes¹

(G. Ferraudi, P. Groutsch² and Ch. Kutal²)

ABSTRACT: Flash photolysis $\lambda_{\text{excit}} \geq 240$ nm reveals that a long lived transient species ($t_{1/2} \sim 10$ sec) mediates in the decomposition of $\text{Co}(\text{tfa})_3$, tfa=trifluoroacetylacetone, in deaerated cyclohexane. Such species was tentatively assigned as a metastable cobalt(III)-carbonion complex which decomposes in cobalt(II) products. Species which donate hydrogen more easily than methanol or cyclohexane, namely $\text{HSn}(\text{n-Bu})_3$ or 2-propanol, are able to inhibit the formation of the transient. Moreover, the decay of the species is accelerated by methanol or 2-propanol. A mechanism, based on the formation of cobalt(III)-carbonion complexes as one alternative reaction channel, is proposed. The photochemistry of the cobalt(III) diketonate complexes is compared with that of the corresponding Rh(III) and Cr(III) complexes.

-
- (1) Submitted for publication in Inorganic Chemistry
 (2) Department of Chemistry, University of Georgia
-

VIII. (NDRL-2190) A Laser Flash Photolysis Study of Electron Transfer Reactions of Phenolate Ions with Aromatic Carbonyl Triplets¹

(P.K. Das and S.N. Bhattacharyya)

ABSTRACT: Light-induced electron transfer reactions from phenolate ions to a variety of carbonyl triplets have been studied in aqueous acetonitrile using 337.1 nm laser flash photolysis. In particular, the effects of carbonyl triplet nature and substitution in phenolate ions have been examined in respect of both kinetics and primary photoproduct yields. The rate constants for electron transfer are found to be in the range, $2 \times 10^9 - 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The quantum yields of primary photoproducts (phenoxy radicals and radical anions of carbonyl compounds) are essentially unity except with p-bromo- and p-iodophenolate ions. With p-iodophenolate ion, the yields of ketone-derived radical ions are in the range 0.3-0.5, and remain practically unchanged on increasing temperature from 23 to 75°C. This result suggests the involvement of heavy atom induced intersystem crossing and/or back electron transfer at some stage(s) of the electron transfer reaction mechanism.

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

IX. (NDRL-2191) Intramolecular Electron Transfer and Dehalogenation of Anion Radicals. IV. Haloacetophenones and Related Compounds¹

(D. Behar and P. Neta)

ABSTRACT: Halogen substituted acetophenones and several other carbonyl and carboxyl derivatives were reduced with e_{aq}^- in irradiated aqueous solutions to produce the anion radicals. In certain cases, reduction by $(CH_3)_2CO^-$ was also used. The anion radicals undergo intramolecular electron transfer and dehalogenation to yield inorganic halide ions. The rates of these reactions varied over a wide range (10^1 - 10^7 s⁻¹) and were strongly dependent on the nature of the halogen and the other substituent and their relative positions in the molecule. The results obtained here are discussed along with previous measurements on cyano and nitro derivatives. The rate of dehalogenation is found to be dependent on the electron affinity of the other substituent on the ring. Hammett's substituent constants do not correlate with the observed rates. However, spin density distribution in the anion radicals, as derived from ESR parameters, yields a good qualitative correlation. Increased spin density on the ring carbon bearing the halogen is accompanied by an increase in the rate of C-X bond scission. The spin density represents in this case the negative charge density, since protonation of the anion radicals results in minor changes in spin densities but causes a dramatic decrease of the rate of dehalogenation.

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

X. (NDRL-2192) Controversies in the Tunneling Mechanism¹

(K. Funabashi)

ABSTRACT: Contrary to Tachiya's assertion, the decay law of the tunneling mechanism for hydrated electrons can not be obtained as a special case of the random-walk mechanism, in which the number of steps required for reaction is restricted to one. The difference between the tunneling and random-walk mechanism can be traced back to those of the physical picture for the hydrated electron and the underlying quantum mechanics of excess electrons in polar molecular aggregates; quantum mechanics for rigid and nonrigid potentials. The latter difference also leads to a new interpretation of the absorption spectra of hydrated electrons.

(1) Submitted for publication in the Japanese Journal of Radiation Chemistry

XI. (NDRL-2193) Electron Transfer Reactions from Aromatic Carbonyl Triplets to Paraquat Dication¹

(P.K. Das)

ABSTRACT: The rate constants for electron transfer reactions from several aromatic carbonyl triplets to paraquat dication leading to the formation of paraquat radical ion have been measured by nanosecond laser flash photolysis and are found to be in the range, $1 - 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

(1) Submitted for publication in Tetrahedron Letters

XII. (NDRL-2194) Radiation Chemical Studies of Ni-glycine. Hydrogen Abstraction by OH Radicals and Oxidation by Br_2^- ¹

(S.N. Bhattacharyya and P. Neta)

ABSTRACT: Reactions of hydroxyl radicals with Ni(II)-glycine complexes were studied by pulse radiolysis and by product analysis. Radiolytic degradation of the complexes in N_2O saturated solutions leads to the formation of carbonyl compounds. The nature and yield of these products indicate that the transient formed by reaction of OH with the complex undergoes disproportionation. The optical absorption spectrum of this transient exhibit a maximum below 250 nm, which is similar to that observed with glycine alone. The reaction of Br_2^- with the complex is found to be too slow to be observed by pulse radiolysis. However, the reaction occurs in steady-state radiolysis and yields different products than those observed with OH. Specifically, the yield of formaldehyde is appreciably higher in the presence of Br_2^- . It is concluded that Br_2^- oxidizes the metal center of the Ni(II)-glycine complex to Ni(III), whereas OH reacts by hydrogen abstraction to form Ni(II)-coordinated glycine radical.

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

XIII. (NDRL-2195) Resonance Raman Scattering of Semiquinone Radical Anions¹
(G.N.R. Tripathi)

ABSTRACT: The time resolved electronic absorption spectra of p-benzosemiquinone (PBSQ) and 2,5-di-t-butyl-p-benzosemiquinone (DTBSQ) radical anions are obtained in pulse radiolysis. The same radicals have been generated chemically in a flow system. The Raman spectra are excited by tuning a pulsed dye laser in the electronic absorption region. A time adjusted gate electronics has been used for the temporal resolution of the Raman spectra from fluorescence. The resonance effect has been utilized to record the Raman spectra of unstable semiquinone radical anions, 10^{-3} - 10^{-4} M in concentration. The observed Raman spectra and excitation profile are interpreted to assign the electronic and the vibrational transitions in the radicals. The semiquinone radical anions are fairly stable on photo-irradiation above 330 nm.

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

XIV. (NDRL-2196) Rate Constants for Reactions of Aliphatic Carbon-Centered Radicals in Aqueous Solutions^{1,2}
(A.B. Ross and P. Neta)

ABSTRACT: Rate constants have been compiled for reactions of various transient aliphatic radicals produced mostly by radiolysis in aqueous solutions. In certain cases the radicals have been produced by photolysis or by a thermal chemical reaction. Data are included for aliphatic carbon-centered radicals only, i.e. substituted alkyl radicals in the broad sense, but not for oxyl or aminyl radicals. Reactions of the aliphatic radicals with inorganic and organic compounds are included.

(1) Submitted for publication to NSRDS-NBS

(2) Supported by Environmental Research and Development and the Office of Standard Reference Data of the National Bureau of Standards

XV. (NDRL-2197) Direct, Continuous Observation of Light Dependent Changes in the Intravesicular pH of Bacteriorhodopsin Proteoliposomes¹

(D.H. Bell, N.R. Clement², L.K. Patterson and J.M. Gould²)

ABSTRACT: Anionic soybean phospholipid vesicles incorporating the light-driven proton pump bacteriorhodopsin have been formed by a sonication procedure with the pH sensitive membrane-impermeant fluorescence probe 8-hydroxy-1,3,6-pyrenetrisulfonate (pyranine) entrapped within the intravesicular aqueous compartment. Illumination of the reconstituted proteoliposomes caused changes in the fluorescence intensity of entrapped pyranine indicative of an increase in hydrogen ion concentration within the proteoliposomes. The fluorescence change had a half-time of 15-30 seconds. The maximum extent was linearly proportional to the actinic light intensity, the amount of bacteriorhodopsin present during sonication, and the duration of the sonication period. The rate of the light-dependent fluorescence change was enhanced by the K⁺ ionophore valinomycin, and was abolished by the uncoupler gramicidin. It is concluded that the fluorescence intensity of vesicle-entrapped pyranine can be employed as a useful probe for continuous, real-time measurements of hydrogen ion concentration within reconstituted proteoliposomes.

(1) Submitted for presentation at the 25th Annual Meeting of the Biophysical Society, Denver, Colorado, February 22-25, 1981.

(2) Department of Chemistry, University of Notre Dame

XVI. (NDRL-2198) Bibliographies on Radiation Chemistry: II. Studies of the Chemistry of Semiquinones^{1,2}

(A.J. Swallow,³ A.B. Ross and W.P. Helman)

ABSTRACT: This bibliography lists about 280 papers dealing with the formation, properties and reactions of free radicals containing the 1,2- or 1,4-benzosemiquinones moiety, produced in irradiated systems. Chemical, biological and electrochemical generation of the intermediates are not covered. Papers on reduction of quinones or oxidation of hydroquinones containing no quantitative information on the semiquinone intermediates are likewise not included. The bibliography was prepared by a search of the Radiation Chemistry Data Center bibliographic data base.

(1) Submitted for publication in Radiat. Phys. Chem.

(2) Supported by Environmental Research and Development and the Office of Standard Reference Data of the National Bureau of Standards

(3) Paterson Laboratories, Christie Hospital and Holt Radium Institute, Manchester, England

XVII. (NDRL-2199) Photoinduced Dimerization of Macrocyclic Complexes¹

(S. Muralidharan and G. Ferraudi)

ABSTRACT: The triplet state of benzophenone oxidizes $\text{Ni}([\text{14}] \text{aneN}_4)^{2+}$ to a Ni(III) intermediate which subsequently produces the dimer of the complex as a product. The nature of the product was confirmed by structural studies. $[\text{Ni}(\text{13-At})]^+$ reacts with the triplet of fluorenone and ^2E state of $\text{Cr}(\text{bipy})_3^{2+}$ forming also a dimer in a reaction that involves different intermediates. Intermediates in the photoinduced oxidations of the macrocycles have been investigated by flash photolysis. The mechanism of the photoinduced oxidation is discussed in terms of the reported properties of the macrocycles.

(1) Submitted for publication in the Journal of Inorganic Chemistry

XVIII. (NDRL-2200) Analysis of Mechanisms for the Cyclic Cleavage of Water by Visible Light¹

(M.H. Dung and J.J. Kozak)

ABSTRACT: The cyclic cleavage of water by visible light via coupled redox catalysts in colloidal systems has recently been reported by Grätzel and coworkers. In this paper we present an in depth analysis of a mechanism for the consequent H_2 and O_2 production, focusing on the factors which may affect the stability of the photostationary state, the enhancement in the kinetics due to the presence of colloiddally-dispersed noble metal (oxides), and the sensitivity of the yield to the system parameters (intensity and illumination of the source). Emphasis is placed on comparison with the experimental data reported for the H_2 and O_2 production. The analysis and, especially, our simulations show that the underlying, coupled chemical network, when triggered by the absorption of light, behaves as a true synergetic system; for example, increasing the efficiency of the reactions via the introduction of a colloiddally-dispersed catalyst enhances the effect of increasing the intensity of the radiation source. Our simulations show that there may be an upper limit on the effectiveness of this synergetic effect in producing H_2 and O_2 via a cyclic, water-cleavage reaction.

(1) Submitted for publication to the Journal of Photochemistry

XIX. (NDRL-2201) Pulse Radiolysis Conductivity Measurements in Aqueous Solutions with Nanosecond Time Resolution¹

(E. Janata)

ABSTRACT: A dc-conductivity apparatus is described which allows high precision time resolved conductometric measurements to be made beginning ~5ns after a fast electron pulse over a pH range from 3 to 11.5. A time resolution of 1.4 ns has been achieved by using a new type of cell made of glassy carbon and improved detection electronics. A rate constant of $k = 1.18 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ has been determined for the neutralization reaction $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ at pH = 10.64.

(1) Submitted for publication in Radiat. Phys. and Chem.

XX. (NDRL-2204) Intramolecular Electron Transfer and Dehalogenation of Anion Radicals¹

(P. Neta and D. Behar)

ABSTRACT: Aromatic compounds containing an electron affinic group on the ring and a halogen atom either on the ring or on a side chain were reduced by hydrated electrons or by $(\text{CH}_3)_2\text{COH}$ radicals to produce initially the corresponding anion radicals. These radicals, with the unpaired electron delocalized over the ring and the substituent (NO_2 , CN , COCH_3 , COC_6H_5 , CO_2^- , CHO), have finite lifetimes and undergo an intramolecular electron transfer whereby the negative charge becomes localized on the halogen atom to results in dehalogenation. The first order rates of dehalogenation were determined by kinetic spectrophotometric pulse radiolysis for the various halogens attached at various positions on the ring or the side chain. The rates ranged from $>10^7$ to $<1 \text{ s}^{-1}$ and were strongly dependent on the structure of the anion radical. The general trends are $\text{I} > \text{Br} > \text{Cl} > \text{F}$; $\text{O} > \text{p} \gg \text{m}$; $\text{ArCH}(\text{CH}_3)\text{X} > \text{ArCH}_2\text{X} > \text{ArCH}_2\text{CH}_2\text{X} \sim \text{ArX}$; and $\text{CO}_2^- > \text{CN} > \text{COCN}_3 > \text{CHO} > \text{NO}_2 \sim \text{COC}_6\text{H}_5$. The results indicate the importance of the C-X bond dissociation energies and the spin density distributions on the anion radicals in determining the rates of dehalogenation.

(1) Submitted for presentation at the Third International Symposium on Organic Free Radicals, Freiburg, Germany, Aug. 31-Sept. 4, 1981

XXI. (NDRL-2205) Trapped Electrons in Non-rigid Potentials; Solvated Electrons¹

(K. Funabashi)

ABSTRACT: The concept of the small polaron is applied to the hydrated electron. Inadequacies of the existing single-site formulation are exhibited by the linear response theory of Kubo as applied to the calculation of the d.c. mobility and the absorption spectrum. In the new approach, the key step is simply to recognize the degeneracy of the ground vibronic states for the hydrated electron, or alternatively to allow the excess electron to be localized at any intermolecular site of the liquid, reflecting the non-rigidity of the potential. The orientational polarization model is used to show that the conventional $(1s) \rightarrow (2p)$ transition and the electron transfer transition in the non-rigid potential could have an identical transition energy of about 2eV, but the line width for the electron transfer mode is larger by about 50%.

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

XXII. (NDRL-2206) Studies of Radiation Induced Peroxidation in Model Lipid Systems¹

(L.K. Patterson)

ABSTRACT: Studies of irradiation induced lipid peroxidation in fatty acid micelles, both from these laboratories and others, are briefly summarized. Steady state measurements have shown the dependence of hydroperoxide yield on the state of aggregation in the lipid and the degree to which the reactive sites are closed packed. Chromatographic measurements obeyed the square root dependence of yield on dose rate confirming the proposed chain mechanism. Application to antioxidant studies have demonstrated the highly efficient blockage of the peroxidation chain by α -tocopherol and the subsequent prooxidant effect of the product formed. Time resolved studies have been used to determine rate information for $\cdot\text{OH}$ -lipid interaction, radical transfer within the lipid, radical peroxidation, lipid radical movement across the micellar boundary, chain termination, and radical interaction with α -tocopherol. Compli-

mentary laser studies have demonstrated, in contrast to $\cdot\text{OH}$ behavior, the comparatively high degree of selectivity exhibited by alkoxy radicals toward allylic lipid sites.

(1) Submitted for presentation at the Gordon Conference on Oxygen Radicals in Biology and Medicine, Ventura, California, January 11-16, 1981.

XXIII. (SR-56) Porphyryns and Chlorophylls I) Electron Transfer in Isotropic Solutions. II) Triplet State in Liquid Crystals¹
(V. Grebel)

ABSTRACT: I. One-electron oxidations of various metalloporphyrins in dichloroethane solutions were studied by kinetic spectrophotometric pulse radiolysis. Co(II)-TPP was found to produce Co(III)TPP while the Cd(II), Cu(II), Pb(II), and VO complexes, like the ZnTPP and MgTPP, yield the cation radicals. Ni(II)-TPP is oxidized at the metal center in the presence of pyridine but at the ligand in its absence. The Co(II)TPP by the above cation radicals was also followed. The rate constants for these reactions were found to be mostly in the range of $3-5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, much lower than the expected diffusion-controlled rates.

II. An EPR study of the photoexcited triplet state of porphyrins, Chl a and the covalently linked dimer of Zn pyrochlorophyllide a, in a liquid crystal, is reported. The metalloporphyrins interact to form excimers. The low intramolecular energy transfer rate in the dimer ($<10^6 \text{ s}^{-1}$) suggests that the unfolded form predominates.

(1) Submitted to The Hebrew University of Jerusalem in partial fulfillment of the requirements for the Degree of Master of Science, October 1980. Experiments in Part I were conducted at the Radiation Laboratory, University of Notre Dame.

Other investigations in progress include:

XXIV. Hyperfine Coupling Constants in Methyl Radical

(D. M. Chipman)

A new computer program has been completed which allows ab initio calculation of both isotropic and anisotropic hyperfine coupling constants (hfcc) in doublet radicals by a single-excitation configuration interaction method. This incorporates the results of a theoretical derivation of the explicit form of the spin density natural orbitals in this model, thereby providing an unambiguous means of separating core and valence electron contributions to the hfcc.

The method has been applied to methyl radical, with some interesting results. For planar methyl, calculations with a good split-valence basis set give $a(^{13}\text{C}) = 30.4 \text{ G}$ and $a(^1\text{H}) = -31.3\text{G}$ as compared to the experimental results of 28.0 and -24.5G , respectively. The anisotropic hfcc agree even more closely with experiment, as does the variation of the isotropic hfcc with bond angle. The value of $a(^{13}\text{C})$ for planar methyl is calculated to have a surprisingly large contribution of -34.1G from the 1s core electrons on carbon, which is balanced by a $+64.6\text{G}$ contribution from the valence electrons. The relative weight of the core and valence contributions to the spin polarization part of the hfcc is found to be insensitive to large changes in the bond angle in methyl radical, but does depend on the bond length. This suggests that semiempirical methods such as INDO, in which the use of a single parameter to describe both the core and valence contributions prevents them from varying independently, will not be able to satisfactorily predict the dependence of hfcc on changes in bond lengths.

XXV. Theoretical Calculations on 4-membered Heterocyclic Ring Systems

(D. J. Pasto¹ and D. M. Chipman)

Ab initio calculations have been performed on cyclobutane and on a variety of heterocyclic ring systems derived from cyclobutane. The compounds studied involve a methylene, oxygen, sulfur or a carbonyl group at one ring position and, in addition, all possible combinations of

two of these groups at the 1- and 3- ring positions. It has been possible to rationalize the orbitals in all of these systems in terms of simple interactions among the orbitals of the constituent fragments, which were calculated separately. This approach also provides quantitative information on the relative importance of through-bond and through-space interactions between the 1- and 3- positions. A variety of arguments and calculations are presented to show that previous literature assignments of the first two ionization potentials in 1,3-cyclobutadione, involving the symmetric and antisymmetric combinations of the nonbonding pairs of electrons on the oxygen atoms, are in the incorrect order.

(1) Department of Chemistry, University of Notre Dame

XXVI. Absorption Spectra of Solvated Electrons in THF

(H. Karasawa and K. Funabashi)

Solvated electrons in ammonia and water have been known to have separate absorption bands in UV region in addition to the main band in the visible (or IR) region. There are some indirect experimental evidences that trapped electrons in 3MP and MTHF also have additional UV absorption bands. In order to find out the generality of the two-component-structure of the absorption spectra for solvated electrons, the optical absorption spectra of solvated electrons in THF solutions of potassium with dicyclohexano-18-crown-6 have been studied. Preliminary results indicate a new absorption at ~ 560 nm in addition to the main band at ~ 2000 nm. Spectroscopic characterization of this new transition is being investigated.

XXVII. Track Theory of Heavy-Ion Radiolysis

(J.A. LaVerne and A. Mozumder)

We are developing a track model which separates the contribution to the total differential radiolytic yields in water arising from the track core and from secondary electrons (delta rays). We have applied the model in the determination of the ferric ion yield in aerated ferrous sulfate solutions irradiated with helium, deuteron and proton ions.

Different ions having the same charge-to-velocity ratio deposit equal amounts of energy per unit pathlength in the track core. Also two ions of equal charge-to-velocity ratio have essentially the same delta-ray spectrum if the maximum transferrable energy ($2mv^2$) is large compared to the mean excitation potential (I). Thus the contribution to the differential ferric ion yield for these ions can be taken to be the same. To determine the delta ray contribution we must know the integral ferric ion yield for low energy electrons. No measurements of the integral ferric ion yield have been made for electrons with initial energy less than 5.7 keV, i.e., that from tritium beta particles. Much qualitative work has been done on the radiolysis of low energy electrons and we are currently making estimations of the integral ferric ion yield with low energy electrons.

XXVIII. Electron Thermalization in Liquid Argon

(A. Mozumder)

The technique of pseudo-Maxwellian solution of the Boltzman transport equation for hot electrons in gases as developed earlier by this author is now being extended for use in liquefied rare gases. As is well known in these systems elastic collisions appear in two different forms - one for momentum relaxation (σ_1) and another one for the energy loss (σ_0). They are related by the structure factor which is well known only for LAr. Further the scattering cross sections in the liquid and in the gas are generally different. Recent transport experiments of Doke et al are being analysed to give the relevant cross sections as functions of impact energy. They will be used to give the thermalization time and positional broadening using the following equation written in a simplified form:

$$D(t) = (3N)^{-1} \langle v/\sigma_1(v) \rangle$$

$$\frac{d\langle T \rangle}{dt} = \frac{2}{3k} \langle \sigma_0 \left[\frac{1}{2}mv^2 - \frac{3}{2}kT \left(\frac{4}{3} + \frac{1}{3} \frac{v}{\sigma_0} \frac{d\sigma_0}{dv} \right) \right] \rangle$$

$$\xi = \int_0^t D(t^1) dt^1$$

$$n(\vec{r}) = (4\pi\xi)^{-3/2} \exp(-r^2/4\xi)$$

In the above equations $\langle \dots \rangle$ denotes the average value over the distribution function and the symbols have their usual meanings as detailed in an earlier paper (J. Chem. Phys. 72, 1657 (1980)). The aim is to obtain the effective electron temperature $\langle T \rangle$ and width of position distribution $\xi^{1/2}$ as functions of time.

XXIX. Hot Electron Cooling in Molecular Gases

(A. Mozumder)

Unlike rare gases, electron cooling in molecular gases is provided mainly by inelastic processes, the final thermalization being dominated by vibrational and rotational excitation. Since in most cases rotational spacing is quite small rotational de-excitation is also important. In the extreme long-time scale momentum transfer collisions may contribute significantly to the energy-loss rate. Otherwise a kind of dichotomy seems to be operative; that is inelastic processes determine cooling rate and therefore the thermalization time-scale whereas elastic collisions determine the diffusion co-efficient and togetherwith the thermalization time give the positional broadening at thermalization.

Basic formulas for electron-induced excitation have been compiled from the literature for H_2 which is the first molecular gas being studied. Rotational excitation cross-section has been obtained from Takayanagi and Itikawa. De-excitation cross-sections are derived from excitation cross sections using microscopic reversibility paying due attention to degeneracy factors which is very important for rotational levels. As a byproduct of this study a time-dependent rate for excitation (and de-excitation) under electron impact has been formulated. These rates involve a pair of well-defined levels of the molecule and in the long-time limit the rates of excitation and de-excitation exactly cancel each other obeying detailed balance.

XXX. Electron Capture in Rare Gases in Competition with Thermalization

(A. Mozumder)

In the gas phase electron attachment cross-section for a variety of nondissociative and certain dissociative reactions varies as some inverse power of the velocity. This concept has been used to extend earlier work of the author (J. Chem. Phys. 72, 1657, (1980); 72, 6289 (1980)) to estimate the extent of epithermal scavenging in a rare gas in competition with thermalization when the scavenger is present as a minor component. For the surviving fraction electron cooling rate is the same as in the pure gas while the scavenging rate is to be calculated using a time-dependent velocity distribution function (pseudo-Maxwellian) and a velocity dependent attachment cross-section as follows:

$$k(t) = \int 4\pi v^3 \sigma_r(v) \left(\frac{m}{2\pi k_B \langle T \rangle} \right)^{3/2} \exp(-mv^2/2k_B \langle T \rangle) dv$$

$$\sigma_r(v) = Av^{-\beta}$$

In the above equations $\langle T \rangle$ is the time-dependent effective electron temperature obtained as in the earlier studies and the parameters A, β are available from swarm data. Numerical integration of rate equations up to the thermalization time gives the probability of escaping epithermal scavenging. Study of about a dozen scavengers under progress at present indicate: (i) epithermal scavenging is ubiquitous, time-dependent and varies exponentially with the scavenger concentration, (ii) generally, epithermal scavenging decreases with gas temperature and (iii) for very reactive molecules such as CCl_4 or SF_6 relative scavenger concentration need to be ~ 1 ppb or less if significant hot electron scavenging is to be avoided in rare gas systems. Electron attachment-detachment along with thermalization is also being investigated in rare gases taking SF_6 as an example.

XXXI. Electron Attachment in Nonpolar Liquids

(W. H. Hamill)

A fascinating feature of electron attachment in nonpolar liquids is the possibility to change electron energy ϵ and mobility μ isothermally by choice of the medium over a range >0.5 eV and $>10^4$ cm²V⁻¹s⁻¹. This changes the rate constant by several orders of magnitude, often giving a maximum in k . This has been interpreted as an effect of ϵ , by analogy with the gas phase, but the "one-over-v" law describes the time dependence. When ϵ is high and mobility μ is low, $k \propto \mu$. For low ϵ and large μ , k is often much less but not thermally activated and only exoergic attachment occurs. To examine the role of μ , molecule and ion have different configurations, requiring time θ , while the residence time of e^- is $\tau \propto \mu^{-1}$. In terms of $e^- + A \xrightleftharpoons[1]{2} (e^-, A) \xrightarrow{2} \text{product}$ and $k = k_1[k_2/(k_{-1} + k_2)] = k_1[1 - \exp(-\tau/\theta)]$. Since $k \propto \mu$, $k \rightarrow \text{const.}$ at large μ for very efficient acceptors ($\theta \approx 10$ fs, e.g. SF₆). For inefficient acceptors ($\theta \approx 1$ ps, e.g. C₂H₅Br), following an initial increase in k with increasing μ , $\exp(-\tau/\theta)$ decreases rapidly at $\mu > 1$ cm²V⁻¹s⁻¹.

XXXII. Structures of Metal-Water Bimolecular Complexes

(J. Bentley)

The recent observation by Margrave and coworkers of matrix IR spectra of metal-water complexes prompted the application of a previously proposed (NDRL-2066) semiempirical electrostatic model to predict their structures and binding energies. However, experimental characterizations of this kind of complex do not exist, and the existing theoretical studies are so divergent in basis set and accuracy as to provide an unsatisfactory data base for the model. To remedy this, the minimum energy C_{2v} structures of the complexes M...OH₂ (M=Li, Be, B, Na, Mg, Al) have been calculated using uniform basis sets for the entire series. To compensate for deficiencies in the basis sets, the function counterpoise correction of Bernardi and Boys has been applied. The results are as follows: (i) The dissociation energies of the complexes can be estimated using only the electrostatic potentials of their constituents. (ii) Calculations which do not give a good representation of water's dipole moment give quite inaccurate energies. (iii) The counterpoise correction decreases the dissociation

energy by 0.7 to 1.9 kcal/mole. Thus, previous reports of bound MgOH_2 and BeOH_2 complexes [Frurip and Curtiss, Chem. Phys. Lett. 75 69 (1980)] are probably in error.

XXXIII. Electron Spin Densities for LiOH_2 in Argon Matrices

(J. Bentley)

In conjunction with the foregoing study on metal water complexes, the electron spin densities and hyperfine coupling constants for lithium and hydrogen in the complex $\text{Li} \dots \text{OH}_2$ have been calculated. Agreement with the data of Margrave et al in argon matrix is quite good. The ESR spectra indicate two forms of the complex, one of which disappears when the matrix is annealed. The present calculations strongly suggest that the difference between the two is in the configuration of the matrix cavity rather than in that of the complex. Attempts are under way to characterize the matrix cavity by means of a model due to Adrian.

XXXIV. CO Desorption and Adsorption on PT(III)

(D. H. Winicūr, J. Hurst¹, C. A. Becker¹ and L. Wharton¹)

The Low-Energy Molecular-Beam-Scattering (LEMS) data previously reported has been re-analysed using a new power-law functional form to relate the surface coverage to fractional attenuation of the helium probe beam. This form produces equivalent coverage values for the kinetic desorption and equilibrium adsorption experiments which are consistent with the values reported in the literature.

The first-order Arrhenius desorption rate constant is $1.6 \times 10^{14} \exp(-31.1 \text{ kcal/mole/RT}) \text{ sec}^{-1}$. The value obtained for the activation energy is independent of the coverage model used. The temperature dependence of the equilibrium adsorbed CO between 400°K and 600°K indicated that the adsorption energy decreases linearly with coverage with an average value of $31.1 \pm 1.2 \text{ kcal/mole}$. The agreement between these values (which also agree with the thermal desorption measurements of McCabe and Schmidt) provides evidence that the proposed functional form is reasonable.

(1) University of Chicago

XXXV. Resonance Raman Scattering of Semiquinone Radical Anions
(G. N. R. Tripathi)

The physico-chemical properties of semiquinones are of interest because of their role as radical intermediate in the important biological processes such as photosynthesis and mitochondrial electron transport. The optical spectra of semiquinone and related radical anions have been obtained in pulse radiolysis. The unstable semiquinone radical anions have also been generated chemically in a flow system and their resonance Raman spectra have been recorded. Raman spectra of 12 halogen, methyl and COOH substituted semiquinones have been obtained and analysed. Characteristic differences in the spectra are observed depending on the nature of the substituents and the symmetry of the molecules. The resonance enhancement of the 8a phenyl vibration in all the semiquinones has been assigned to the resonant electronic transition as ${}^2B_{3g} \rightarrow {}^2B_{1u}$ and not ${}^2B_{2g} \rightarrow {}^2A_u$ as suggested recently by Jaffe et al (1975) on the basis of CNDO calculations.

XXXVI. Construction of a Seven Meter Spectrograph for the Study of Reactive Intermediates in the Gas Phase
(J. L. Hardwick)

A high resolution spectrograph has been constructed and tests are in progress to determine its optical characteristics. The spectrograph consists of collimating optics with a focal length of 1.9 m; camera optics with a focal length of 7.0 m; and a 632 line/mm grating, 350 mm wide, blazed at 50° . Near the blaze angle, the aperture of the collimating optics is approximately f/8; the equivalent focal ratio for photographic detection is f/29 due to magnification of the image of the slit. Preliminary tests using a low pressure mercury lamp indicate that a resolution of 0.04 cm^{-1} can be attained without difficulty near the blaze of the grating, while resolution near 0.02 cm^{-1} can be achieved at higher grating angles with considerable loss of light. Thus, the resolution obtainable for most molecular spectra should be limited by Doppler width and pressure broadening rather than by instrumental resolution. This spectrograph is intended for examining intermediates present in flames, discharges and laser induced photodecompositions in the gas phase.

XXXVII. Radical Reactions in Combustion Chemistry

(D. H. Winicur and J. Hardwick)

The methoxy radical is an important intermediate in the photochemical reactions in the atmosphere and in the combustion of hydrocarbons. However, because of its instability, there have been very few direct measurements of its properties and no measurements of the rates of its reactions. A technique, using the reactions between metastably excited Ar^* (and Kr^*) and CH_3OH , in a flowing, cold-cathode discharge, has recently been reported to provide CH_3O radicals in sufficient quantity to yield spectral measurements. We have constructed a prototype flowing, cold-cathode discharge tube and have observed a very bright flame using an Ar^* and $\text{Ar}^* + \text{N}_2$ discharge. Encouraged by this initial success, we are attempting to quantify the discharge conditions and are proceeding to optimize the apparatus for the production of CH_3O radicals.

XXXVIII. Studies of Exciplexes by Microwave Dielectric Absorption

(R. W. Fessenden, N. Selvarajan and S. Vaidyanathan)

The microwave dielectric absorption method has been used to investigate the nature of any intermediates formed when excited states of aromatics such as anthracene and pyrene and also benzophenone are quenched by various amines in benzene solution. With the aromatics and amines such as dimethylaniline, relatively large dielectric absorption signals were seen and the decay periods matched those of the well-known exciplex fluorescence. The amplitudes suggest a dipole moment of the exciplex of about 10 D. Within the response time of the apparatus (~ 30 nsec) no instances of dark exiplexes were found (i.e., a dielectric signal with no corresponding fluorescence). Benzophenone was studied in combination with various amines. In the one case of DABCO (1,4-diazabicyclo[2.2.2]octane) a large signal with a decay half life of 60 nsec was found. From the optical spectrum (and the polar nature), the intermediate must be an ion pair (BP^- , DABCO^+) which then decays into a pair of neutral radicals. Further studies of this interesting intermediate are in progress.

XXXIX. Laser Photolysis of Aqueous Systems

(V. Nagarajan and R. W. Fessenden)

The laser flash photolysis apparatus is being used to study the behavior of various intermediates in aqueous solution with the aim of further clarifying reactions only partially understood from pulse radiolysis experiments. For example, a major concern in the latter has been on the mechanism of oxidation of various substrates by OH radical. In many cases, such as with bromide and chloride, an intermediate adduct has been demonstrated. Flash photolysis in a charge-transfer-to-solvent band results in the directly oxidized substrate and a solvated electron (which can be scavenged). A first example is iodide which is readily photolysed at 248 nm with the Kr-F excimer laser. Observation of the formation of I_2^- from $I + I^- \rightarrow I_2^-$ directly yields the rate constant of $1.1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. Addition of up to 0.1 M base has no effect on this reaction confirming that the equilibrium $I + OH^- \rightleftharpoons IOH^-$ favors the I atom. Further studies using 196 nm (Ar-F) to study the bromide and chloride systems are planned.

XL. Reactions Between Hydroxyl Radicals and α -Methyl-D-Glucopyranoside in Aqueous Solution

(K. P. Madden and R. W. Fessenden)

The major free radical product in 77K γ -irradiated single crystals of α -CH₃-D-glucopyranoside (α MeGlu) is the deprotonated C6 primary hydroxyalkyl radical. This radical, upon warming, undergoes a 1,2 hydrogen shift to produce a C5 secondary oxyalkyl radical. It is of interest to determine under which conditions this rearrangement might occur in aqueous solution.

In situ photolysis of H_2O_2 has been used to generate α MeGlu radicals in neutral aqueous solution for ESR studies. These radicals have been identified as the C7 primary oxyalkyl radical, the C2 secondary hydroxyalkyl radical, and the C6 primary hydroxyalkyl radical (for numbering scheme, see structure below). Studies of the reactions of these transient species,

particularly the conversion of the C6 primary hydroxyalkyl radical, are in progress.

α -CH₃-D-GLUCOPYRANOSIDE

XLII. Laser Flash Photolysis Study of Hydrogen Bonding Equilibria Involving Phenols

(K. Bobrowski and P. K. Das)

Utilizing the fact that the bimolecular rate constant (k_q) of the quenching of p-methoxyacetophenone triplet by a phenol is enormously decreased when the latter is hydrogen-bonded, we have developed a laser flash photolytic method of studying hydrogen bonding phenomena with phenols. Employing this method, we have determined, in various nonpolar solvents, the equilibrium constants for hydrogen bond formation between several phenols and a number of substrates with moderate to strong polar character (e.g., acetone to dimethylsulfoxide). The extent of decrease in the quenching rate constant (k_q) in the case of a particular phenol correlates well with the corresponding decrease in the phenolic O-H frequency on hydrogen bond formation with the same set of polar substrates.

XLIII. Hydrogen Abstraction by Acetophenone Triplets from Phenols: A Study of Substituent Effect

(N. Selvarajan and P. K. Das)

The nature of carbonyl triplet in acetophenone derivatives can be varied from one of primarily n, π^* type to one of primarily π, π^* type by suitable substitution in the benzene ring as well as in the α -position. We have carried out a laser flash photolysis study of hydrogen abstraction reactions of various α - and p-substituted acetophenone triplets with

phenols in benzene and wet acetonitrile. Although the rate constants (k) for triplet quenching are found to be relatively high (1×10^7 – $9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), the fraction of the quenching events that lead to net hydrogen abstraction (measured in terms of primary yields of phenoxy/ketyl radicals) is found to be in the range 0.2–0.5. The kinetic isotope effect, hydrogen vs. deuterium, is relatively large ($k_{\text{H}}/k_{\text{D}} = 2$ – 3.5), suggesting that the breaking of O–H bond is important in the development of the transition state. The variation of k with the nature of substituent in acetophenone and phenol follows a Hammett type relationship; this variation, however, is not as drastic as in the case of hydrogen abstraction from alcohols and hydrocarbons.

XLIII. Charge Transfer Interaction in the Lowest Singlet Excited State of All-trans Twenty-two Carbon Homologue of Retinal

(G. Hug, P. K. Das and N. Selvarajan)

Although the charge transfer interaction in the excited states of aromatic hydrocarbons has been the subject of numerous photophysical studies, there has been practically no work concerning similar interaction involving the excited states of polyenes. However, insight into the excited state charge transfer phenomena involving polyenes is important because of their implication in many photobiological processes including vision. Using all-trans C_{22} aldehyde ($\phi_{\text{F}} \sim 0.01$, $\tau_{\text{F}} \sim 0.7 \text{ ns}$, $\phi_{\text{T}} \sim 0.5$ in cyclohexane) as a model, we have carried out a study regarding the quenching of its fluorescence and triplet yield by various methyl and methoxy substituted aromatic hydrocarbons as well as a number of amines. The rate constants for quenching are very high (1×10^8 – $7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$); the trend in their variation with ionization potential of the quenchers suggests that the polyenal acts primarily as an electron acceptor.

xLIV. Photophysics of Linear Polyene Aldehydes and Schiff Bases of the Series, $\text{CH}_3-(\text{CH}=\text{CH})_n-\text{CH}=\text{X}$, $\text{X}=\text{O}$ and N-n-Bu

(P. K. Das, R. S. Becker¹ and G. Kogan¹)

The absorption and emission spectra of the polyenals of the series $\text{CH}_3-(\text{CH}=\text{CH})_n-\text{CHO}$ and their n -butylamine Schiff base derivatives are relatively well-resolved at 77K. Four band systems, assigned as arising from transitions to $^1(n, \pi^*)$, $^1\text{B}_u^*$, $^1\text{A}_g^{*+}$ and $^1\text{A}_g^{*-}$ states, have been recognized

in the absorption spectra. Three of these states, viz., $^1(n,\pi^*)$, $^1B_u^*$ and $^1A_g^{*-}$, are located very close to one another in the polyene derivatives with $n=4$ and 5. The radiative behavior of the polyenes, measured in terms of fluorescence quantum yields and lifetimes, is dictated by the relative location of these three low-lying singlet excited states.

(1) University of Houston

XLV. Photoinduced Redox Transformations in Macrocyclic Complexes.

I) The Case of the Rh(III) Phthalocyanines

(S. Muralidharan and G. Ferraudi)

The synthesis of the phthalocyanines of Rh(III) has been extended to new members of the series Rh(ph)X, X:Cl, Br, I, N₃, NCS. The nature of the complexes has been investigated by means of the UV-Vis spectrum, the elemental analysis and oxidative titrations. These complexes are stable in acetonitrile and acetonitrile-2-propanol mixtures for extended periods.

The same transients were photogenerated in irradiations of Rh(ph)Cl, Rh(ph)Br or Rh(ph)I in acetonitrile. Scavenging of the intermediates with characteristic scavengers of X $\cdot$, S $\cdot$ = Cl $\cdot$ or Br $\cdot$, reveals that these radicals are not products of the photochemical reaction. However, the photogeneration of a powerful oxidant was established from its reaction with 2-propanol and Mn²⁺. The transient species, observed in flash photolysis, can be assigned as Rh(III)-ligand radicals. The nature of these species and those of their precursors are being investigated. Product yields will be determined under various medium conditions.

XLVI. A Flash Photolytic Investigation of the Transient Transformations in the Photochemistry of Rhenium-hydride Complexes

(G. Ferraudi and C. Caulton¹)

The photolysis of ReH₅P₃, P=dimethylphosphine, induces the dimerization of the complex with liberation of hydrogen and phosphine:

This photoreaction shows a pronounced dependence in solvent nature, phosphine and complex concentrations. Flash photolysis reveals three transient species with half lives between 400 μ s and 8 ms. The decay of the shorter lived species, assigned as ReH_5P_2 , has been attributed to its reaction with ReH_5P_3 . The nature of the intermediates is being investigated by using appropriate scavengers in continuous wave and flash photolysis.

(1) Indiana University

XLVII. Transient Transformations in the Photoinduced Sensitization of Norbornadiene. The Sensitization by $\text{Ir}(\text{phen})_2(\text{OH})\text{phen}^{3+}$.
(C. Kutal¹ and G. Ferraudi)

The isomerization of norbornadiene to quadricyclene is photoinduced by a number of compounds in their excited states. The photosensitization of norbornadiene by excited states of $\text{Ir}(\text{phen})_2(\text{OH})\text{phen}^{3+}$, excit ≥ 320 nm in CH_3CN , produce transients with $\lambda_{\text{max}} \sim 560$ nm. Such transients have been attributed to an Ir(II) complex. The successive irradiations of the solution generate a new spectrum which is stable in time. The amount of the final species increases non linearly with the number of photons absorbed. Although secondary photolysis can be one of the reasons of the photochemical behavior indicated above, other mechanisms are being investigated.

(1) University of Georgia

XLVIII. The Photochemical Properties of Molybdenum Complexes of Dithiocarbamate Ligands
(R. Richman¹ and G. Ferraudi)

The photochemical transformations of the MoO_2L_2 (L = dithiocarbonate, benzyl acetylacetonate) are being investigated by continuous and flash photolysis. Flash irradiations reveal that the photochemical reactions generate intermediates with half lives in a millisecond range. Moreover, the observed transient transformations depend on the parent compound and medium conditions. Such transformations suggest that complicated photochemical mechanisms are operative. The reactivity of the dithiocarbamate radicals is being investigated under various experimental conditions.

(1) Carnegie-Mellon University

XLIX. Measurement of CIDEP Parameters

(J. P. Hornak and R. W. Fessenden)

The description of the amplitudes of H atom ESR signals is sufficiently developed that measurement of intrinsic enhancement factors (polarization/equilibrium polarization) can be made by comparison of steady-state signal amplitudes with those of a radical like SO_3^- which is unpolarized. Radical concentrations were obtained by numerically integrating the kinetic equations. The intrinsic enhancements for H atoms in acid aqueous solutions are -103 and 75 for low- and high-field lines, respectively, and -45 and 36 for D atoms in acid D_2O . These calculations make use of measured relaxation times and also take into account relaxation by spin-exchange. An attempt was made to use the same formulation to predict the dependence of steady-state ESR signal amplitude upon added reactant as in the work on H atom reaction rates (P. Neta, R. W. Fessenden and R. H. Schuler, J. Phys. Chem. 75 1654 (1971)). However, the calculations predict a more rapid change of amplitude with reactant concentration than was found experimentally. The source of this discrepancy is being sought.

L. Pulse Radiolysis Studies on the Nanosecond Time Scale

(E. Janata and R. H. Schuler)

Improvements in the time resolution of the linear accelerator based time resolved optical and conductometric pulse radiolysis experiment make it possible to examine absorbing transients during a 5 nsec electron pulse and conductance changes shortly thereafter. Detector time constants as determined by numerical synthesis of the recorded Cerenkov emission correspond to sequential RCs of 1.2 and 1.8 nsec for the photomultiplier-amplifier and Biomation 6500. Tests of these approaches are illustrated by direct observation of the growth and decay of the signal due to the hydrated electron in N_2O saturated solutions where the reaction period is 3 nsec and by the protonation of the ketyl anion radical produced by the reduction of acetone which has a period of 9 nsec.

LI. Scavenging Reactions in the Radiolysis of Cyclopentane

(H. Karasawa and R. H. Schuler)

The competitive reactions between galvinoxyl (G) and radioactive iodine (I_2) for cyclopentyl radicals have been re-examined by γ -radiolysis. The relative rate constants for these reactions (k_{R+I_2}/k_{R+G}) were found to be 8.2 at 298K and 11.2 at 199K. The difference of the activation energy is estimated to be only 376 cal/mol. The ratio of the pre-exponential factors is 4.3 which is nearly identical to the value of 4 expected if the relative rates are controlled primarily by a spin selective reaction between cyclopentyl radicals and galvinoxyl, i.e., the singlet but not the triplet electronic state radical encounter pairs undergo reaction.

LII. Radiation Chemistry Studies with Heavy Ions

(J.A. LaVerne and R.H. Schuler)

We have measured the integral ferric ion yield in aerated and deaerated aqueous ferrous sulfate solutions irradiated with helium ions of various initial energy in order to determine the importance of H atom production at high LET's. Helium ions accelerated at the Physics Department heavy ion Van de Graaff accelerator covering the range 21.4 down to 5.3 MeV after window loss were used. Over this region the initial LET of the particle increases from 3.0 to 9.6 ev/Angstrom. The corresponding integral ferric ion yields decrease from 5.12 to 3.70 for the deaerated system and from 7.75 to 4.86 for the aerated system. From these measurements the hydrogen atom yield is found to decrease from 1.3 to 0.6 with the limiting yield for water decomposition estimated as ~ 3.2 or about 10% lower than given by previous studies with cyclotron radiations. This limit is similar to that estimated from previous measurements with carbon ions. Further work with more massive ions is in progress.

LIIII. Oxidation of Substituted Alkyl Radicals by IrCl_6^{2-} , $\text{Fe}(\text{CN})_6^{3-}$, and MnO_4^- in Aqueous Solution. Electron Transfer versus Chlorine Transfer from IrCl_6^{2-}

(S. Steenken and P. Neta)

Alkyl radicals substituted at C_α by alkyl, hydroxyl, alkoxy, and chlorine react in aqueous solutions with $\text{Ir}(\text{IV})\text{Cl}_6^{2-}$ to yield $\text{Ir}(\text{III})$ species. In the case of substitution by hydroxyl and alkoxy, the rate constants are in the diffusion controlled range $((4-6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ and the reaction proceeds by electron transfer. In the case of ethyl and methyl radical and the chloromethyl radicals the rate constants range from 3.1×10^9 for ethyl to $2.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for trichloromethyl and the reaction proceeds by chlorine transfer from IrCl_6^{2-} to the alkyl radical. With iso-propyl and tert-butyl radical the reaction proceeds by both electron and chlorine transfer. Alkyl radicals also react with $\text{Fe}(\text{CN})_6^{3-}$. The rate constants increase with increasing alkylation at C_α from 5×10^6 for methyl to $3.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for tert-butyl. The reaction is suggested to proceed by electron transfer. Rate constants for reaction of MnO_4^- with alkyl radicals are of the order $10^9 \text{ M}^{-1} \text{ s}^{-1}$.

LIV. One-Electron Redox Potentials of Phenols. Hydroxy- and Aminophenols and Related Compounds of Biological Interest

(S. Steenken and P. Neta)

Redox potentials for the one-electron oxidation of substituted phenoxide ions were measured by the pulse radiolysis methods described earlier (NDRL-1945). These studies were expanded to include aminophenols and phenylenediamines and their N-methyl derivatives. Catechols and catecholamines of biological interest, and compounds related to serotonin and tocopherol were examined. Redox potentials were also measured for several antioxidants. The relationship between structure and redox potential is being analyzed. Quantitative correlation of redox potentials with rates of electron transfer is also examined.

LV. Reaction of $\cdot\text{OH}$ with Quinoline

(N. Selvarajan)

In continuation of the work on hydroxylation of aromatics, the reaction of quinoline with $\cdot\text{OH}$, generated radiolytically, has been investigated by pulse radiolysis and gamma radiolysis techniques. Using optical pulse radiolysis studies, the second order rate constants for the oxidation of $\cdot\text{OH}$ adduct of quinoline by one electron oxidants $[\text{IrCl}_6]^{2-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ are estimated to be $2.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $6.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ respectively. From γ -radiolysis studies the yield of the products is determined to be ~ 5.0 . The separation and identification of the reaction products by high pressure liquid chromatographic methods is in progress.

LVI. A Pulse Radiolytic Study of Radical Cations of Retinyl Polyenes

(K. Bobrowski and P. K. Das)

The radical cations of various all-trans retinyl polyenes have been generated by pulse radiolysis in 1,2-dichloroethane, acetone and n-hexane, and studied for their spectra and kinetics of decay and formation. The absorption spectral maxima of the radical cations are in the spectral region, 580-650 nm. In oxygen-saturated solutions, they decay with first-order kinetics with lifetimes in the range 20-50 μsec . The decay processes are found to be of mixed order in solutions saturated with nitrogen and nitrous oxide. In addition to radical cations, transient species with different decay and formation kinetics have been observed with spectral maxima in the range 380-440 nm; these have been tentatively assigned as the products of addition of solvent-derived radicals to the polyene chain and/or of hydrogen abstraction from the methyl groups linked to the polyene chain. The pulse radiolysis of retinal n-butylamine Schiff base in 1,2-dichloroethane is dominated by the formation of protonated Schiff base which absorbs strongly at 430-460 nm, and offers a method of studying the kinetics of protonation of the polyene Schiff base as well as other various bases (e.g. amines).

LVII. Formation of the Phenoxy-type Radical from p-Hydroxycinnamic Acid
(K. Bobrowski)

Addition of OH radicals to aromatic rings carrying hydroxyl groups is particularly interesting because of the possibility of elimination of water from the OH adduct to form phenoxy-type radicals. From the previous studies it was no evidence for the formation of phenoxy radicals from p-hydroxycinnamic acid in the region of pH 1 to 9. The study has been extended to pH range above 9. The transient formed through the reaction of OH with p-hydroxycinnamic acid at pH 10 has the absorption maxima at 545 and 600nm. The same characteristic spectrum was obtained by the reaction of $O^{\cdot -}$ radical-ion with p-hydroxycinnamic acid. With phenols the $O^{\cdot -}$ radicals have been suggested to react by electron transfer to produce the phenoxy radicals. Because the obtained spectrum is quite different from the spectra of phenoxy radicals (usually they absorb in the region 380-410 nm) we have used other oxidizing radicals as $Cl_2^{\cdot -}$, $Br_2^{\cdot -}$ and CH_2CHO to obtain phenoxy radicals from p-hydroxycinnamic acid by direct electron transfer. In all cases the obtained spectra are similar to those previously observed for OH and $O^{\cdot -}$ reactions with p-hydroxycinnamic acid at pH 10 and 14 respectively. Therefore, this spectrum was assigned to the phenoxy-type radical:

Based on previous and present observations it is suggested that the reaction of OH radicals with p-hydroxycinnamic acid in the pH range 1-9 produces mainly addition product to the olefinic side chain (>90%), whereas at pH above 9 addition of OH radicals to the aromatic ring becomes more important (~70%).

LVIII. Determination of the Products of Oxidation of Aniline by Ag(II)

(A. Kumar and P. Neta)

In order to elucidate the mechanism of the oxidation of aniline by Ag(II) it was necessary to develop a method for quantitative determination of the oxidation products. Using HPLC, separation of aniline and the expected oxidation products, hydrazobenzene and benzidine could be achieved. Hydrazobenzene, however, was present in the form of a complex with Ag^+ .

With Ag^+ -aniline N_2O saturated system, hydrazobenzene was found to be the major product of oxidation in contrast to the aniline-OH reaction where the yield of hydrazobenzene was only ≈ 0.1 . In the presence of Ag^+ nearly 40% of the aniline consumed could be accounted for by the formation of hydrazobenzene. The other components due to their very low concentration could not be analysed. Product estimation data under varying experimental conditions suggest the complexation of Ag(II) with aniline to be the primary step in the oxidation. Kinetic analyses of the different steps involved in the reaction is in progress.

LIX. Hydroxyl Radical Reactions with Ni(II) Macrocyclic Complexes.

Generation of Ni(III) and Ligand Radicals

(P. Morliere and L. K. Patterson)

While reactions between anion radicals, Br_2^- or $(\text{CNS})_2^-$, and macrocyclic complexes $[\text{Ni(II)(Cr+4H)}, \text{Ni(II)(CR)} \text{ or } \text{Ni(II)(CR-2H)}]$ may in all cases be interpreted as involving Ni(III) intermediates, oxidation of these complexes by $\cdot\text{OH}$ is more complicated. For $\cdot\text{OH}$ attack on Ni(II)(CR) , dissimilarities in transient spectra compared to Br_2^- reactions and intermediate sensitivity to O_2 indicate only ligand radical formation. The other two complexes, in reaction with $\cdot\text{OH}$, appear to generate mixtures of Ni(III) species and ligand radical. Those Ni(III) intermediates produced here exhibit characteristics comparable to those generated by Br_2^- and $(\text{CNS})_2^-$.

LX. Synthesis and Detection of Nanomolar Quantities of ATP

(D. H. Bell, L. K. Patterson and J. M. Gould¹)

Small amounts of adenosine triphosphate (ATP) can be generated in a system of ATP synthetase-containing proteoliposomes within which a pH gradient has been formed by pulsed ionizing radiation. The precise determinations of the ATP so formed is hindered by the presence of an enzyme present in preparations of ATP-synthetase which results in the production of ATP and adenosine monophosphate (AMP) by reactions that do not require a pH gradient. Also the AMP thus formed inhibits the assay for ATP - an assay of the ATP-dependent luminescence of a luciferin-luciferase complex. In order to interpret the changing levels of luminescence and to correlate these levels with the absolute levels of ATP at any instant, a computer model of the several reactions was developed and tested. The model gave reasonable predictions for the effects of an inhibitor and the effects of varying levels of AMP and ADP.

Since the pulsed radiolysis-dependent generation of ATP requires an active preparation of the ATP-synthetase enzyme, the activity of this enzyme is measured in a similar system which differs only in that the pH gradient is formed by a proton-pumping pigment instead of pulsed radiolysis. To accomplish these experiments, a sample holder has been designed to work in conjunction with the photon-counting sections of a SPEX spectrofluorimeter. Coupled pairs of rotating shutters allow for detection of low levels of luminescence from proteoliposomes that are strongly illuminated.

(1) Department of Chemistry, University of Notre Dame