NDRL--3318

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RADIATION LABORATORY

UNIVERSITY OF NOTRE DAME

QUARTERLY REPORT

July 1 - September 30, 1990

ISSUED

October 16, 1990

MASTER

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

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Dr. T. Nyokong, a Fulbright Fellow from the University of Lesotho, Roma, Lesotho, concluded her appointment and returned to her home institution on 7/15/90.

Dr. N.J.B. Green, who is on leave of absence from the Laboratory at Oxford University, returned for the period 7/16 to 8/24/90 to conduct research.

Prof. B. Brocklehurst of Sheffield University, U.K., joined us for the period 7/16 to 8/7/90 to further his collaboration with Dr. J.A. LaVerne.

Ms. D.L. Kohen joined the Laboratory on 7/18/90 as a summer research assistant. On 8/23/90 she began graduate studies in the Department of Chemistry and Biochemistry.

Dr. D. Weir resigned his appointment on 7/31/90 to take a position with Quality Analytical Laboratories in Downers Grove, IL.

Prof. D.A. Armstrong concluded his sabbatical year with us on 8/15/90 and returned to the University of Calgary.

Mr. V. Rassolov, an incoming graduate student in the Department of Chemistry and Biochemistry, arrived from Moscow on 8/16/90. He expects to study under Prof. R.H. Schuler.

Upon successfully defending her doctoral dissertation (supervised by Prof. R.W. Fessenden), Ms. D. Toublanc resigned her Laboratory appointment and returned to France on 8/16/90.

Prof. H. Altmiller of St. Edward's University, Austin, TX, arrived on 8/21/90 to spend a sabbatical semester with us. He will be working with Dr. G. Ferraudi on inorganic photochemical studies.

Prof. F. Wilkinson of the University of Loughborough, U.K., spent the period 8/27 to 9/10/90 in the Radiation Chemistry Data Center working on a data compilation with Dr. A.B. Ross.

Mr. M. Gray resigned his Research Assistantship on 9/1/90 to accept a consulting position.

Dr. A. Hitachi of Waseda University, Japan, spent the period 9/4 to 9/28/90 in the Laboratory collaborating with Dr. J.A. LaVerne on a heavy-ion radiolysis project.

Mr. P.A. Pluzhnikov resigned his Research Associate appointment on 9/14/90 to accept a position with Syscon International in South Bend.

Ms. Y.M. Wang successfully defended her doctoral dissertation (supervised by Dr. L.K. Patterson) and resigned her Research Assistant appointment on 9/30/90.

Prof. M.V. George concluded his appointment as a Visiting Professor on 9/30/90 and returned to the Regional Research Institute, Trivandrum, India.

Drs. S.M. Pimblott and J.E. Chateauneuf were promoted from Research Associate to Assistant Professional Specialist on 7/1/90 and 8/1/90, respectively.

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Visitors during the quarter included the following:

Dr. G. Foldiak of the Isotope Institute, Budapest, Hungary, was in the Laboratory for the period 6/29 to 7/8/90, collaborating with Drs. Schuler and LaVerne on a heavy-ion radiolysis project.

Prof. K. Hasegawa of Shizuoka University, Japan, spent the period 7/16 to 7/18/90 visiting the Laboratory.

Drs. Q.G. Mulazzani (Institute of Photochemistry and Radiation Chemistry, Bologna, Italy) and G. Buxton (Cookridge Radiation Research Center, University of Leeds, U.K.) visited the Radiation Chemistry Data Center from 7/18 to 7/22/90 to collaborate with Dr. A.B. Ross.

Mr. J. Manak, a graduate student in Notre Dame's Physics Department, used the Laboratory's laser facilities on 7/27/90.

Dr. Z. Vager of the Weizmann Institute, Israel, visited the Laboratory on 8/8/90.

Dr. K. Bobrowski from NIST, Gaithersburg, MD, visited the Laboratory on 8/22-8/23/90.

Dr. H. Yoshida of Oak Ridge National Laboratory spent the period 8/26 to 8/28/90 in the Laboratory, using our gamma and heavy-ion radiolysis facilities.

Publications

L.G. Boulu and J.J. Kozak
Simulations of Energy Transfer and Trapping in Two-Dimensional Disordered Systems
Spatial Inhomogeneities and Transient Behavior in Chemical Kinetics, P. Gray, G. Nicolis, F. Baras, P. Borckmans and S.K. Scott, Eds.; Manchester University Press, p. 700 (1990) [NDRL 2017]

M. Muneer, P.V. Kamat and M.V. George
Electron Transfer Reactions. Reaction of Nitrogen Heterocycles with Potassium
Can. J. Chem. 68, 969 (1990) [NDRL 3018]

K.R. Gopidas and P.V. Kamat
Photophysical Behavior of Ultrasmall CdSe Semiconductor Particles in a Perfluorosulfonate Membrane
Materials Letters 9, 372 (1990) [NDRL 3230]

I. Carmichael
Ab initio Coupled-Cluster Calculations of Isotropic Hyperfine Splitting in Some Diatomic Hydrides
J. Phys. Chem. 94, 5734 (1990) [NDRL 3238]

K.R. Gopidas, M. Bohorquez and P.V. Kamat
Photophysical and Photochemical Aspects of Coupled Semiconductors. Charge-Transfer Processes in Colloidal CdS-TiO_2 and CdS-AgI Systems
J. Phys. Chem. 94, 6435 (1990) [NDRL 3240]

D. Weir
Spectroscopy and Intermolecular Charge-Transfer Reactivities of Excited-State Radicals with Cyano Substituents
J. Phys. Chem. 94, 5870 (1990) [NDRL 3249]

A. Samanta, C. Devadoss and R.W. Fessenden
Picosecond Time-Resolved Absorption and Emission Studies of the Singlet Excited States of Acenaphthylene.
J. Phys. Chem. 94, 7106 (1990) [NDRL 3252]

Q. Sun, G.N.R. Tripathi and R.H. Schuler
Time-Resolved Resonance Raman Spectroscopy of p-Aminophenol Radical Cation in Aqueous Solution
J. Phys. Chem. 94, 6273 (1990) [NDRL 3253]

J.E. Chateauneuf
Spectroscopic and Kinetic Characterization of Diphenyldiazomethane Radical Anion.
J. Phys. Chem. 94, 7177 (1990) [NDRL 3277]

J. Bentley and D.M. Chipman
Calculation of Partial Widths for Autoionization of the $^1P(3s3p)$ Resonance State of Helium
J. Chem. Phys. 93, 1785 (1990) [NDRL 3278]

G. Ferraudi
Photochemical Properties of Metallophthalocyanines in Homogeneous Solution
Chapter 4 in Phthalocyanines Properties and Applications, C.C. Leznoff and
A.B.P. Lever, Ed., VCH Publishers, Inc., p. 291 (1989) [SR 121]

A.B. Ross and B.H.J. Bielski
Sources of Compilations of Rate Constants for Oxygen Radicals in Solution
Vol. 186, Methods in Enzymology, Academic Press, p. 113 (1990)* [SR 123]

*Partially supported by the Office of Standard Reference Data of the National Institute of Standards and Technology.

External Talks and Presentations

G.N.R. Tripathi, "Resonance Raman Spectroscopy of Chemical Transients", Bhabha Atomic Research Centre, Sept. 4, 1990; "Raman Studies of Chemical Reactions", Tata Institute of Fundamental Research, Bombay, India, Sept. 5, 1990.

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

1. (NDRL-3305) Transient Raman Studies of Chemical Reactions: OH Oxidation of Simple Aromatics[1]

(G.N.R. Tripathi)

The reactions of the hydroxyl radical (·OH) are of fundamental interest to radiation chemistry and radiation biology. It is generally believed that the ·OH radicals react exclusively by addition to the aromatic systems. This behavior contrasts with the highly oxidizing nature of the ·OH radical (reduction potential 2.32 V at pH 7) which should generally favor electron transfer. The adduct (hydroxycyclohexadienyl) radicals subsequently react with H^+, OH^- and H_2O to form the radical cation (addition-elimination electron-transfer path). In some hydroxy-aromatics in basic solutions (hydroxy group ionized), direct electron-transfer from the aromatic system to the ·OH radical has also been suggested, but the results can be explained, alternatively, by OH^- catalyzed ionic dissociation of the adducts at a time-scale shorter than the reaction period. We are currently examining the reaction of ·OH radical with some prototype aromatic systems by transient Raman spectroscopy. We find unambiguous evidence for the direct formation of the radical cation in these reactions. Since the covalently bonded OH-adduct cannot dissociate/convert into radical cations, unless reaction with another species is involved, the initial chemical step must involve direct electron transfer. While the radical cation-OH^- pairs, thus formed, can undergo in-cage combination to produce OH-adducts, a fraction which escapes the cage can dissociate into solvated ions. This reaction mechanism, which is significantly different from the conventional mechanism, conforms with the high reduction potential of the OH radical.

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(1) Submitted for presentation at International Conference on Laser Applications in Life Sciences, Moscow, USSR, Aug. 27-31, 1990.

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2. (NDRL-3306) "Radiation Chemistry" in Literature Compilations: Their Wider Value in Free-Radical Research[1]

(P. Wardman[2] and A.B. Ross)

Radiation-chemical techniques have generated a huge amount of quantitative data on free-radical reactivity and physico-chemical properties of radicals. The Radiation Chemistry Data Center at the University of Notre Dame collates and assesses these and other rate, spectral and thermodynamic data, often in conjunction with specialist authors. Most of the data compilations produced by the Center are of relevance not only to radiation chemistry, but also to many other areas of free-radical research where quantitative data are needed. The main activities of the Data Center are reviewed briefly, and the most important data compilations of relevance to free radical biology and medicine are surveyed.

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(1) Submitted for publication to Free Radical Biology & Medicine.

(2) Mount Vernon Hospital, Northwood, Middlesex, U.K.

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3. (NDRL-3307) The Scavenger and Time Dependences of Radicals and the Molecular Products in the Electron Radiolysis of Water: Examination of Experiments and Models[1]

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

Laplace transform techniques have been used to compare the scavenger and the time dependences of e^-_{aq}, OH, H_2 and H_2O_2 produced following the electron radiolysis of water. A new empirical relationship for the variation of these yields on scavenger concentration is presented. Experimental data on the scavenging of e^-_{aq}, OH, H_2 and H_2O_2 have been fitted with the new function and it is found that the inverse Laplace transform of the results for e^-_{aq} and OH do not match the direct experimental measurements of the time dependences of these species. There is no apparent reason for this discrepancy. The accuracy of Laplace transform techniques in nonhomogeneous kinetics was determined by using a deterministic diffusion-kinetic model to calculate the time dependences of the yields of these species in pure water and the dependence of their yields on the concentration of a few selected scavengers. Numerical Laplace transforms of the time dependences of e^-_{aq}, OH, H_2 and H_2O_2 reproduced well the calculated scavenger concentration dependence. The inverse Laplace transform of the new function accurately reproduced the predicted time dependent kinetics of diffusion-kinetic models even when very different initial distributions of e^-_{aq} were used. This function is shown to be an improvement on previous functions, especially at matching the yields at high scavenger concentrations. The parameters derived in the analysis of the available experimental data can be used with the new function or its Laplace transform to easily determine the scavenger concentration dependence or time dependence of any of these species with other scavengers for which the scavenging rate constant is known. The influences of various parameters used in the diffusion-kinetic modeling of the radiation chemistry of water are discussed.

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

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4. (NDRL-3308) Distribution of Primary Ionization and Excitation in Water Radiolysis[1]

(A. Mozumder)

This paper aims at the calculation of entity-specific ionization and excitation probabilities for water radiolysis at low LET with due attention to ionization efficiency and threshold(s). Mean numbers of ionizations and excitations, together with their statistical fluctuations, are provided for a given energy loss ε which may be further averaged over the distribution of ε. Explicit computations are presented for the gas phase while the procedure for the liquid phase is broadly indicated.

The probability $\omega(\varepsilon)\Delta\varepsilon$ that an energy loss between ε and $\varepsilon+\Delta\varepsilon$ will occur on the complete absorption of a primary radiation has been calculated for electron radiolysis of water from fundamental principles. If the energy spent in an ionization process is denoted by I', the maximum number of ionizations corresponding to energy loss ε is given by $n_m \approx \varepsilon/I'$. Calling the probability for $(n_m-\nu)$ ionizations and η excitations at energy loss ε $P(N_m-\nu,\eta;\varepsilon)$, the overall ionization and excitation probability is given by

$$W(k,\eta) = \sum_{\varepsilon} P(k,\eta;\varepsilon)\ \omega(\varepsilon)\Delta\varepsilon.$$

We have evaluated P as a product of a probability of a given number of ionizations and a conditioned probability of having another given number of excitations. Each of these factor probabilities can be given as a Bernoulli distribution in terms of the maximum number of events and the normalized probability of occurrence of an event (ionization and excitation). In the gas phase, the energy-dependent occurrence probabilities may be obtained from cross-sections of ionization, excitation and other processes involving neither ionization nor excitation. The liquid phase calculations depend on experimental ionization efficiency (up to ~ 9.3 eV), W-value of ionization and a plausible form of variation of event occurrence with energy.

It is found that a median spur (20-25 eV) in liquid water has the maximum probability of having one ionization and one excitation while a typical energy loss in the gas phase (30 eV) results in 1 or 2 ionizations and 0-2 excitations. Fates of ionizations and excitations leading to the primary species are speculated.

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(1) Submitted for presentation at 7th Tihany Symposium on Radiation Chemistry, Balatonszeplak, Hungary, Sept. 9-15, 1990 and also to be published in Proceedings of 7th Tihany Symposium on Radiation Chemistry.

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5. (NDRL-3309) Correlation Effects in Simple Liquids[1]

(R. Atkinson[2], P. Clifford[2] and N.J.B. Green)

A stochastic model of single particle motion based on the velocity autocorrelation function (VACF) is proposed. Recent simulations of the probability density for changes in direction are discussed in terms of this model. In all cases but one the theoretical results are in excellent agreement with the simulations. It is concluded that the measures of directional change proposed do not show any behavior that cannot be explained in terms of the model and an empirical VACF.

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(1) Submitted for publication in Molecular Physics.

(2) Oxford University.

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6. (NDRL-3310) Study of a Semi-continuum Model for the Hydrated Electron[1]

(S. Pommeret and Y. Gauduel[2])

Kevan's structural model for the solvated electron has been studied in association with the spherical part of a continuum potential via an imaginary time Splitting Operator Method (SOM). The study focuses on the influence of the continuum potential representing the second solvation shell interaction with the electron. The continuum potential is computed in the self-consistent approximation. The temperature dependence of the continuum potential allows us to extend our study from 77 K to 300 K. The gyration radius of the solvated electron is found to be of the same order as computed by their simulation methods, and for the best value of the cavity radius more than 60% of the charge is inside the cavity. The results of the present computation are then compared to those obtained by using a full simulation approach or the semi-continuum theory. In the present work, it is interesting to note that at 300 K we have found results that are in good agreement with those computed by using a Molecular Dynamics approach for the medium.

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

(2) Ecole Polytechnique, Palaiseau, France.

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7. (NDRL-3311) The Radiolysis of Cyclohexane with ^{4}He Ions[1]

(J.A. LaVerne, R.H. Schuler and G. Foldiak[2])

The role of cyclohexyl radicals in the radiolysis of cyclohexane has been studied. Neat solutions and solutions with added iodine have been irradiated with ^{60}Co gamma rays and with helium ions of 5 MeV (LET = 90 eV/nm) to 20 MeV (LET = 30 eV/nm). The yields of cyclohexene, bicyclohexane and cyclohexyl iodide have been determined at very low doses using gas chromatographic-mass spectrometric techniques. Gamma radiolysis studies show that the yields of cyclohexene and bicyclohexane decrease from 3.12 and 1.76 molecules/100 eV to 1.74 and 0.27 molecules/100 eV, respectively, with the addition of 0.1 mM iodine. With 10 MeV helium ions, the addition of 0.1 mM iodine there is a much smaller decrease in the yields of cyclohexene and bicyclohexane, from 2.25 and 1.10 molecules/100 eV to 1.93 and 0.79 molecules/100 eV, respectively. The lifetime of the cyclohexyl radical is about 1 μs at this concentration of iodine and the results suggest that the radical combination processes are largely complete in helium ion tracks. The yield of cyclohexyl iodide does not increase with further addition of iodine in gamma radiolysis, which could be due to the interference of iodine with precursors to the cyclohexyl radical. Cyclohexyl iodine yields increase with increasing iodine concentration using 10 MeV helium ions which is expected since the iodine can scavenge more radicals from the track before they recombine. Iodine apparently does not significantly interfere with ionic processes in the tracks of heavy ions. The yields of cyclohexene and bicyclohexane decrease with increasing iodine concentration and at 40 mM they appear to reach the limiting values of 0.48 and 0.20 mplecules/100 eV, respectively, for gamma rays and 0.61 and 0.30 molecules/100 eV, respectively, with 10 MeV helium ions. The similarity in yields for the two types of radiation suggests that the production of cyclohexene and bicyclohexane can occur to a minor extent via processes not involving radical precursors. At 40 mM of iodine the lifetime of the cyclohexyl radical is about 2 ns and most cyclohexyl radicals should be scavenged. There is probably a minor, fast ionic process for the production of some of the observed cyclohexene and bicyclohexane.

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(1) Submitted for presentation at 7th Tihany Symposium on Radiation Chemistry, Balatonszeplak, Hungary, Sept. 4-10, 1990 and also to be published in Proceedings of 7th Tihany Symposium on Radiation Chemistry.

(2) Institute of Isotopes, Budapest, Hungary.

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8. (NDRL-3312) Structure of the Photoproduct from the Cycloadduct of 2,3-Diphenyl-2,3-epoxy-1-indanone and Dibenzoylacetylene[1]

(D. Ramaiah,[2] W.H. Pearson,[3] P.K. Das and M.V. George)

A single crystal x-ray analysis of the photoproduct, from the cycloadduct (1) of 2,3-diphenyl-2,3-epoxy-1-indanone and dibenzoylacetylene, has shown that its structure is 3,3a-dibenzoyl-3a,8b-dihydro-2,8b-diphenylindeno[1,2-b]furan-4-one (8a) and not the earlier reported benzoxacinone structure (3a). Reasonable pathways for the formation of 8a and analogous products are presented.

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

(2) Regional Research Laboratory (CSIR), Trivandrum, India.

(3) Department of Chemistry and Biochemistry, University of Notre Dame.

9. (NDRL-3313) Photochemistry of Sensitizing Dyes. Spectroscopic and Redox Properties of Cresyl Violet[1]

(D.I. Kreller and P.V. Kamat)

Photosensitizing properties of cresyl violet have been investigated by characterizing singlet and triplet excited states and the reduced and oxidized forms of the dye by picosecond and nanosecond laser flash photolysis. The dye readily forms a charge transfer complex with amines with complexation constants in the range of 49 - 3350 M^{-1}. The dye in its singlet and triplet excited states has lifetimes of 2.46 ns and 68 μs respectively. The excited triplet is quenched by ground state dye molecules with a bimolecular rate constant of 1.45 x 10^9 $M^{-1}s^{-1}$. The semioxidized radicals of the dyes have been generated by oxidation of CV^+ with azide radicals ($k = 1.6 \times 10^{10}$ $M^{-1}s^{-1}$) in a pulse radiolysis experiment. The semireduced dye has been generated by quenching of triplet dye with triphenylamine ($k = 1.4 \times 10^9$ $M^{-1}s^{-1}$). Photoelectrochemical reduction of cresyl violet in colloidal TiO_2 suspension has also been carried out, with a quantum yield of 0.013.

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

10. (NDRL-3314) Ultrafast Photochemical Events Associated with the Photosensitization Properties of a Squaraine Dye[1]

(P.V. Kamat, S. Das[2], K.G. Thomas[2] and M.V. George)

The photosensitization properties of a squaraine dye are elucidated by means of transient absorption and emission spectroscopy techniques. The charge injection from excited dye into the conduction band of TiO_2 semiconductor occurs within the laser pulse duration of 18 ps ($k > 5 \times 10^{10}$ s^{-1}). The quick recombination between the dye cation-radical and the injected charge ($k = 3.7 \times 10^9$ s^{-1}) is a major limiting factor in controlling the efficiency of sensitization.

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(1) Submitted for publication in Chemical Physics Letters.

(2) Regional Research Laboratory, Trivandrum, India.

11. (NDRL-3315) Novel Phototransformations of Bridgehead-Dimethyl-Substituted Dibenzobarrelene. Structure of the Photoproducts[1]

(C.V. Asokan,[2] S.A. Kumar,[2] S. Das[2], N.P. Rath[3] and M.V. George)

Single crystal X-ray diffraction studies have revealed that the phototransformation products of 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (1) are correctly represented as 1,5-dibenzoyl-4,8-dimethyl-2,3:6,7-dibenzocyclooctatetraene (9), the dibenzopentalene derivative 13 and the pentacyclic peroxycarbinol 17 and not the earlier reported structures, 1,4-dibenzoyl-5,8-dimethyl-2,3:6,7-dibenzocyclooctatetraene (3), the benzonaphthalene derivative 6 and the carbinol 5, respectively. Both singlet state-mediated "tri-π-methane" rearrangement and the triplet state-mediated "di-π-methane" rearrangement of 1 could give rise to a 1,4-diradical intermediate 8, which could then lead to the cyclooctatetraene 9 by a Grob-type fragmentation or undergo a 1,2-rearrangement to the dibenzopentalene 13. The pentacyclic peroxycarbinol 17 could arise through the oxygen-quenching of one of the diradical intermediates derived from 1, followed by extensive rearrangements.

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

(2) Regional Research Laboratory, Trivandrum, India.

(3) University of Missouri-St. Louis.

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12. (NDRL-3316) Molecular Orbital Studies of Hyperfine Coupling Constants in the H_2CN and H(HO)CN Radicals[1]

(D.M. Chipman, I. Carmichael and D. Feller[2])

Isotropic magnetic hyperfine splittings have been evaluated for the closely related H_2CN and H(HO)CN radicals from *ab initio* molecular orbital models. Uncertainties in the equilibrium geometries appear to have little effect on the carbon and nitrogen splittings but may affect the large methylene hydrogen splittings by up to several Gauss. Vibrational averaging is estimated to provide corrections on the order of only 1 Gauss or less at all nuclei. Direct, spin polarization, and electron correlation effects all contribute about equally to the large methylene hydrogen splitting in each radical, as well as to the large difference in this splitting between the two radicals. The electron correlation contribution is the most difficult to calculate, and neither of two distinct procedures utilized to study that effect provides a fully quantitative description at the limit of currently feasible calculations.

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

(2) Pacific Northwest Laboratory, Richland, WA.

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13. (NDRL-3317) A Laser Flash Photolysis Study of Aromatic Nitrones. Triplet State Properties and Reactivity with Singlet Oxygen[1]

(D.R. Cyr, T. Mathew,[2] K. Ashok,[3] P.K. Das and M.V. George)

Results of a nanosecond laser flash photolysis study of a series of aromatic nitrones in solutions at room temperature are presented. Direct laser flash excitation (337.1 or 308 nm) of nitrone solutions in benzene or methanol results in ground state bleaching attributable to photocyclization to oxaziridines. The quantum yields of this process are estimated at 0.1-0.3 in methanol. From rate constants of triplet quenching by nitrones, their triplet energies are located at 1.4-2.0 eV. Except in the case of a cyclic nitrone (2 in Scheme 1), no transient absorption phenomena due to nitrone triplets are observed as a result of the extensive quenching of sensitizer triplets; thus, the triplets of noncyclic nitrones are very short-lived ($\tau_T < 10$ ns), possibly due to structural relaxation analogous to that in olefin triplets. With zinc tetraphenylporphyrin as the sensitizer, there is evidence for electron transfer quenching in which the nitrones act as donors. No ground-state bleaching is observed in the course of triplet sensitization, suggesting that photocyclization to oxaziridines does not occur from the triplet state. The nitrones are moderately efficient quenchers of singlet oxygen, the corresponding bimolecular rate constants being in the range $(0.5-8) \times 10^7\ M^{-1}s^{-1}$ in various solvents.

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

(2) Regional Research Laboratory (CSIR), Trivandrum, India.

(3) Indian Institute of Technology, Kanpur, India.

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14. (SR-138) Publications and Reports of the Notre Dame Radiation Laboratory

The bibliography summarizes the reports issued by the Notre Dame Radiation Laboratory (NDRL) from its inception in 1946 through June 30, 1990. Reports from Notre Dame during the period to June 30, 1976, are covered by NDRL 1 through NDRL 1056 (pages 1-53). Reports NDRL 1101 through NDRL 1662 on pages 54-82 (originally RRL 1 through RRL 562) cover reports issued from the Mellon Institute Radiation Research Laboratories at Carnegie-Mellon University during the period January 1, 1958 to June 30, 1976. The two laboratories were merged July 1, 1976, and reports NDRL 1701 to NDRL 3299 (pages 83-175) cover reports issued after the merger. The Special Reports series, beginning on page 176, provides archival documentation for various items such as book chapters, theses, computer programs and other items not cited in the NDRL report series. The author index, included on pages 185-218, covers all authors, including co-authors from other institutions. This bibliography is maintained on the Laboratory's computers (currently the VAX 11/780) as file [REPORT]ALLREPTS.LAB and is currently searchable for alphanumeric strings or to prepare bibliographies of individual authors. In addition, publications issued since 1983 are keyworded for preparation of topical bibliographies.

15. (SR-139) Microwave Absorption of Photoinduced Transient Species and their Relaxation Behavior[1]

(D.B. Toublanc)

The microwave absorption technique, initially developed by Fessenden et al., was applied to the determination of rotational relaxation properties and dipole moments for several relevant polar systems in nonpolar solvents. Measurements of the dielectric dispersion to loss ratios were performed at microwave frequencies close to 9.2 GHz. In some cases, measurements were carried out at 3.1 GHz to confirm or complete the information otherwise gathered.

Deviations from the ideal single relaxation Debye behavior, smaller for rigid quasi-spherical ground state ketones, larger for ground and excited state molecules that exhibited internally rotating groups, were observed in most cases. The relatively large dielectric dispersion to loss measured for the former in viscous solvents indicated that these solutes interacted little with the neighboring molecules, and tumbled rapidly in this viscous environment. Observation of a large dispersion component of the transient microwave signal also provided evidence for a fast internal dipole moment reorientation affecting the charge transfer states of triplet Michler's ketone and singlet 9,9'-bianthryl. Since the relaxation behavior, quantified by means of a relaxation function $g(\tau)$, significantly affects dipole moment calculations, new moments were calculated for these systems, and found to be below the commonly accepted figures by 5 to 10 D for bianthryl. The charge transfer states observed upon formation of anthracene/diethylaniline or pyrene/diethylaniline exciplexes were also investigated and a suitable value of the relaxation function obtained. This was done by fitting the dispersion to loss values observed at two different frequencies to a theoretical model allowing for a distribution of relaxation times. The dipole moments calculated with this new function (about 10 D) agree with solvent shift or electrooptical measurements performed by other groups.

The present method was further exploited to yield dipole moments of several substituted phenoxyl radicals in benzene. The chloro analogs of the parent phenols were taken as models for the relaxation function used in the calculations. Hence, measurements on ground states at just one frequency were necessary to evaluate $g(\tau)$. The large influence of para substituents on the relaxation of the phenoxyls, and the inductive effects caused by diverse substituent groups were assessed.

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(1) Submitted to the Graduate School of the University of Notre Dame in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy.

Other investigations in progress include:

16. Partially Diffusion-controlled Reactions of Ions in Spur Kinetics

(S.M. Pimblott and N.J.B. Green)

Several of the reactions of importance in spur kinetics are not fully diffusion-controlled and the first encounter of such pairs will not necessarily result in reaction. In the modelling of spur kinetics the possibility of encounter without reaction must be considered. The survival probability of a geminate pair is described by the adjoint to the diffusion equation and the treatment of partially rather than fully diffusion-controlled reactions requires only the selection of the appropriate boundary conditions. Modelling reaction in spurs is a many-body problem. Conventional deterministic treatments incorporate the effects of unreactive collisions only to the extent that they are implicit in the homogeneous rate constant while more recent stochastic models have ignored any influence on the kinetics. We have previously considered the Monte Carlo simulation of the geminate encounter of radicals that do not always react. The incorporation of unreactive encounters significantly increased the computer time required for Monte Carlo simulation, relative to the diffusion-controlled case, as the probability of a reflective collision was assessed after each timestep. A more efficient technique has been developed which models the kinetics using similar methods to those developed for diffusion-controlled reaction. Monte Carlo simulations of geminate ion-pairs have been performed. The simulations predict the same kinetics as numerical solutions of the adjoint equation with the corresponding boundary conditions. We are now examining several many-body systems similar to those found in radiation chemistry and photochemistry. The Monte Carlo methods will be used in conjunction with more approximate analytical techniques based upon the independent pairs approximation.

17. Scavenging Kinetics and the Laplace Transform Relationship

(S.M. Pimblott and N.J.B. Green)

The validity of Laplace transform relationships between the scavenged yield and time-dependent kinetics for radiation chemistry and photochemistry have been tested using stochastic and deterministic models. The connection is strictly valid only for a single pair of reactants and when the scavenging reaction is first order with a time-independent rate constant. The accuracy of the LT method has been tested for multi-particle systems and the effect of a time-dependent rate coefficient for scavenging has been assessed. For small numbers of particles the extent of any discrepancies found between either the true decay kinetics and the ILT of the scavenger yield or the scavenged yield and the LT of the kinetics depends upon the rate constants for the various possible (re)combination reactions. The smaller the rate constant for the combination of like species relative to the recombination reaction, the more accurate the LT relationship. When only recombination reactions occur, or when recombination dominates the reaction of like particles as in water radiolysis, the agreement is excellent. In the prototypical single-species system where only like species can combine there is considerable disagreement. The incorporation of a time-dependent rate constant for scavenging involves only a transformation of scale and the use of LT methods with this modification is exact for an isolated pair.

18. Spur Overlap in Nonhomogeneous Kinetics

(S.M. Pimblott)

Mathematical flaws in conventional deterministic models for spur kinetics have recently led to a great deal of interest in stochastic alternatives. For the most part these stochastic treatments involve some form of Monte Carlo simulation. The only exception to this is a master equation formulation based upon the independent pairs approximation and thus far this technique has only been applied to isolated spurs. A significant fraction (over 10%) of the energy lost by a high energy electron in water is in events larger than 100 eV so to model realistic radiation chemistry one must consider the possibility of an extended distribution of reactants. The modelling of multi-spur systems is straightforward using simulation techniques and it should not introduce any problems not of importance in isolated spurs. In a master equation formulation each additional spur introduces an additional dimension to the state space and a 'new' rate coefficient for interspur reactions has to be evaluated. A master equation describing reaction in a two-spur system has been formulated and has been solved for a number of idealized systems. The kinetics have been compared with those predicted by simulation and by conventional deterministic models. Full random flights and approximate independent reaction times simulations agree almost exactly and the discrepancies between the stochastic simulations and the deterministic treatments are of the order expected from previous calculations. The master equation results show a significantly larger error than expected. The error, while smaller than those of the deterministic models, is about 5%. The origins of this error are under investigation.

19. Track Structure and the Distribution of Energy Losses in Gaseous Hydrocarbons

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

The radiolysis of hydrocarbons has been a field of continuing interest since the 1920s. One region of considerable importance is the energy loss by the radiation particle to the medium. This strongly influences, amongst other things, the period of fast kinetics immediately following radiolysis as the kinetics depend strongly on the spatial distribution of the reactive ions and radicals and so on the structure of the radiation track. The stopping powers, the inelastic mean free paths and the distributions of energy loss events for electrons in a variety of gaseous alkanes have been calculated using experimentally based dipole oscillator strength distributions. The results show very little difference between the members of the homologous series C_nH_{2n+2} where n = 2, 4, 6 and 8. The integrated path length of a 1 MeV electron in gaseous octane is only 5% larger than it would be in ethane vapor of the same density. Similarly the stopping powers and mean free paths differ by less than 10%. The distribution functions describing the probability of an energy loss by an electron with a specific energy, E, are in the order ethane > butane > hexane > octane. In any of the hydrocarbons the function is practically unaffected by the size of E for E > 10 keV. The integrated distribution of energy loss events along the whole track of a high energy electron in a hydrocarbon is also insensitive to the incident electron energy above 10 keV and is not significantly affected by the value of n. The results for the alkanes have been compared with previous calculations for the various phases of water. There are large differences even compared to the vapor phase, for instance, the inelastic mean free path is smaller by a factor of about 2 in the alkanes. Comparison of the energy loss distributions for the complete energy degradation of an electron show that, while the most probable events have the same energy, the distribution of possible events is much narrower in the alkanes than in water vapor.

20. Diffusion and Reaction of Electron-cation Pairs in Aromatic Crystals

(S.M. Pimblott and A. Mozumder)

The geminate survival probability of a reacting pair is generally described using the adjoint to the diffusion equation. For most problems it is acceptable to use an isotropic diffusion coefficient and dielectric constant. We recently presented a series of transformations to facilitate the solution of the adjoint diffusion equation when dealing with reactive species and with media for which anisotropic diffusion and dielectric tensors are necessary. The important constants in this treatment are the elements of the so called p matrix which is obtained from the diffusion and dielectric tensors. Originally we considered the geminate electron-hole recombination in anthracene crystals and in this case the p matrix was (0.126, 0.441, 0.433). We are now modelling geminate recombination in a number of other aromatic crystals, in particular naphthalene. For naphthalene the p matrix is (0.1391, 0.4656, 0.3953) which shows considerably more anisotropy than the p matrix for anthracene. The increased anisotropy is apparent in the solution of the transformed adjoint equation. Whereas the contours of constant survival probability were almost spheroidal for anthracene they are clearly ellipsoidal for naphthalene. Calculations including an external field presently are underway.

21. Quenching in Liquid Argon: Relative Scintillation Yield at Different LET

(A. Hitachi[1] and A. Mozumder)

Relative scintillation yield in LAr is maximal for relativistic heavy ions of the Ne-La group. At low LET it decreases due to electrons escaping recombination. At high LET it decreases again due to biexcitonic quenching. At the same LET quenching is more efficient for slower ions. The underlying theory is based on the following hypotheses: (1) exciton formation, directly or on ion recombination, (2) competition between exciton diffusion and self-trapping, (3) scintillation from self-trapped excitons. It is necessary that recombination must occur before self-trapping since exciton lifetime is independent of LET, an experimental observation.

Recombination time can be divided into electron stopping to subexcitation energy, followed by motion to the classical turning point (CTP) and return to the recombination distance r_0. Because of inefficient recombination several passes through CTP and r_0 are needed to significantly complete the recombination process. Based on detailed dynamics our estimated time for electronic stopping is ~ 1 fs and therefore negligible. For α-particles, the time for a full pass to go to CTP and return to r_0 is ~ 40 fs. Recombination efficiency, taken to be the ratio of the experimental to the Debye rate, is ~ 0.1. Thus the computed recombination time scale for α tracks is ~ 400 fs, which is less than the self-trapping time of free excitons (~ ps) which is required. No quenching is expected in the track penumbra where ~ 25% of energy is deposited for nonrelativistic particles.

The simplified equations for exciton diffusion and reaction are

$$\partial n/\partial t = D\nabla^2 n - kn^2 - n/\tau \qquad (1)$$

and

$$\partial n'/\partial t = n/\tau \qquad (2)$$

where n,n′ are respectively the free and self-trapped exciton density; D = free exciton diffusion coefficient, k = specific quenching rate and τ = self-trapping time. Equations (1) and (2) are solved under gaussian approximation taking for liquid Argon $D = 1\ cm^2/s$, $\tau = 1$ ps and $k = 4 \times 10^{-8}\ cm^3s^{-1}$. The computed survival probability against quenching, when combined with 75% energy deposition in the core, gives a relative scintillation yield for α-particles as 0.8, compared with the mean experimental value of 0.7. We are investigating the ways to improve the model which will also be applied to relativistic particles.

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22. Ionization and Excitation Distribution in Spurs: Rôle of Physical Parameters

(A. Mozumder and S.M. Pimblott)

In earlier quarterly reports we gave reasons for seeking a distribution in discrete numbers of ionizations and excitations in spurs and arrived at an approximate distribution. Briefly the reasons are based on the thresholds and efficiencies of ionization and the requirement of stochastic kinetics. The maximum number of ionizations (n_m) and the maximum number of excitations η_m conditioned on $n_m-\nu$ ionizations are determined by spur energy ε, average energy needed for ionization and excitation, etc. Under energy conservation the excitation distribution is geometric and the ionization distribution is binomial.

The parameters needed for the calculation of the distribution function are the ionization potential (I), photoionization efficiency as a function of energy (η), mean excitation energy of the positive ion ($<ex>^+$), average energy spent in an excitation process ($<ex>$), cross-sections for inelastic processes ($\sigma_{ion}, \sigma_{ex}, \sigma_v$, etc.), ratio δ of mean electronic and vibrational excitation energy, etc.; many of these parameters are phase-dependent. In the gaseous phase of water $I = 12.6$ eV and $<ex>^+ = 4.4$ eV, obtained by comparison with the asymptotic W-value (29.6 eV). Photoionization efficiency is available experimentally. The inelastic cross sections are energy-dependent and appear through the reduced parameters $p \triangleq <\sigma_{ex}>/[<\sigma_{ex}>+<\sigma_v>]$ and $q \doteq <\sigma_{ex}>/[<\sigma_{ion}> + <\sigma_{ex}>]$. In the gas phase these cross-sections may be taken from Hayashi's compilation (IAEA-TECDOC-506, International AEA, Vienna, 1989) in which, however, σ_{ex} is acknowledged to be rather uncertain. We have therefore fitted the q-values to the experimental W-value measurement of Combecher (Radiat. Res. <u>84</u>, 189, 1980) according to a theoretical formula. Mean values of electronic and vibrational excitation energies are found to be 7.7 and 0.513 eV giving $\delta \approx 15$. Thus, <u>for the gas phase</u>, we obtain at low LET, $G_{ion} = 3.57$ and $G_{ex} = 3.87$ giving $G_{ex}/G_{ion} = 1.08$ compared with the experimental values $G_{ion} = 3.30$, $G_{ex} = 3.95$ and $G_{ex}/G_{ion} = 1.20$.

In the liquid phase of water we argue for I = 8.3 eV by linear extrapolation of experimental results (Nikogosyan et al., Chem. Phys. <u>77</u>, 131, 1983). Also we extrapolate $\eta = 0.4$ at 9.8 eV which is the photionization efficiency in the gas phase at the ionization potential. Beyond 9.8 eV, gas phase η values are used with an energy shift 12.6-9.8 = 2.8 eV and with local averaging to smooth out resonances. Again $\langle ex \rangle^{+}(\ell) = 4.2$ eV is obtained by comparing with asymptotic W-value of ionization (20.8 eV). Ionization and excitation cross-sections in liquid water are taken from the work of Ritchie et al. (Proc. 6th Symp. Microdosimetry, 345, 1978) but σ_v is assumed phase independent. The q-values so obtained are subjected to the same adjustment as in the gas phase with an asymptotic value $q_{\infty} = 0.047$. The calculated G-values in the liquid phase are $G_{ion} = 5.73$ and $G_{ex} = 2.13$ which are comparable to those obtained by Kaplan et al. by a different method (Radiat. Phys. Chem. <u>36</u>, 493, 1990). The experimental values are $G_{ion} = 4.8$ and $G_{ex} \approx 0.8$. Therefore a very significant cage recombination is indicated for primary radical decomposition.

23. Dispersive Time in Radiation Chemistry

(A. Mozumder)

When a chemical process occurs with a time-dependent probability density such that the first moment exists then that moment can be used to scale the rate of that process and the process is regular, or non-dispersive. Examples are the usual first-order kinetics, fluorescence decay, radioactivity, etc. When the first moment diverges no scaling can be applied and the reaction time is termed dispersive. There are different reasons for dispersive time which are ubiquitous in radiation chemistry. In general dispersive times lead to time-dependent specific rates except that in the case of homogeneous second-order kinetics it need not be. A significant number of dispersive-time reactions originate from relaxation phenomena (mechanical, dielectric, glass transitions, etc.), as has been stressed by Plonka (Lecture Notes in Chemistry No. 40, Springer-Verlag, Berlin, 1986). However this is not always true. A closely connected question is the random fluctuation in reaction rates. In the following paragraph we submit a partial list of dispersive time reactions in radiation chemistry. We are in the process of analyzing these reactions with a view to understanding their general features.

1. Geminate recombination (fully or partially diffusion-controlled): both e-ion and neutral. 2. Geminate recombination by tunnelling at low temperatures, although the escape probability is zero. 3. Dose-dependent homogeneous second-order reactions, with or without time-dependent reactivity. 4. Radical reactions in polymer matrices below the glass transition temperature. 5. Non-exponential waiting time distribution in electron mobility (transport). 6. Kinetics of trapped electron decay in ice. 7. Certain types of radiation-induced isothermal luminescence decay. 8. Lifetime distribution in cations in micelles. Undoubtedly further additions can be made to this list.

24. Structure of Charged Particles Tracks

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

Over the past few years we have demonstrated the use of dipole oscillator strength distribution (DOSD) in determining the structure of electron tracks in water. This has been made possible in part because of the availability of DOSD over a wide span of energy and in part because of a reliable connection found by Ashley between DOSD and the differential inelastic collision cross-section. We have determined the spur size distribution in all phases of water, both in the differential and integral senses, and a clear phase effect has been shown at low energies. Using the same framework low-energy electron range and range straggling have been computed in the gas phase for some isomeric hydrocarbon molecules. In the next phase of our work we are turning our attention to the track-structure of heavy-ions. It is expected that the spur distribution in the penumbra of such ions will be somewhat different from that of low-LET, high-energy electrons. It is also expected that such a distribution will depend, to a certain extent, on the geometric or dynamical definition of a core and a penumbra. Our immediate objective is to investigate the sensitivity of penumbra structure on such definitions and also to examine the dependence of the spur size distribution upon the incident particle charge and velocity.

25. Magnetic Hyperfine Constants for Solitons in Polyacetylene from Ab Initio Calculations

(B. Kirtman,[1] M. Hasan[1] and D. Chipman)

Solitons play a fundamental role in conductivity and other properties of lightly doped trans-polyacetylene (t-PA), a material of considerable current interest in materials science. Yet, direct quantitative characterization of the neutral π radical defect has proved elusive. Of primary interest is the spin distribution inferred from magnetic hyperfine coupling constants (hfcc) measured by ENDOR spectroscopy. Unfortunately, the three active experimental groups provide widely different and mutually incompatible interpretations of their ENDOR spectra. This motivated our theoretical study using the methods of ab initio quantum chemistry.

We modelled the infinite radical polyene chain by the set of finite segments C_5H_7, C_9H_{11}, $C_{13}H_{15}$, $C_{17}H_{19}$, $C_{21}H_{23}$ chosen so that the soliton is symmetrically located at the chain center. Geometries were obtained by extending ab initio multiconfiguration results available for C_5H_7 and C_9H_{11} to the larger polyenes using interpolation and extrapolation factors derived from ROHF/MNDO calculations. This approach leads to limiting C-C single and double bond lengths in $C_{21}H_{23}$ that agree very well with experimental t-PA values.

Hfcc calculations were done by single excitation configuration interaction. A [6s3p1d|4s1p] contracted Gaussian basis set specifically designed for hfcc calculations was employed for the three smallest polyene radicals. For the two largest radicals a more tractable double zeta basis, which yields almost identical isotropic hfcc after uniform scaling, was used. Estimated uncertainties in the extrapolated geometries lead to insignificant variation of the calculated hfcc.

By the time $C_{21}H_{23}$ is reached, the sequence of computed hfcc is essentially converged for all CH units from the center of the chain to well beyond the half-width of the spin distribution, thus allowing for accurate extrapolations to the infinite polyene. The ab initio half-width of about three CH units is much narrower than any of the experimental values, whereas the coupling at the central proton is much larger. Our results also suggest directions for improving the experimental analyses, particularly in correcting oversimplified assumptions about the shape of the hfcc distribution and about the anisotropy variation along the chain.

Possible theoretical errors due to basis set incompleteness and higher order electron correlations have been estimated. Although the latter will shift the hfcc toward better agreement with experiment, the effect is too small to account for the discrepancy. Thus, the interpretation of the experimental ENDOR spectra remains in doubt. The large discrepancy between theory and current experimental interpretations raises the possibility that interchain interactions heretofore omitted from consideration could be significant.

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26. Polarized Cyclohexadienyl Radical Spectra in the Photolysis of Naphthalene Carboxylic Acids and Anhydride

(A. S. Jeevarajan, and R. W. Fessenden)

In a continuation of the ESR studies of the photolysis of aromatic acids (NDRL-3110), several derivatives of naphthalene have been studied. The reactions are similar to those of the benzene derivatives giving radicals by net H addition to the ring. These radicals are essentially cyclohexadienyl radicals with a benzene ring fused at the 1,2 or 2,3 positions to give a nine-center π system. These spectra give additional insight into the photochemical mechanism and provide an opportunity to study the electronic structure of these more complex, conjugated radicals.

Three compounds have given interpretable spectra, 1,4-naphthalene dicarboxylic acid, 1,8-naphthoic anhydride, and 1,4,5,8-naphthalene tetracarboxylic acid. Photolysis of 1,4,5,8-naphthalene tetracarboxylic acid and 10% 2-propanol in water gave the ESR spectrum of the anion radical and that of a hydrogen adduct at position 2 of the ring. The low-field lines of this steady-state esr spectrum appeared in emission and the high-field lines in absorption. This pattern is like that found with the benzene carboxylic acids and related compounds and is believed to arise from the cross reaction of the H adduct radical with the radical from the 2-propanol. The hyperfine constant (hfc) of the methylene protons is 28.9 G, lower than the value in most cyclohexadienyl radicals derived from benzene derivatives. Even at pH 13, one carboxyl proton is still present, suggesting a proton bridging between two carboxyl groups. When acetone was used as a sensitizer, the anion radical concentration was increased 20-fold and a hydrogen adduct to position 1 of the ring was found. In this case, the hfc of the methylene proton is even smaller at 20.9 G.

When 1,4-naphthalene dicarboxylic acid and 10% 2-propanol in water was photolyzed, an anion radical and the hydrogen adduct at position 1 were obtained. When acetone was added, the anion radical yield increased 3 times. The hfc of the methylene proton at 18.2 G is also very small.

Photolysis of 1,8-naphthoic anhydride in 2-propanol showed the presence of an anion radical and the polarized spectrum of the hydrogen adduct at position 2. The hfc of the two methylene protons is 30.1 G.

27. The ^{13}C Hyperfine Constants of $H_2N\dot{C}HCO_2^-$

(J. Jeevarajan and R. W. Fessenden)

As part of an effort to identify the radical formed by reaction of SO_4^- with glycine through its ^{13}C hyperfine constants, we have measured the ^{13}C constants of the radical $H_2N\dot{C}HCO_2^-$ which is formed by the reaction of OH with glycine. The normal form of the radical is well known and has the hyperfine constants, $a^H(CH) = 13.70$, $a^N = 6.09$, $a^H(NH) = 3.60$ and 3.19 G. The value of $a^H(CH)$ is unusually small for a substituted alkyl radical. Radiolysis-ESR experiments were performed with samples of glycine which were enriched with ^{13}C at the 1 or 2 position. The resulting spectra were analysed and the values of the hyperfine constants were found to be $a^C(2-C) = 15.00$ G and $a^C(1-C) = 7.33$ G. In each case, the spectra of the isotopically substituted radicals were described by the same values for the other constants within 0.01G as determined by a least-squares procedure using about 40 of the 48 lines. The value for the constant at the 2 carbon (the nominal radical site) is very much smaller than the 30-40 G for most substituted alkyl radicals. It appears that a considerable amount of the spin density must be shifted to the nitrogen. It should be noted that the ^{13}C constants for the form $+H_3N\dot{C}HCO_2^-$ from the crystal are much more normal at 45 G (J. R. Morton, J. Am. Chem. Soc. 86, 2325 (1964)).

28. An ESR Study of Hydrogen Atom and Hydroxyl Radical Trapping by DMPO in Aqueous Solution

(H. Hu and K.P. Madden)

Nitrone compounds have many advantages as free radical spin traps. They are insensitive to light and oxygen, soluble in a large number of solvents, and have spin adducts that are inherently stable since a carbon atom separates the nitroxide function from the trapped radical. DMPO (5,5-dimethyl-1-pyrroline-N-oxide) is a popular nitrone spin trap. It reacts to give relatively stable spin adducts from most carbon-, nitrogen-, and oxygen-centered parent radicals. We have initiated a study of DMPO spin trapping in aqueous solution starting with radicals from water radiolysis. The ESR spectrum of the DMPO-hydroxyl radical adduct has a g factor of 2.00562 and hyperfine couplings of 14.98 ± 0.01 G to the nitroxide nitrogen and the beta methylenic proton. The ESR spectrum of the DMPO-hydrogen atom adduct has a g factor of 2.00545 and hyperfine couplings of a^{N}_{N-O} = 16.52 ± 0.07 G, $a^{H}_{C-H_\beta}$ = 22.74 ± 0.02 G and $a^{H}_{C-H_\gamma}$ = 0.44 ± 0.03 G to the nitroxide nitrogen, the beta protons, and the gamma methylenic protons. In neutral aqueous solution, bubbling the solution with nitrous oxide reduces the yield of H adduct to about seven times less than the solution purged with nitrogen. This suggests that the hydrated electron may add directly to DMPO, followed by protonation to give the same spin adduct as direct hydrogen atom addition to DMPO.

29. A Time-Resolved ESR Study of Alkyl Radical Spin Trapping by 2-methyl-2-Nitrosopropane

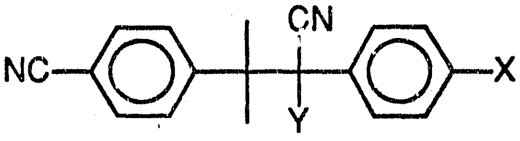
(K.P. Madden)

Hydroxyl radicals react with dialkyl sulfoxides at near diffusion-controlled rates to produce sulfinic acid radicals, which in turn fragment to produce quantitative yields of alkyl radicals. Using this reaction to produce parent alkyl radicals we have measured the trapping rate of methyl, ethyl, n-propyl and isopropyl radicals in neutral aqueous solution using the nitroso trap 2-methyl-2-nitrosopropane. The trapping rates were 1.7 x 10^7, 5.3 x 10^7, 6.9 x 10^7, and 4.6 x 10^7 M^{-1} sec^{-1}, respectively. The increase in trapping rate in the series methyl, ethyl, n-propyl follows the increase in electron-releasing power as these primary radicals become more highly substituted. The influence of steric effects is observed in the trapping of the isopropyl radical, where the greatly increased electron releasing capacity of this secondary alkyl radical is counteracted by greater steric hindrance in the radical-trap encounter complex.

30. Thermal Cleavage of Radiolytically Generated Radical Anions

(J.E. Chateauneuf and P. Maslak[1])

Studies have begun on the pulse radiolytic reduction of cyano-substituted diphenylethanes of the form, 1, in order to gain insight on internal bond strengths of radical anions by observation of unimolecular fragmentation patterns.



1

The radical anions of such compounds undergo thermal mesolytic cleavage of the central carbon-carbon ethane bond to yield anion and free radical fragments. For example, compound Y = Me, X = CF_3 was found to be directly reduced by the solvated electron following pulse radiolysis of pure MeOH, although no UV-visible absorption was observed that could be attributed to the resulting radical anion. Instead, two independent absorption bands (λ_{max} = 300 and 360 nm) were observed that coincide with the p-cyanocumyl radical and the respective anion. Pulse radiolytic reduction of 1 also occurred in CH_3CN, where the absorptions of both radical and anion were found to appear with identical growth kinetics, 1.5×10^7 s^{-1}. Similar experiments with compound Y=Me and X=H resulted in a considerably slower growth rate, 2×10^6 s^{-1}. Therefore, experiments thus far indicate that cleavage rates of $1^{\cdot -}$ are XY substituent dependent. Cleavage rates of other such compounds are being investigated.

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31. Time-Resolved Raman Study of the Hydroxyl Radical Reactions with Fluorophenols in Aqueous Solution

(Y. Su, G.N.R. Tripathi and R.H. Schuler)

The fluorine atom, because of its high electronegativity, exerts a profound effect on the charge distribution in fluorinated aromatic radicals and, as a result, the chemical properties, such as acidity constants, redox potentials, dehydroxylation and bimolecular reaction rate constants, are greatly altered. Raman studies of the fluorophenoxyl radicals, produced by pulse radiolysis in aqueous solution, are in progress so that the chemical behavior of these radicals can be understood from their molecular structure. These studies are also expected to provide an insight into the mode of OH attack on aromatic systems. Our preliminary studies show that about 35% of the OH radicals produced on radiolysis of water react with pentafluorophenoxide to form the tetrafluoro-p-benzosemiquinone radical anion, and about 50% of the OH radicals react to produce pentafluorophenoxyl radical. The remaining OH radicals probably form the tetrafluoro-o-benzosemiquinone radical anion. The Raman detection of the latter radical is possible only in its protonated form and, therefore, studies in acidic solutions are in progress. The ·OH and N_3· radical oxidation of tetrafluorohydroquinone in basic solutions results in similar yields of the p-benzosemiquinone radical anion, showing that the electron transfer is the primary reaction channel in both cases. Further studies are in progress.

32. Sequential Biphotonic Photochemistry of Re(I) Complexes

(M.R. Feliz, H. Altmiller and G. Ferraudi)

Flash photolysis of $Re(CO)_3$(4-phenylpyridine)$_2$Cl has shown that the generation of the photoproduct, λ_{max}= 420 nm, takes place in parallel with that of the emissive charge transfer state. A reducing radical is also generated in such a photoredox process and it has been scavenged with Cu(TIM)$^{2+}$. These results implied the presence of more than one excited state in the photophysics of the Re complex. A photoproduct, identified as a dimeric Re complex, has been isolated by liquid chromatography and characterized by means of its elemental analysis, UV-Vis and IR spectra. Action spectra based on the quantum yields of CO, Cu^{I}(TIM)$^{+}$ produced in the scavenging of radicals, and the dimeric Re photoproduct have been measured in order to establish the role of these electronic states. The quantum yield of emission is being investigated as a function of the photonic energy. Similar photochemical and photophysical experiments are being conducted with $Re(CO)_3$(4-cyanopyridine)$_2$Cl where we expect to have an order of electronic levels different than in the 4-phenylpyridine complex. These studies will establish a basis for comparison in further studies of the Re(I) complexes' photoreactions under sequential biphotonic excitations.

33. Magnetic Field Effects in the Photochemistry of Cr(III) Complexes

(M. Perkovic and G. Ferraudi)

Previous studies from this Laboratory have shown that intense magnetic fields change the rates of the ground and excited state reactions involving coordination complexes. These perturbations on the photoreactivity and emission of the ligand field states are being investigated with $Cr([14]aneN_4)(CN)_2^+$, $Cr(CN)_6^{3-}$, $Cr([15]aneN_4)(CN)_2$, and other related compounds of Cr(III) as a function of the ligand field strength and symmetry. In a continuation of previous experiments on the $(^2T_1, {}^2E)$ phosphorescence from $Cr([14]aneN_4)(CN)_2^+$ doped in $t\text{-}Rh([14]aneN_4)(CN)_2^+$, we have investigated the photophysics of $Cr(NH_3)_4(CN)_2^+$ under similar experimental conditions. The single exponential decay observed with and without the magnetic field (6 Tesla at 77 °K) stands in contrast with a double exponential and a single exponential decay in the respective presence and absence of the field for the $\{14\}aneN_4$ complex. Since these differences are probably related to the effect of distinctive tetragonal splittings of the $^2T(O_H$-parentage) and $^2E(O_H$-parentage), we are investigating the magnetodynamic effects on the trans-$Cr(en)_2X_2^+$, X=NCS,CN, family of compounds. Time-resolved magnetic circular dichroism (TRMCD) spectra of the excited states of the Cr(III) complexes are expected to give information about the nature of the magnetic field perturbation. We have made, therefore, CD and MCD spectral measurements of d-$Co(en)_3^{3+}$ and Zn(phtalocyanine) respectively while measurements of the complexes' TRMCD spectra are in progress.

34. Picosecond Spectroscopic Detection of Diphenylcarbenium Ion

(J.E. Chateauneuf)

Recently, Kirmse, Kilian and Steenken (JACS **1990**, *112*, 1699) have demonstrated that diarylcarbenium ions can be generated by protonation of diarylcarbenes in aqueous solutions. Nanosecond laser flash photolysis (LFP) of several p-substituted diphenyldiazomethanes in CH_3CN/H_2O solutions resulted in the absorption spectra of the corresponding cations. The parent diphenylmethyl cation ($Ph_2\overset{+}{C}H$) was, however, not observed due to rapid reactivity with H_2O.

In this laboratory, picosecond LFP has resulted in the detection of $Ph_2\overset{+}{C}H$. Both 266 and 355 nm ps LFP of Ph_2CN_2 in 1:1 $CH_3CN{:}H_2O$ solution has resulted in the transient absorption spectrum of $Ph_2\overset{+}{C}H$, $\lambda_{max} = 435$ nm. Confirmation that the spectrum observed was that of $Ph_2\overset{+}{C}H$ was obtained by independent generation of $Ph_2\overset{+}{C}H$ by photolytic (266 nm) heterolytic cleavage of Ph_2CHCl. The carbenium ion decayed with first order kinetics ($\tau = 750$ ps) in 1:1 $CH_3CN{:}H_2O$ as a result of nucleophilic attack by H_2O.

By far more significant, however, was the observation of $Ph_2\overset{+}{C}H$ generated by diazophotolysis in neat alcohols. In initial experiments, $Ph_2\overset{+}{C}H$ was observed in MeOH, EtOH and i-PrOH with lifetimes of 40, 700 and 800 ps, respectively. These observations represent the first direct evidence of a protonation mechanism in the O-H bond insertion reaction of carbenes with alcohols.

35. Photochemistry and Photoelectrochemistry of Squaraine Dyes

(B. DeLaBarre, M.V. George and P.V. Kamat)

Squaraine dyes are useful in various technological applications such as xerography, solar cells and optical recording media. The photophysical and photochemical behavior of bis(2,4-dihydroxyphenyl) squaraine (DHPS) and bis(2,4,6-trihydroxyphenyl) squaraine (THPS) are being investigated in aqueous and nonaqueous media. These dyes have a strong absorption in the visible with absorption maxima at 568 and 562 nm for DHPS and THPS respectively in methanol. Interaction of these dyes with colloidal TiO_2 leads to the appearance of a red-shifted charge-transfer band. The apparent association constants for the association between DHPS-TiO_2 and THPS-TiO_2 in acetonitrile were 1000 M^{-1} and 3000 M^{-1}, respectively. Excitation of this complex with 337 nm laser pulse led to the production of anion radical of the dye. Photochemical and photoelectrochemical processes are currently being studied with the aid of laser flash photolysis.

36. Photosensitization of TiO_2 Colloids with Squaraine Dyes. A Picosecond Laser Flash Photolysis Study.

(P.V. Kamat, S. Das,[1] K.G. Thomas,[1] and M.V. George)

The charge transfer from singlet excited squaraine dye (Bis(4-dimethylamine-2-hydroxyphenyl squaraine, SQ) into the conduction band of a large bandgap semiconductor and the recombination of injected charge with the dye cation-radical have been time-resolved in the subnanosecond time domain with the aid of picosecond laser flash photolysis. The kinetic and mechanistic details of such ultrafast charge transfer events are important in controlling the properties of photosensitizing dyes.

The dye SQ strongly interacts with TiO_2 colloid as indicated by the appearance of a charge transfer absorption band around 670 nm. The association constant as determined by the Benesi-Hildebrand method is 2700 M^{-1}. The quenching of fluorescence emission ($\phi_f = 0.84$) of SQ by TiO_2 colloids indicates an efficiency of 90% for the charge injection process. Formation of

$SQ^{\cdot +}$ (abs. max 580 nm) is seen within the laser pulse duration of 18 ps. when TiO_2-SQ complex is excited with a 532-nm laser pulse. The cation radicals have been independently characterized in pulse radiolysis experiments. Time-resolved transient absorption spectra recorded upon 532-nm excitation of SQ in colloidal TiO_2 suspension indicate a rapid back reaction between the injected charge and $SQ^{\cdot +}$ ($k = 3.7 \times 10^9\ s^{-1}$). Such a short-lived injected charge within the semiconductor particle highlights the problems associated with the photosensitization of large bandgap semiconductors with squaraine dyes.

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37. Photochemistry and Photophysics of ZnO Colloids

(P.V. Kamat)

High concentrations of quantized ZnO colloids (up to 0.1 M) have been prepared in ethanol solutions. These colloids exhibit strong absorption below 340 nm and the onset of absorption is dependent on the particle size. The smaller particles are highly fluorescent with an excitonic emission at 410 nm and a broad emission around 500 nm. 266-nm laser pulse excitation of ZnO colloids leads to the appearance of a broad absorption band in the red and infrared region. This absorption, which is readily quenching by dissolved N_2O, is attributed to the trapping of electrons at the ZnO surface. Charge trapping and interfacial charge transfer processes in quantized ZnO colloids are currently being studied with time-resolved transient absorption and emission spectroscopy techniques.

38. Semiconductor Assisted Photodegradation of Nitrophenols

(M.S. Dieckmann, K.A. Gray and P.V. Kamat)

Degradation of colored pollutants such as nitrophenols are being studied over oxide surfaces such as TiO_2, ZnO, Al_2O_3 and SiO_2. Colored pollutants offer a unique advantage because they may be able to sensitize large bandgap semiconductors such as TiO_2 and ZnO and themselves undergo photodegradation. Preliminary studies indicate that nitrophenols adsorbed over TiO_2 particles when irradiated with visible light undergo rapid degradation. Both the number and position of substituent nitro groups influenced the rate of photodegradation. Diffuse reflectance laser flash photolysis studies will be carried out to elucidate the mechanistic and kinetic details of the photodegradation of nitrophenols over various support materials.

39. Stability of Chlorophyll a in Spread Monolayers

(C. Mingotaud and L.K. Patterson)

The reactivity of chlorophyll a (Chl-a) in spread monolayers has been studied at the N_2-water interface, using HPLC analysis. It has been shown that pH, ionic strength of the subphase and monolayer surface pressure modify the stability of Chl-a in Langmuir films.

The pathway of degradation for Chl-a is controlled by subphase pH. At pH lower than 7, Chl-a is transformed to pheophytin and for pH higher than 8 formation of a new product, supposedly a partially hydrolyzed Chl-a, occurs. This new compound has never been obtained before in solution, where the complete hydrolysis of the chlorophyll is observed.

The speed of the reaction in strongly influenced by the subphase ionic strength and by the surface pressure. Indeed, a small change in the ionic strength from 2×10^{-3} to 3×10^{-3} M markedly increases the degradation of Chl-a at pH = 10.8 (after the reaction, the monolayer contains 45% of the new compound in the first case and at least 90% in the second). On the other hand, the compression of the monolayer accelerates the reaction for the lowest pressure, but significantly decreases the speed of degradation at higher pressures. This behavior may be related to changes in homogeneity of the monolayer.

40. Monolayer Studies with Phthalocyanines

(A.-F. Mingotaud and L.K. Patterson)

Two metal-phthalocyanines (M = Al or Zn) bearing long chains through sulfonamide bonds have been synthesized from the phthalocyanine tetrasulfonate. Force-area isotherms of pure monolayers at the air/water interface show collapse pressures of 62 mN/m and 48 mN/m, respectively. The corresponding areas/molecules are 66 $Å^2$/molecule and 39 $Å^2$/molecule. Thus, the Al-phthalocyanine seems to lie more parallel to the water surface. Steady-state and time-resolved fluorescence measurements have been carried out with these compounds in solution and in monolayers. These indicate little aggregate formation in the layer.

Long-chain derivatives of methylviologen have been synthesized to study electron transfer. The compound having two C18 chains forms a monolayer with a collapse pressure of 61 mN/m and a corresponding area/molecule of 86 Å^2. This relatively large area/molecule reflects the electric repulsion between molecules bearing two positive charges. To date no electron transfer from the phthalocyanine singlet state has been observed.

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