AUSTRALIAN INSTITUTE OF NUCLEAR SCIENCE AND ENGINEERING

14th ANS RADIATION CHEMISTRY CONFERENCE

9-11 NOVEMBER 1998

LUCAS HEIGHTS - AECS THEATRE

In association with the Australian Section RACI
David Sangster first became involved in radiation chemistry in 1948 as an Australian CSIR officer at Harwell, England. Subsequently, at Harwell he worked in several areas of atomic energy research. In 1957, during the initial stages of the establishment of the Australian Atomic Energy Commission at Lucas Heights, David joined the AAEC to continue this work. In 1961, he recommenced his research in the area of radiation chemistry, continuing in this field with his transfer to CSIRO in 1982 until the present time.

He is the co-author with Professor J.H.O'Donnell (University of Queensland) of a very successful textbook "Principles of Radiation Chemistry" and he has written several scientific papers ranging from industrial applications to the effect of radiation on aqueous solutions. His recent research interests include radiation crosslinking of polymers and radiation grafting to provide a bio-compatible surface which will be acceptable within the human body.

The Australian Institute of Nuclear Science and Engineering (AINSE) would like to pay special tribute to Mr. David Sangster's significant contribution to the field of radiation chemistry over this extensive period. The worldwide response to this conference marks the high esteem in which he is held by his colleagues throughout the scientific community. The collaborative research he has undertaken with AINSE scientists from various universities throughout Australia and New Zealand has been considerable and many AINSE Fellowship and Studentship holders are appreciative of the enormous contribution he has made to their research careers.

Although David Sangster is planning to retire in 1989 from his CSIRO appointment, we are sure his interests in radiation chemistry research will continue. The Institute, Council members, RACI Polymer Division, and conference participants wish David good health and much happiness in the years to come.
OVERSEAS VISITORS

PROFESSOR DAVID ARMSTRONG
Professor David Armstrong is Professor of Physical Chemistry and Dean of Science at the University of Calgary, Canada. His interests include radiation chemistry of gases, electron capture and ionic recombination reactions, pulse radiolysis of aqueous solutions, and one and two electron transfer processes in systems of biological importance.

DR. KLAUS-DIETER ASMUS
Dr. Klaus Asmus was born in 1937. In 1965 he graduated Dr-Ing from the Technical University of Berlin. He was a research Fellow at the Mellon Institute, Pittsburg 1966-8 before returning the following year as a research scientist to the Hahn Meitner Institute, where he has been head of the department of radiation chemistry. His research interests are in radical chemistry and the reactions of sulphur containing species, particularly those important in the radiation biology field. He last visited Australia and New Zealand in 1985.

THE LORD DAINTON
The Lord Dainton was born in Yorkshire. After graduating from Oxford and Cambridge he became a pioneer in the field of radiation chemistry. In 1950 he was appointed Professor of Physical Chemistry at Leeds University, Vice-Chancellor at Nottingham University in 1965 and Professor of chemistry at Oxford University in 1970. He has held many positions of distinction in the U.K., including Chairman of the University Grants Committee, Chairman, Council for Scientific Policy and Advisory Board of the Research Council, Chairman of the British Library Board, Chairman of the National Radiological Protection Board, Chancellor of Sheffield University and a Fellow of the Royal Society. In 1986 he was elevated to the peerage. His scientific interests include chain reactions, photo-chemistry, polymers and radiation chemistry. In the 1960s he visited Australia in connection with a Vice-Chancellors Conference and attended the AINSE Radiation Chemistry Conference. Some of his former students are prominent in Australian science to-day.

DR. E. MARTIN FIELDEN
Dr. E. Martin Fielden graduated from the University of Manchester and then worked as a postdoctoral Fellow with Dr. Baxendale at Manchester University before going to join Professor Jack Boag in the U.K. He is now head of the Division of Molecular Processes, Medical Research Council, Radiobiology Unit at Harwell. His research interests include superoxide reactions in cells and DNA strand breakage detection analysis.
OVERSEAS VISITORS

DR. ALAN CAMPBELL LING
Dr. Alan Campbell Ling was born in London and became an American citizen in 1980. He graduated from the University of London with a PhD in 1966. He then accepted a postdoctoral Fellowship with Professor John Willard at the University of Wisconsin, before taking up an appointment as A/Professor at West Virginia University. In 1975 he moved to San Jose State University, California, where he became Professor of chemistry and Dean of the school of science. In recent years, Dr. Ling has received many honours and awards. He has been visiting Professor at Wayne State University and during 1985-6 was a visiting scientist at Lucas Heights. His interests include radiation chemistry, radiation biology, fire extinguishants and the chemical evolution of life.

PROFESSOR SEIZO OKAMURA
Professor Seizo Okamura graduated from Kyoto University where he subsequently became Professor of Polymer Chemistry. After his retirement, he became Director of the Osaka Centre for Radiation Research. He has occupied many important positions in Japan. His interests include the effect of radiation on polymeric systems. He visited Australia in 1968.

PROFESSOR WOLFRAM SCHNABEL
Professor Wolfram Schnabel graduated from the University of Cologne and is now in the Radiation Chemistry department, Hahn-Meitner Institute for nuclear research Berlin and Professor at the Technical University, Berlin. His scientific interests include polymer chemistry, photo-chemistry, radiation chemistry and chemical kinetics.

PROFESSOR VIVIAN STANNETT
Professor Vivian Stannett was born in England and in 1957 became a U.S. citizen. In 1950 he graduated from the Polytechnic Institute of Brooklyn. Until recently he was Professor of Chemical Engineering and Dean of the Graduate School, North Carolina State University. He has held several important scientific positions in the U.S. His interests include radiation processing and effects of radiation on polymers. Previously visited Australia in 1974 for the AINSE Radiation Chemistry Conference.

DR. HARRY SUTTON
Dr. Harry Sutton was born in New Zealand and graduated from the University of Newcastle and Durham University. He spent some time at Leeds University before being appointed Senior Lecturer at Edinburgh University. He returned to N.Z. to take up an appointment at the Institute of Nuclear Sciences, DSIR, New Zealand in charge of radiation chemistry. His scientific interests include radiation chemistry, radiation biology and food preservation. He has previously attended several AINSE Radiation Chemistry Conferences.
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**Conference President**

Professor D.H. Napper  
University of Sydney

**Conference Committee**

- Professor D.H. Napper  
  University of Sydney
- Dr. R. Cooper  
  University of Melbourne
- Dr. G.S. Laurence  
  University of Adelaide
- Assoc. Professor M.A. Long  
  University of New South Wales
- Professor J.H. O'Donnell  
  University of Queensland
- Mr. D.F. Sangster  
  CSIRO
- Dr. R.B. Gammon  
  AINSE
- Dr. D.D. Cohen  
  AINSE

**Conference Secretary**

Mrs. J. Watson  
AINSE
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<td>Review</td>
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Friday 11th November, 1988 - Lucas Heights

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<td>2.00 - 2.40</td>
<td>51</td>
<td>New Light on the Mechanisms for Luminescence Emission in Electron-Irradiated Ice. T.I. Quickenden (Univ. of W.A.)</td>
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<td>2.40 - 3.00</td>
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<td>The Temperature Dependence of the Luminescence from Electron Pulse-Irradiated H$_2$O Ice. M.G. Bakker (Argonne Nat. Lab.), A.J. Matich, T.I. Quickenden (Univ. of W.A.)</td>
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CLOSING DISCUSSIONS

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Chairman: Professor J.H. O'Donnell

Professor D.H. Napper
Conference President
ABSTRACTS
Radiation and Chemistry

by

D.F. Sangster

Division of Chemicals and Polymers
CSIRO, Lucas Heights Research Laboratories
MENAI NSW 2234 Australia

Abstract

The passage of high energy ionising radiation - gamma rays and electron beams - through materials produces excited states and free radicals. Since the amounts of these species can be quantified and their production can be controlled, the utilisation of radiation chemical techniques provides a facile means of studying their chemical reactions and of utilising these in industrial applications. This is illustrated by investigations using pulse radiolysis or gamma radiation in such fields as organic, metal-organic, polymer, excited state and biological chemistry and by industrial applications principally in the polymer field.

Radiation chemical techniques have proved effective in investigations on the hydroxylation of aromatic compounds, the structure of alcohol-alkane solutions, polymerising species, excited states in gases and in cryogenic solids, ice structure, kinetics of polymerisation, redox reactions in organometallic compounds, unusual valence states and superoxide reactions.

Commercial applications have proved economically viable in the crosslinking, degradation and grafting of polymers and in the polymerisation and curing of monomers. Radiation grafting of prosthetic devices has been an effective means of obtaining a biocompatible surface.
The ascorbate radical is produced by the one-electron oxidation of ascorbic acid and the dimerised radical decays by disproportionation to ascorbic acid and dehydroascorbic acid. Generation of the ascorbate radical by reduction of dehydroascorbic acid would allow the reaction of the radical with oxidising metal ions to be followed. It has proved impossible to generate the ascorbate radical by the one-electron reduction of dehydroascorbic acid, but in the course of the study a number of reactions of other radicals produced by pulse radiolysis of ascorbic acid have been observed. Electrochemical methods confirmed the irreversibility of the oxidation of ascorbic acid and the inability to reduce dehydroascorbic acid. Dehydroascorbic acid rapidly undergoes a series of isomerisations and dehydrations which are the probable reason for the non-reversibility of the system.

In the course of the studies the formation of a vanadium(III)-ascorbate complex was observed; the formation of metal-ascorbate complexes provides a common initial step in the metal ion oxidation of ascorbic acid.
POLYMERISATION OF MICROEMULSIONS

by

R.A. Mann, R.G. Gilbert and D.H. Napper
School of Chemistry,
University of Sydney,
N.S.W., 2006, Australia

and

D.F. Sangster
CSIRO Division of Chemicals and Polymers
Lucas Heights, N.S.W., 2232, Australia

Abstract

Microemulsions have been extensively studied since their introduction by Hoar and Schulman [1] in 1943. In contrast to conventional emulsions, microemulsions are optically transparent or translucent and thermodynamically stable. They can be formed spontaneously by mixing oil and water in the presence of surfactant and cosurfactant. The dispersed phase in an oil-in-water (o/w) microemulsion comprises oil droplets less than 50nm in radius.

Polymerisation of o/w microemulsions was introduced in 1981 by Atik and Thomas [2] and since then a range of chemical initiators have been used in conjunction with various o/w microemulsions. Despite these studies the mechanisms of particle formation and growth have not been well established. This paper describes the first kinetic investigation of these systems using gamma-radiolysis as the initiation system. Radiation is a convenient source of primary free radicals whereby the effects of electrolytes and other solutes on the microemulsion can be avoided. In addition, it can be effectively switched on or off at will, making it possible to observe the relaxation of polymerisation to the thermal rate.

The effects of monomer concentration, dose rate and relaxation on the kinetics, particle size distribution and molecular weight distribution were investigated for sodium dodecyl sulfate/pentanol and hexadecyltrimethylammonium bromide/hexanol microemulsions of styrene in water. It was observed that the polymerisation rate shows only two intervals, increasing to a maximum before falling. Latex particles are reasonably small (10-40nm in radius) containing only one or two molecules of a relatively high molecular weight (1-2x10^6). They are believed to be formed predominately within the microemulsion droplets, but also within the aqueous phase at high dose rates.

References

ELECTROCHEMICAL MONITORING OF THE TRANSIENT PRODUCTS OF PULSE RADIOLYSIS

by

T.A. Green and T.I. Quickenden
Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands, W.A., 6009.

D.F. Sangster
CSIRO Division of Chemicals and Polymers, Lucas Heights Research Laboratories, Private Mail Bag 7, Menai, N.S.W., 2234.

Abstract

In conventional pulse radiolysis experiments, the decay kinetics of transient species is commonly monitored by spectrophotometry, electron spin resonance, or conductivity measurements. More recently (1,2) electrochemical methods such as chronoamperometry, and chronocoulometry have been used to study the products of radiolysis. These techniques can provide electrodic kinetic data about transient radical species which would be difficult to obtain by other means. Such techniques also provide an independent means of evaluating homogeneous rate constants. This paper will describe some results obtained by applying chronoamperometry to the transient species formed during the irradiation of aqueous solutions using pulsed electrons produced by the Van de Graaf electron accelerator at Lucas Heights.

(1) A. Henglein, Electroanal. Chem. 9, 163 (1976).
SUPEROXIDE RADICAL REACTIONS
WITH METAL COMPLEXES

by
P.J. McLay, P.M. May and G.T. Heftet

School of Mathematical and Physical Sciences
Murdoch University
Murdoch, 6150, Western Australia

Abstract

The bisdioxopiperazine anticancer drug Razoxane is known to interact synergistically with the anthracycline antitumour agent Adriamycin. Co-administration of the drugs alleviates the dose-limiting cardiotoxicity of Adriamycin. Redox cycling of the quinone moiety of Adriamycin with consequent formation of reactive oxygen species in the tissues is thought to be the cause of this toxicity. It has been postulated that the metal complexes of the biological metabolite of Razoxane reduces Adriamycin cardiotoxicity by reacting with generated superoxide radicals before this species or its disproportionation products can produce cellular damage.

The kinetics of the reaction of superoxide with the hydrolysed metabolite of Razoxane, ICRF 198, and structurally similar compounds ICRF 175, EDTA and DTPA, together with their Zn^{2+}, Cu^{2+} and Fe^{3+} complexes has been studied. The results show that there is little, if any, reaction between superoxide and the free ligands and the zinc complexes. Reaction with copper complexes is slow. On the other hand, the ferric complexes tend to react moderately rapidly with superoxide (with the exception of the DTPA complex). The possible biological significance of the results is considered. Other experiments indicate that at physiological pH the perhydroxyl radical HO₂ rather than the superoxide anion O₂⁻ is largely responsible for this reaction.
Redox Reactions, Reduction Potentials and Bond Dissociation Free Energies of Some Radicals in Aqueous Solutions

by

D.A. Armstrong,
P.S. Surdhar,
S.P. Mezyk

University of Calgary, Canada

ABSTRACT

Single electron reduction potentials are important for assessing rates and mechanisms of reactions. Because free radicals are relatively short lived in aqueous solutions, few experimental values of $E^0$ are available for these species. Several values have been calculated from gas phase data, but this requires the use of similarly structured stable molecules (e.g. Ar for Cl$^-$ and CH$_3$Cl for CH$_3$S$^-$) as models to obtain the free energies of solution of the radicals. Also, there is often considerable uncertainty in the bond dissociation energies and other required thermodynamic data. We have begun a programme of measuring $E^0$ for free radicals, including sulphur centered species. The reduction potentials will be reported and some redox reactions of RS$^-$ radicals will be discussed.
THEORETICAL STUDIES OF ELECTRON THERMALIZATION IN RARE GASES

by

L.A. Porter and R. Cooper,
Department of Physical Chemistry
The University of Melbourne
Parkville, Victoria

and

Derek Y.C. Chan
Department of Mathematics
The University of Melbourne
Parkville, Victoria

Abstract

The pulse irradiation of a sample of gaseous helium produces a large number of secondary electrons, which lose energy by collision with gas atoms. Once the energy of an electron falls below the lowest threshold for electronic excitation of helium (19.8 eV) the rate of energy loss drops, since energy is lost only by elastic collisions with the gas. Such lower energy electrons are termed subexcitation electrons.

We have studied the thermalization of subexcitation electrons in helium using a Monte Carlo simulation procedure. This has allowed us to determine the electron energy distribution function, N(E,t), as a function of time, starting from the initial subexcitation spectrum proposed by Platzman.1 As expected, the distribution eventually approached the Maxwell-Boltzmann form as the average electron energy approached thermal.

The results of this simulation have been used to calculate the relative conductivity to microwaves of the irradiated helium sample, and the results have been compared successfully with experimental data determined by this research group.

References

ELECTRON THERMALISATION IN OXYGEN

by

Ronald Cooper
Department of Physical Chemistry
University of Melbourne

Horatio Rodrigo
Division of Manufacturing Technology
CSIRO Preston Victoria

and

John M Warman
Interuniversity Reactor Institute
Technical University of Delft
DELFT The Netherlands

Ionisation phenomena in gases are controlled by a variety of electron energy loss processes such as thermalisation, attachment -or, capture- processes and ionic recombination. Electron capture by oxygen has been a process examined thoroughly by both radiation chemists and physicists. The simple Bloch-Bradbury mechanism;

\[ e^- + O_2 \rightarrow O_2^- \]
\[ O_2^- \rightarrow O_2 + e^- \]
\[ O_2^- + O_2 \rightarrow O_2^- + O_2 \]

predicts a second order dependence on Oxygen pressure of the electron capture rate. This is in contrast to most other species which show a simple bimolecular capture rate constant e.g. \[ e^- + SF_6 \rightarrow SF_6^- \quad K = 1.25 \times 10^{14} \text{M}^{-1} \text{s}^{-1} \]

In contrast with many other systems which show a maximum capture rate at thermal energies, oxygen will capture "hot" electrons. This means that in irradiated gases a mixed kinetic mechanism will be operating resulting in complex observations of the rates of electron disappearance.

In this study we have used a Febetron pulse radiolysis system together with microwave conductivity detection to monitor the concentration and the mobility of electrons in irradiated oxygen.

At high pressures the electron disappears with simple pseudo first order kinetics corresponding with the known thermal electron capture rate constant of \[ 2 \times 10^{-30} \text{cm}^6 \text{s}^{-1} \]. At lower pressures (less than 50 torr) the kinetics become non-exponential but can be satisfactorily resolved into a first power oxygen pressure dependent thermalisation process preceding and overlapping the square power capture process. From this we can determine the thermalisation time in oxygen gas.
OXIDATION OF HALOCARBONS TO CIO SPECIES

by
P.R. Pettit and R. Cooper,
Department of Physical Chemistry
The University of Melbourne
Parkville, Victoria

Abstract

Pulse radiolysis is a convenient technique in the study of gaseous systems, allowing for the generation of gaseous free radicals and examination of their subsequent reactivity. Using a Febetron 706 electron source, halocarbon molecules were irradiated to form simple halocarbon radicals and halogen atoms. For example:

\[
\begin{align*}
\text{CCl}_4 & \rightarrow \text{CCl}_3 + \text{Cl} \\
\text{CFCl}_3 & \rightarrow \text{CFCl}_2 + \text{Cl} \\
\text{CF}_2\text{Cl}_2 & \rightarrow \text{CF}_2\text{Cl} + \text{Cl}
\end{align*}
\]

The reactions of these radicals with oxygen are of special interest in atmospheric ClO\textsubscript{x} chemistry. The CIO free radical has been identified as an important participant in the ozone destruction cycle. It has sharp absorption in the near I.R. allowing easy identification by absorption spectroscopy, used in these studies to examine the rate of formation of CIO in an electron-pulsed mixture of argon, oxygen and a halocarbon.

The observed kinetics of formation are complex, but are seen to be consistent with the mechanism:

1. CCl\textsubscript{4} \rightarrow CCl\textsubscript{3} + Cl
2. CCl\textsubscript{3} + O\textsubscript{2} \rightarrow CCl\textsubscript{3}O\textsubscript{2}
3. CCl\textsubscript{3}O\textsubscript{2} + Cl \rightarrow CCl\textsubscript{3}O + CIO
4. CCl\textsubscript{3} + Cl \rightarrow CCl\textsubscript{4}

The validity of this mechanism has been confirmed by kinetic simulation using LARKIN,\textsuperscript{1} a computer program, and also by comparison with existing experimental data.

References

DIRECT OBSERVATION OF THE DYNAMICS OF THE FORMATION
OF ELECTRONIC EXCITED STATES IN GASES

by
Ronald Cooper
Department of Physical Chemistry
University of Melbourne

Studies of light emission from irradiated gases can be used to probe fundamental excitation processes, identify the products of these processes, and study the subsequent chemical reaction of these energetic species.

An early paper on emissions from pulse irradiated pure rare gases (et al and Sangster) showed that electronic excited states of argon, neon etc were produced by a direct process and a slower one involving ion recombination.

\[ \text{ie} \quad \text{Ne} \rightarrow \text{Ne}^* + \text{Ne}^+ + e^- \]

\[ \text{Ne}^+ + e^- \rightarrow \text{Ne}^* \]

These results came from pulse radiolysis experiments using a Febetron 706 pulsed electron beam facility. The questions which arose from these observations were directed towards the nature of the fast or direct formation process.

Picoscound pulse radiolysis experiments showed that the fast process was indeed pressure dependent and showed a delayed formation of excited states at low pressures. This was subsequently shown to be due to collisional deactivation of higher excited states created by some faster process.

At extremely low pressures—less than 5 torr—the emission is produced by a process whose kinetics are pseudo first order in rare gas pressure. The rate constants for this process are too high for atom-atom collisional rate processes and were shown to be due to secondary electrons of high kinetic energy ($< 10$ eV).

In gaseous mixtures with a vast excess of one component, the rate of production of emission from the minor component is shown to be linearly dependent on its pressure. Bimolecular rate constants for the production of excited states of nitrogen, aromatic hydrocarbons such as anthracene, tetracene, terphenyl etc in excesses of helium, or neon all are much greater than the expected maximum values for collisional processes involving atoms and/or molecules.

The subexcitation electron is the species responsible for these fast excitation processes in dilute mixed gases.
COMMON PRODUCTS FROM \(\gamma\)-RADIOLYSIS AND
UV PHOTOLYSIS OF METRONIDAZOLE

Douglas E. Moore* and Brian J. Wilkins*

'Department of Pharmacy, The University of Sydney
and
'School of Pharmacy, Central Institute of Technology,
Trentham, New Zealand

Abstract

Metronidazole (1-hydroxyethyl-2-methyl-5-nitroimidazole, MET), an antibacterial drug with activity against anaerobic infection, has been studied as an agent for the sensitization of hypoxic cells to damage by X- or \(\gamma\)-rays. The molecular mechanism of the biological action of MET and other nitroheterocyclic compounds is believed to be initiated through reduction (electron capture) by the nitro group (1). The possibility that biologically significant intermediates are formed on metabolism or radiolysis has stimulated the effort to define the products of chemical, metabolic and radiolytic reduction of MET and related compounds (2).

Photolytic reaction of MET has proved to involve a less complex sequence of reactions thereby enabling quantities of the major products to be isolated for identification purposes (3). The photochemical reaction proceeds through two unstable intermediates, a hydroxyimino-ketone and a ring-cleaved hydrolysis product before recyclization to a 1,2,4-oxadiazole. These compounds were also found following \(\gamma\)-radiolysis of metronidazole, being about 25% of the products. Saturation of the solution with nitrous oxide had no significant effect on the yield of imino-ketone, although it increased the overall rate of disappearance of MET in radiolysis. Conversely, the imino-ketone was not detected on addition of sodium formate or propan-2-ol to the radiolysis, but an increased yield of other products was observed. It is suggested that formation of the imino-ketone and oxadiazole in photolysis and radiolysis does not proceed via the nitro radical anion as first transient species.

References

The Maturation of Radiation Chemistry

by

F.S. Dainton
(Oxford)

ABSTRACT

For almost half a century after the discovery of X-rays and radioactivity little was known about detailed mechanisms responsible for radiation chemical change in fluids. In gases attention was focussed on measuring ionic yield, M/N, but in liquids, because the mean excitation potential, W, was unknown, even this was impossible. Impelled by the needs of protection and therapy the radiation chemistry of dilute aqueous solutions was much studied and led to valid concepts of indirect action, competition, protection (also implying sensitisation) but, with one notable exception, the nature of the primary chemical species remained a mystery to all investigators.

Less than two decades later the situation was transformed. Precision calorimetry and chemical dosimetry allowed yields, expressed as G values, to be measured for liquids and therefore the effects of temperature, phase, polarity, solvent structure, LET and solute nature to be ascertained. In aqueous systems it was inferred from the known reactivities of solutes such as Fe\(^{2+}\), Ce\(^{IV}\), O\(_2\), HCOO\(^-\), CH\(_2\)CH\(_X\) etc. that the primary chemical species available to react with solutes were H, OH, H\(_2\) and H\(_2\)O\(_2\) and the dependance of their G values on the above variables was explored. However in the 1950s certain remarkable effects of pH emerged, interpretable on the basis that OH, HO\(_2\) and even H could ionise and that the conjugate base had different reactivity. By studying the effects of neutral salts on rate constant ratios of "H" with two different solutes, it was shown that e\(^-\)\(_{aq}\) is the primary reducing species in water, and, in the same year, pulse radiolysis revealed the optical spectrum and made possible the determination of absolute rate constants of the primary and related odd-electron species. The physical and chemical properties of the electron in liquids, glasses and micelles are now better known than those of most common chemicals, it can be "titrated" by N\(_2\)O and the properties used to explore motion in glass-forming liquids, selective solvation and ion-atmosphere relaxation times.

Parallel, though less spectacular, advances have taken place in our knowledge of non-aqueous condensed systems but many problems remain.

I will tell as much of this exciting story as 45 minutes permit. The question as to whether the excitement will diminish and the emphasis be on applications in the future is one to be answered only by the younger chemists present!
Radiation Chemistry of Polymers at the University of Queensland

James H O'Donnell

Department of Chemistry, University of Queensland, Brisbane 4067

High energy radiation produces a variety of chemical reactions in polymers. These reactions include (1) main chain scission, (2) chain crosslinking, (3) elimination of small molecular products, and (4) structural changes in the polymer molecules.

The objective of the research program on radiation chemistry of polymers at the University of Queensland has been to understand the mechanisms of degradation and to quantitatively relate the nature and rate of degradation to molecular structure in various series of polymers and copolymers.

The properties of polymer materials are particularly dependent on molecular weight and special emphasis has been given to determination of the radiation chemical yields (G values) for scission and crosslinking. Molecular weight distributions and averages obtained by various methods including ultracentrifuge sedimentation have been utilised with equations deduced by extension and modification of theoretical expressions.

The radiation chemistry is greatly influenced by the presence of particular radiation sensitive or resistant groups, e.g. sulfonyl, carboxyl, and aromatic. The quantitative effects of such groups have been determined.

Structural changes in the irradiated polymers have been observed by 13C NMR spectroscopy, including solid-state spectroscopy. New chain ends resulting from scission and crosslinks have been determined in ethylene-propylene copolymers and diene polymers. Free radical reactions play an important role in radiation degradation of polymers and have been investigated by ESR spectroscopy.

This research program at the University of Queensland has always been closely linked to the Lucas Heights Laboratories through AINSE and the personal involvement of David Sangster in the AAEC and then CSIRO.

Session V Thursday 9.00 - 9.40 a.m. 13R
THE EFFECT OF ADDITIVES ON GAMMA-RADIATION CROSSLINKING OF LOW MOLECULAR WEIGHT POLYBUTADIENE RESIN.

B.M. SMITH¹, J.L. GARNETT², and R.P. BURFORD¹

¹ School of Chemical Engineering
² School of Chemistry
University of New South Wales
P.O. Box 1, Kensington, N.S.W., 2033, Australia.

ABSTRACT

The range of end use applications of elastomers is extended by their ability to be crosslinked or vulcanised. Vulcanisation was originally the process whereby sulphidic crosslinks were introduced into unsaturated elastomers, but today, vulcanised rubber is prepared by a variety of processes. The methods include heating the polymer in the presence of sulphur or free radical generators, or exposing the rubber to ionising radiation.

The inclusion of additives when compounding radiation crosslinked rubbers increases the crosslinking efficiency of the radiation, by providing a method for overcoming degradation, favouring crosslinking. With the incorporation of the right additive, it is possible to economically upgrade the performance of lower grade materials to match or surpass the performance of more expensive materials. In the proposed paper the role of novel additives in radiation cross-linking of a typical elastomer will be discussed.
AN ESR STUDY OF RADIATION INDUCED CROSSLINKING IN POLYPROPYLENE

by

W. Ken Busfield and Peter J. Pomery

Division of Science and Technology, Griffith University, Qld.  
Polymer and Radiation Group, University of Queensland.

Abstract

Post gamma irradiation grafting has long been recognised as a valuable method of producing graft copolymers to enhance surface and/or physical properties. The mechanism and site of grafting is of particular interest, particularly in semi-crystalline polymers in which multiple phases are present. The majority of studies have been directed towards polyethylene, whereas other polymers such as polypropylene, PP, have received less attention.

It has long been recognised that ESR provides a valuable probe into studies of the reaction mechanisms resulting from ionising radiation, and in this paper we report the use of ESR to probe the mechanism of the post-irradiation grafting of butadiene onto irradiated polypropylene. Because of the importance of polymer morphology on grafting reactions, both quenched and annealed polypropylenes have been examined over a range of grafting temperatures.

Examination, analysis and kinetic studies of the radicals produced in irradiated polypropylene have been identified as alkyl type and allyl type, the proportion of each being dependent on the irradiation temperature, thermal treatment and nature of sample, i.e. annealed or quenched. There is an observed transformation of alkyl to allyl type radicals which, in annealed PP, have a maximum stability at 318 K, are situated predominantly at crystal boundaries, and appear to be of major importance in the grafting reaction with butadiene. However, it also appears that stable alkyl radicals trapped in the crystalline core are also important in long term post irradiation grafting.

Session V Thursday 10.00 - 10.20 a.m. 15R
The Radiation Chemistry of Poly(Methyl Methacrylate)

by


Polymer and Radiation Group,
Department of Chemistry,
University of Queensland.

Abstract

In the past, the study of the radiation chemistry of poly (methyl methacrylate) has been mainly limited to the atactic polymer. Using mainly GC to detect volatiles produced on γ irradiation, and ESR to detect the radicals, a mechanism has been proposed which involves scission of the side chain and then of the backbone, so that the molecular weight of the polymer decreases.¹,²

Some work has been done on the isotactic polymer which indicates that as well as the side chain scission mechanism there is also possibly scission of the backbone leading to racemization.³ In this work we have sought to investigate this effect further, using GC, ESR, and NMR, of the isotactic PMMA because of instrumental advances in the twenty years since the work was published. As well, the effect of irradiation on the syndiotactic polymer is also being investigated.

3) Thompson, E.V., Polym. Lett. 1965, 3, 675

16R Session V Thursday 10.20 - 10.40 a.m.
Pulse Radiolysis and Flash Photolysis Studies on Chlorine Containing Polymers

by

W. Schnabel

Hahn-Meitner-Institute, Berlin GMBH, D-1000 BERLIN 39
Federal Republic of Germany

ABSTRACT

Various chlorine containing polymers have attained interest with respect to applications as resist materials in UV, X-ray or electron lithography. In order to elucidate reaction mechanisms and kinetics of radiation-induced reactions in these polymers we have started some time ago investigations with various aromatic and aliphatic polymers. This paper concerns mainly results obtained with poly-4-chloromethyl-styrene, PCMSt, and with poly(3,3,3-trichloroethyl methacrylate), PTCMA.

Flash photolysis of PCMSt in tetrahydrofuran solution at $\lambda_{\text{inc}} = 266$ nm (flash duration: 20ns) revealed the formation of benzyl type radicals which formed crosslinks.

\[ \text{CH-CH}_2^- \xrightarrow{\text{hv}} \text{CH-CH}_2^- + \text{Cl}^- \quad (1) \]

\[ 2 \text{P}_1^* \xrightarrow{} \text{P}_1-P_1 \quad (2) \]

Macroradicals formed according to reaction (3) presumably contributed to crosslinking.

\[ \text{Cl}^- + \text{CH-CH}_2^- \xrightarrow{} \text{CH-CH}_2^- + \text{HCl} \quad (3) \]

\[ 2 \text{P}_2^* \xrightarrow{} \text{P}_2-P_2 \quad (4) \]

Crosslinking was also observed with a copolymer of styrene with 28 mol % 4-chlorostyrene. In this case quenching of excimers of styrene repeating units by CMSt units resulted in the formation of additional benzyl radicals. Exciton migration along the chain in styrene blocks is assumed to promote quenching.
When PTCMA was irradiated in O₂-free dioxane solution by 100 ns pulses of 16 MeV electrons at concentrations below 0.04 base mol/1, main-chain scission occurred. G(S)=3.7 was equal to 0(0) observed with solid PTCMA indicating that main-chain scission was induced mainly by the direct action of radiation on the polymer. Interestingly, PTCMA crosslinked at polymer concentrations higher than 0.04 base mol/1. Since crosslinking was not observed in CH₂Cl₂ solution it was concluded that PTCMA acts as an electron scavenger in dioxane solution and that crosslink formation is due to the combination of lateral macroradicals that are formed via dissociative electron capture processes involving mainly electrons that otherwise recombine with parents ions.

\[
\begin{align*}
\text{CH}_3 & \quad + \text{e}^- \quad \rightarrow \quad \text{CH}_3^- \\
\text{O}=\text{C}-\text{O}-\text{CH}_2-\text{CCl}_3 & \quad \rightarrow \quad \text{O}=\text{C}-\text{O}-\text{CH}_2^-\text{CCl}_2 \\
\text{(P}) & \\
2 \text{P}_3^- & \quad \rightarrow \quad \text{P}_3^-\text{P}_3 \\
\end{align*}
\]

In the presence of O₂, main-chain scission was the predominant process in all cases. From kinetic measurements it was inferred that, in this case, the combination of PO₂ radicals is the rate determining step in the consecutive series of reactions leading to chain cleavage.

REFERENCES

1. Q.Q. Zhu and W. Schnabel, Polym, Degrad. Stab., in print
POLYMERISATION BY UV LASER

by

George L. Paul, David I. Klick, M. Alfred Akerman,
Darko Supurovic, and Haruki Tsuda.

Centre for Industrial Laser Applications
School of Physics
University of New South Wales
Kensington, NSW 2033
Australia

Abstract

Current UV curing technology for coatings involves the use of lamps to excite a photoinitiator in a mixture of monomers and oligomers. The polymeric chain reaction makes effective economic use of the UV photons. The same principle can be applied using a UV laser as the source of the photons. The high cost of the laser produced photons may be justified if there is an advantage in the use of the laser.

A series of experiments which has resulted in a patent for the Commonwealth will be described. Clear coatings of 7 μm thickness were irradiated with various wavelengths, pulse repetition rates and fluences. Coatings were cured over a range of 7 orders of magnitude of fluence, to as low as 10^{-4} mJ/cm². Cost estimates demonstrate that the laser has advantages over certain types of UV lamp.

Pigmented coatings were also cured by laser, and a prototype dye laser was developed to enable commercial curing.
LARGE DOSE
RADIATION EFFECTS ON MOLTEN
ISOTACTIC POLY(PROPYlene)

by
J.V. Hanna and W.K. Busfield

Division of Science and Technology,
Griffith University,
Nathan, Qld. 4111.

ABSTRACT

The ability of high resolution $^{13}$C NMR to effectively detect the triad and pentad stereosequences in isotactic poly(propylene) (PP) has allowed the high energy, radiation induced change to this stereoregularity (i.e. structural racemization on the macroscopic scale) to be monitored. Preliminary studies (1) involving the irradiation of highly isotactic PP (>93% isotactic, 70% crystallinity) up to the gel dose indicated extensive structural change, with the loss of isotactic, and concomitant increase in heterotactic and syndiotactic species, being represented by the following large triad G values:

\[
\begin{align*}
G(-ISO) &= 64 \pm 3 \\
G(+HET) &= 38 \pm 3 \\
G(+SYN) &= 24 \pm 3
\end{align*}
\]

Further solid state irradiations of this isotactic PP(2) indicated that the above triad G values were highly dose rate and morphology dependent, however, no real temperature dependence was apparent.

It has been known for some time that molten PP does not undergo gelation whilst irradiated in the molten state (3). This provides an excellent approach to study the racemization phenomenon in PP, to arbitrarily high doses above the gel dose. Pronounced first order behaviour is exhibited in the triad populations over a dose range of \( \sim 2000kGy \) (4), with initial G values describing stereoregular change now greatly increased to:

\[
\begin{align*}
G(-ISO) &= 202 \pm 5 \\
G(+HET) &= 108 \pm 5 \\
G(+SYN) &= 94 \pm 5
\end{align*}
\]

The insensitivity of these G values to temperature in the solid state, coupled to the large increases for the molten state G values, is attributed to a morphology effect rather than a temperature dependence. The rise of \( G(-ISO) \) from 64 to 202 is commensurate with an increase in proportion of the radiation-susceptible phases (amorphous and interlamellar surface regions) participating in racemic change.

(1) W.K. Busfield, J.V. Hanna, J.H.O'Donnell, A.K. Whittaker

Session VI Thursday 12.00 - 12.20 p.m.
Studies of the Oxidative Degradation of Polystyrene Systems.

P.J.Farrington, D.J.T.Hill, J.H.O'Donnell and P.J.Pomery

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Abstract

The radiation chemistry of polystyrene has held the interest of polymer chemists for many years. Work from this laboratory has shown the remarkably low radiation chemical yields in the gamma radiolysis of polystyrene and in further work we have seen that styrene offers a protective effect in many of its copolymers, and that polystyrene displays synergism in some of its blends. Contrary behaviour has been observed on exposure to the natural environment, where polystyrene degrades quite rapidly and its presence can sensitize the degradation of more durable polymers. As a part of the groups' continued interest in the radiation degradation of polymers, the process of "natural" weathering (long wavelength, ultra-voilet photolysis in an oxygen rich atmosphere) is now under investigation.

The photo-oxidation of polystyrene, poly(α-methylstyrene) and poly(p-methylstyrene) has been examined. The molecular weight changes that accompany degradation have been studied using gel-permeation chromatography, the formation of new functionalities followed spectrophotometrically, and the volatile products evolved determined using gas chromatography. The mechanistic and kinetic implications of this work will be presented.
RADIATION-INDUCED CATIONIC POLYMERIZATION OF VINYL AND RING-OPENING MONOMERS IN THE LIQUID STATE

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Abstract

The initiation of cationic polymerization with high energy radiation was first shown by Charlesby's group with liquid isobutylene in 1957. Both cobalt 60 gamma and electron beam radiations were studied. Subsequent research by a number of laboratories over the years has given a reasonably clear picture of various processes involved. Many questions remain however. This aspect will be briefly reviewed.

Work on the effect of solvents and the value of this initiation method for studying "free," i.e. unpaired cations will be reviewed.

Recently we have extended our earlier work with vinyl monomers to ring opening polymerization. In particular the 6, 8 and 10 membered dimethyl siloxanes and hexachlorocyclophosphazene have been studied. Details of this work, largely unpublished will be presented.
THE USE OF MONTE CARLO TECHNIQUES TO PREDICT DNA DAMAGE

by

D.E. Charlton,
Peter MacCallum Cancer Institute,
Melbourne, Australia

J.L. Humm and H. Nikjoo,
MRC Radiobiology Unit,
Chilton, U.K.

Abstract

The generation of double strand breaks (dsb) in the DNA of cells exposed to ionising radiations is generally agreed to be one of the major sources of damage leading to cell death. To calculate such events in the DNA requires a detailed knowledge of the radiation field and a model for the mechanism by which breaks are produced.

The radiation field can now be obtained by the use of computer codes which simulate the paths of ionising particles and their delta ray flux and produce the co-ordinates of each ionisation and excitation in the path. Strand breakage can be modelled by assuming that particular ionisation and/or excitation events in the DNA produce a break.

In this work a technique for calculating dsb will be described based on the results of an experiment by Martin and Haseltine (1). In this experiment the single strand breaks most removed from the decay of an $^{125}\text{I}$ atom incorporated into the DNA was measured using sequencing gels. The distribution of distances from the decay to the break was reported. This experiment was simulated using data on individual electron spectra emitted from $^{125}\text{I}$ and the electron track code of Paretzke (2). The experimental results could be fitted if it was assumed that a single strand break occurred if more than 17.5 eV was deposited in a volume representing the sugar-phosphate moiety of the DNA back bone.

Using this result single strand breaks in each DNA strand following the decay of incorporated $^{125}\text{I}$ can be identified. These, if an opposite strands and separated by a few base pairs, will produce a double strand break. Patterns of single strand breaks following the decay of incorporated $^{125}\text{I}$ were examined and dsb scored for several thousand individual decays. Near the site of the decay 0.89 dsb/decay was calculated. This compares with a measured value of approximately one.

*On leave from Concordia University, Montreal.

References

ROLE OF CHARGE MIGRATION IN DNA

by
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Abstract

The radiation chemistry of DNA has been extensively studied, the main reason being that DNA is the prime cellular target for lethal radiation damage. This damage is due partly to a direct effect and partly to an indirect effect. The indirect effect is caused by ionization in the surroundings of DNA leading to the reaction of OH radicals or organic radicals with DNA, whereas the direct effect is caused by ionization of the DNA itself with the subsequent formation of a radical cation in the nucleobases, the sugar moiety or in the phosphate ester groups. The relative contribution of the modes of cell deactivation is the subject of much debate.

I onizing radiation is known to create a number of lesions in DNA including DNA single and double strands breaks, creation of base free sites and modification of the DNA bases themselves. Henner et. al. (1) using DNA sequencing techniques, have studied the sites of DNA strand breaks induced by radiation. Their results have shown that strand breaks occur uniformly (±20%) along the DNA strand regardless of sequence. Gregoli et. al (2) and Symons (3), have shown that charge migration occurs via stacked bases in DNA with thymine being the eventual sink of a long range electron transfer and guanine being the sink for a short range positive hole transfer. It is believed that the fate of the radicals produced by this charge migration phenomenon, ie. T\textsuperscript{−} and G\textsuperscript{+}, may lead to strand breakage in the DNA.

This paper will present results we have obtained on the \textsuperscript{−} radiolysis of DNA and will deal with aspects of this observed charge migration phenomena.

Interpretation of Polymerization Kinetics with Radical Initiation.

by

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Abstract.

Australian studies have contributed very greatly to recent gains in understanding of the processes involved in polymer formation from solution and from emulsions. The greatest part of the work was done by the Sydney University school but it has relied heavily on measurements made at AINSE and on the wisdom and counsel of DFS. Although Monash Chemistry is very much the late arrival in this area, we presume to suggest in this paper both an analysis of the past and also the directions in which future work appears to us to be heading.

Specifically, we wish to discuss the evidence which is emerging from studies with accurate measurement of the rates of monomer use and of detailed particle size distributions throughout the polymerization process. Some comparisons may also be made between particle nucleation in such studies and particle nucleation in general.
Review of 1988 RADTECH Radiation Curing Conference

by

S. Bett
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ABSTRACT

The 1988 RADTECH conference was held in New Orleans in May of this year. The theme of "Radiating Advantages" was appropriately embraced by the large number and wide variety of the presentations given to the 1,200 strong delegation.

Highlights of the conference were:

* The large number of delegates attending with a wide variety of backgrounds and interests including: academic institutions, industrial chemists, marketing and sales executives and end-users.

* "Testimonials" to the technology (particularly EB) by very large corporate users including 3M, Tetrapak and Willamette.

* Best technical paper of the conference entitled "Vinyl Ether Functionalised Urethane Oligomers: An Alternative to Acrylate Based Systems" by S. Lapin of Allied-Signal Engineered Material Research.


These highlights together with a summary of the cross section of papers presented will be discussed.
"Fenton-like" Reactions of Iron and Copper at Neutral pH

by

H.C. Sutton

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ABSTRACT

Oxidations of organic compounds involving hydrogen peroxide, reducing radicals such as superoxide, and metal catalysts are believed to contribute to biological damage. Examples include inflammatory disease and the injury caused on restoring oxygen to tissues which have been temporarily deprived of it. Such oxidations are commonly thought to be mediated by OH\(^-\) produced in cycles such as:

\[
\begin{align*}
H_2O_2 + L-Fe^{2+} &\rightarrow L-Fe^{3+} + OH^- + OH^- \\
L-Fe^{3+} + O_2^- &\rightarrow O_2 + L-Fe^{2+}
\end{align*}
\]

in which the Fenton reaction (1) is the crucial and rate determining step.

Whilst reaction (1) is thermodynamically possible at pH 7 for ligands (L) such as EDTA which bind much more strongly to Fe\(^{3+}\) than to Fe\(^{2+}\), the evidence for OH\(^-\) formation in such circumstances is questionable. It is even more questionable for biologically available ligands such as citrate. Recent studies show that organic oxidations can be mediated by supposedly Fenton-like reactions in the absence of thermodynamically suitable ligands, and where kinetic evidence rules out OH\(^-\) as the intermediary. Studies of formate oxidation induced by reacting H\(_2\)O\(_2\) with Cu\(^+\) also show that OH\(^-\) is not produced, but limited oxidation occurs by a different mechanism.

Evidence will be presented to show that the oxidant produced in such circumstances is not OH\(^-\) but probably a peroxy compound of Fe\(^{2+}\) or of Cu\(^+\), which has different reactivity. In some cases it may be the result of a two electron oxidation to Fe(IV) or ferryl ion. The implications of this conclusion in "site specific" reactions will be considered. These, also, are commonly attributed to localised production of OH in Fenton-like reactions, and reaction at nearby sites.
RADIATION INDUCED SCISSION AND DEPROPAagation IN POLY-ALPHA-METHYlstyrene.

By R. W. Garrett, D. J. T. Hill and T. T. Le.
Polymer and Radiation Group, Department of Chemistry
University of Queensland, Brisbane. 4067.

Abstract

The ceiling temperature for alpha-methylstyrene is 61°C, so that polymerization can take place below this temperature, but above this temperature the reverse depropagation reaction in equation (1) is favoured.

\[ P_n' + M \xrightarrow{\text{--}} P_{n+1}' \]  

(1)

Poly-alpha-methylstyrene does not undergo spontaneous depropagation unless a chain propagation radical is first present. The thermal degradation of poly-alpha-methylstyrene occurs at a significant rate at temperatures above 200°C, because above this temperature thermal initiated random chain scission takes place. This process has been studied by several workers who have reported that depropagation to monomer occurs almost exclusively (1.2.3).

Gamma irradiation of poly-alpha-methylstyrene results in chain scission and the formation of chain propagation radicals. So that spontaneous depropagation under these conditions can occur at a significant rate at temperatures below 200°C, but greater than the ceiling temperature. For example at room temperature no significant depropagation occurs.

In this paper we report studies of the thermal and radiation degradation of poly-alpha-methylstyrene.


Session IX Thursday 4.40 - 6.15 p.m.
THE RADIATION DEGRADATION OF COPOLYMERS
OF STYRENE AND METHACRYLIC ACID

by


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Abstract

This group has previously studied the radiation degradation of poly(acid)s including poly(methacrylic acid), which contain the radiation sensitive carboxylic acid group. Studies of the radiation chemistry of styrene-methyl methacrylate copolymers have shown that the styrene units exhibit a protective effect, with lower yields of radicals and volatile products than expected from the composition of the copolymers and the radiation chemistry of the homopolymers.

Since poly(methacrylic acid) is highly radiation sensitive (G(CO + CO) approximately 11) it was decided to extend our studies of protective effects to examine styrene-methacrylic acid copolymers. The microstructure of these styrene-methacrylic acid copolymers has been well established, but very little work has been found on the effect of gamma radiation on these copolymers. Electron Spin Resonance measurements of radical concentrations at room temperature showed no protective effect. Gas Chromatography was used to measure the major volatile products, carbon monoxide and carbon dioxide from the copolymers and homopolymers. Gel Permeation Chromatography was used to characterize the copolymers and measure G(X) and G(S).

SIDE CHAIN EFFECTS IN SCISSION OF POLY(OLEFIN SULFONE)S BY RADIATION

by


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University of Queensland, Brisbane, Australia, 4067.

Abstract

Poly(olefin sulfone)s undergo bond scission in the backbone chain as the result of absorption of high energy radiation and are among the most radiation-sensitive polymers known. As such, they have found industrial applications in the field of microelectronics for the production of lithographic masks. 1

In this work, the poly(olefin sulfone)s with longer side chains (C6 - C18) are being studied.

Poly(butene sulfone), where the side chain is small, undergoes scission with the release of sulfur dioxide on irradiation and has a G(S) of approximately 12. Poly(ethylene) undergoes crosslinking upon irradiation and has a G(X) equal to 3 and G(S) equal to 1. The polymers under investigation have a radiation sensitive backbone as in poly(butene sulfone) and long side chains similar to a chain of ethylene units. Therefore, these polymers may undergo main chain scission and side chain crosslinking.

A variety of techniques such as viscometry, osmometry, gel permeation chromatography and NMR have been used to characterize these polymers.

RADIATION DEGRADATION OF CROSS-LINKED POLY(METHYL METHACRYLATES)

by


Polymer and Radiation group, Department of Chemistry, University of Queensland, Brisbane, 4067.

Abstract

Cross-linked poly(methyl methacrylate) has been made for use in dental resins, with Ethylene glycol dimethacrylate (EGDMA) and Tri-ethylene glycol dimethacrylate (TEGDMA) as cross-linkers.

Radiation of EGDMA-MMA and TEGDMA-MMA copolymers and TEGDMA and EGDMA homopolymers by $^{60}$Co gamma-radiation is expected to produce volatile products similar to those produced from gamma-irradiation of PMMA according to well known mechanisms. The radicals produced from chain scission may be identified by ESR. For example the propagating radical of PMMA due to chain scission is identified in the conventional 9-line spectrum. Radicals produced from branch scission and further reactions may also be predicted from analysis of the gaseous products by gas chromatography.

For example:

\[
\begin{align*}
\cdot\text{COOCH}_3 & \rightarrow \cdot\text{CH}_3 + \text{CO}_2 \\
\cdot\text{COOCH}_3 & \rightarrow \cdot\text{OCH}_3 + \text{CO} \\
\cdot\text{COOCH}_3 & \rightarrow \cdot\text{H} + \text{HCOOCH}_3 \\
\cdot\text{OCH}_3 & \rightarrow \cdot\text{H} + \text{HCHO} \\
\cdot\text{OCH}_3 & \rightarrow \cdot\text{H} + \text{CH}_3 \text{OH}
\end{align*}
\]

Thus the major gaseous products from the irradiation of PMMA are: $^2$

$\text{H}_2$, $\text{CO}_2$, $\text{CO}$, $\text{CH}_4$, $\text{MeOH}$, $\text{CH}_3\text{OCH}_3$, $\text{CH}_3\text{COOCH}_3$, $\text{HCO}_2\text{Me}$. Using similar mechanisms, it can be predicted that the ethylene glycol dimethacrylate side chain may produce ethylene glycol, ethane and ethanol in addition to these.

In this poster we report gas and radical yields, and propose production mechanisms for the identified volatile products of gamma radiolysis of these cross-linked methyl-methacrylates.

References


RADIATION (UV) DEGRADATION OF COPOLYMERS

by


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Abstract

As part of the GIRD projects on "Polymer Performance and Degradation in Hostile Environments", this group is investigating the effects of long wavelength UV-B radiation on the physical and chemical properties of styrene copolymers. The copolymers being studied include styrene-co-acrylonitrile, paramethylstyrene-co-acrylonitrile and alpha-methylstyrene-co-acrylonitrile. Different compositions were prepared at 60°C in benzene by free radical polymerisation. Copolymer composition and microstructure were determined by 13C NMR spectroscopy.

Thin films (20-50 µm), cast from appropriate solvents in a Doctor's Knife apparatus, were irradiated in a Q-U-V Accelerated Weathering Tester equipped with UV-B lamps. The long wavelength UV-B radiation is typical of that found in sunlight. Changes in tensile properties were determined on an Instron, and molecular weight changes by GPC. When these changes, attributed to chain scission and/or crosslinking especially in the styrene units, are related to copolymer composition, the protective effect of acrylonitrile can be established. The formation of carbonyl and hydroperoxide groups were monitored by FT-IR spectroscopy and volatile products were identified by GC. UV-VIS spectroscopy provided information on the formation of conjugated unsaturated groups.

Applied stress during irradiation results in enhanced degradation of the copolymer films. The Q-U-V allows us to determine the effects of changing environments, such as temperature and humidity, on the creep rate. Cut-off filters are used to isolate various regions of the UV-B radiation with a view to identifying the sites of radiation absorption.

References

THE SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF MICROPOROUS ALUMINOPHOSPHATE CATALYSTS

by


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Kensington, Australia

Abstract

Previous researchers have reported the development of new catalytic materials, known by the acronym AIPOs. These microporous solids have topologies similar to zeolites. Unlike zeolites, however, these new materials are synthesized hydrothermally in mildly acidic (pH 3-6) gel. This fact suggests the possibility of incorporating a variety of different elements into the framework of the solid, thus producing new bifunctional catalysts.

The aim of this project was to prepare a variety of XAIPO catalysts with different elements incorporated in the catalyst framework. X denotes the element incorporated in the solid. Figure 1 illustrates the elements tested.

These materials were characterized by ICPAES, Solid-State Magic Angle Spinning N.M.R., X-ray diffraction and BET adsorption techniques. Although no direct evidence is given, the results of these tests are consistent with the element being included in the framework of the solid. A total of 60 different metals were tested of which 48 produced stable XAIPO catalysts.

The activity of these catalysts in the oxidative coupling of methane to form higher hydrocarbons was measured. Of the 48 different XAIPOs tested, PbAIPO was the most active and yields of 11% higher hydrocarbons were obtained. Some other XAIPOs which were active include MnAIPO, SnAIPO and BiAIPO.

The yield of higher hydrocarbons increased by using mixed metal XAIPOs, some examples of mixed metal XAIPOs which showed activity are:

- PbMnAIPO
- PbMnSnAIPO
- PbMgAIPO
- PbMnNiAIPO

1. US patent #4,310,440

Session IX Thursday 4.40 - 6.15 p.m.
RADIATION INDUCED TRITIUM LABELLING OF MOLECULES CONSTRAINED IN MICROPOROUS CATALYSTS

by

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Abstract

Radiation induced exchange between tritium gas or tritiated water and an organic substrate has been used in the past as a method of producing tritium labelled compounds. The so-called Wilzbach technique utilised the self radiolysis of the tritium beta radiation to induce the exchange. The method suffered from the serious disadvantage that many very high specific activity byproducts were produced and a rigorous purification procedure was necessary to obtain a satisfactorily labelled product.

Our recent work with microporous zeolites and aluminophosphates as catalysts for hydrogen isotope exchange has led to our consideration of their use for constraining organic compounds within their pore structure during a radiation induced reaction. A number of organic substances have been adsorbed into an ALPO microporous crystalline solid and exposed to curie levels of tritium gas. The apparatus is arranged such that a minimum proportion of the organic exists external to the pore. The results show that the organic substance can indeed be labelled with tritium by such an exposure technique and the amount of byproduct formation is often very small. Toluene, for example, can be labelled with as little as 1% of the activity in byproducts. These results contrast markedly with the conventional Wilzbach gas phase system. It would appear that the constraining influence of the micropore may enhance geminate recombination reactions and thus make reformation of the parent molecule more likely. Thus in a labelling reaction byproduct formation is minimised.

The results are compared with ALPO catalysed exchange itself, and the distinction in the tritium distribution patterns between those of radiation induced and catalytic induced exchange is highlighted.

A study of the radiation chemistry of these systems is continuing.
LUMINESCENCE FROM ELECTRON-IRRADIATED ALKALINE EARTH OXIDE CRYSTALS

by

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Abstract

Luminescence from alkaline earth oxide crystals, particularly CaO and MgO, have been studied extensively in recent years. Such studies are important in understanding the effect of the interaction of radiation with insulating materials, and the formation of defects therein. It is now well established that F-type defect centres in these crystals are responsible for many of these emissions. In the case of the alkaline earth oxides, such centres involve the displacement of oxygen ions, followed by electron trapping and relaxation of the excited F-type centre. A luminescent band at ~ 375 nm observed in both CaO and MgO, has been shown to be due to electron trapping by an anion (oxygen) vacancy, and relaxation of an excited F+ centre. The origin of an emission band observed only in MgO at ~ 235 nm is not as well understood.

In the present study, the temperature dependence of light emissions from electron-irradiated CaO and MgO has been studied by time resolved luminescence spectroscopy after nanosecond irradiation with 0.2 to 0.6 MeV electrons. Emissions in CaO at 375 nm at both 293 K and 83 K, showing similar threshold characteristics for atomic displacement, have been attributed to the displacement of oxygen ions and subsequent electron trapping, resulting in the formation of F+ centres. The threshold energy of 0.31 ± 0.02 MeV corresponds to an oxygen displacement energy of 53 ± 5 eV. A 380 nm emission in MgO, also attributed to oxygen displacement and F+ centre formation, shows similar displacement thresholds for the two temperatures. However a 235 nm emission which is observed only in MgO shows a significant temperature effect, with a threshold energy of 0.30 ± 0.02 MeV at 293 K, and 0.41 ± 0.02 MeV at 83 K. It is proposed that the 235 nm emission at 293 K is also due to oxygen displacement, with a threshold of 52 ± 5 eV, and that the 83 K emission results from the displacement of magnesium ions leading to the formation of V-type centres.

References

TEMPERATURE EFFECTS ON GASEOUS ION RECOMBINATION

by

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Abstract

Gaseous ion-electron recombination rate data is only available for low pressures (less than 0.1 atm). Temperature variation has been observed in some simple systems and generally shows a decrease of recombination rate with increasing temperature. The rate constant for electron-ion recombination in noble gases was measured as a function of temperature (173K-373K), over a range of pressures (50 - 760 torr).

The gases were ionized using a short electron beam pulse, and the rates of recombination were determined by two methods:

(i) a microwave conductivity technique, which determines electron concentration specifically as a function of time; and
(ii) the measurement of optical emission in gases where such emission occurs upon ionic recombination: \( M^+ + e^- \rightarrow M^* \rightarrow M + hv \).

These techniques enabled us to determine rate coefficients at pressures up to one atmosphere for the first time.

The results obtained showed that in He and Ne the rate constant is slightly dependent on pressure, indicating a "radiative" recombination rate with coefficient \( \alpha_2 \), and a "third-body assisted" recombination rate, with coefficient \( \alpha_3 \).

\[
\begin{align*}
\alpha_2 & \quad M^+ + e^- \rightarrow M^* \rightarrow M + hv \quad \text{Radiative Recombination} \\
\alpha_3 & \quad M^+ + e^- + M \rightarrow M^* + M \quad \text{Third-body Assisted Recombination}
\end{align*}
\]

The total recombination coefficient \( \alpha \) can then be expressed as:

\[
\alpha = \alpha_2 + \alpha_3[M]
\]

where [M] is the bulk gas number density.

Current theories predict a negative dependence of \( \alpha \) on temperature. Experimentally, the observed dependence was negative at low temperatures but there is evidence for a change at higher temperatures.
New Instruments for Measuring Chemical Reaction Rates
in $\gamma$ Fluxes

Computer-Control of a Calorimeter and Simple Dilatometer.

by

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Monash University
Clayton, Victoria, Australia

Abstract

Two new instruments which have been developed for study of polymerization kinetics and which are useful both outside and inside a $\gamma$ flux will be presented. The microcalorimeter is listed among AINSE facilities (No 20). It measures the rate of enthalpy change, and this is normally proportional to the rate of chemical reaction. The development of this instrument has enhanced its capabilities and examples of new phenomena uncovered by its use will be displayed.

An automated dilatometer which is simple in concept and reliable in behaviour has also been developed by us and will be shown.

Both devices are suited to use, for example, in H11 or in GATRI, or with normal chemical environments.
KINETICS OF DISSOLUTION OF IONIC SUBSTANCES
by B.A.W. Colter and I.R. Wilson
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Abstract

The first association of Monash Chemistry and AINSE arose from attempts of our colleague, the late A.L. Jones, to investigate reports by Spitsyn that tracer labelled BaSO₄ is orders of magnitude more soluble in water than the unlabelled salt.

Careful studies with various methods of preparation established the role of particle size depending on the speed of precipitation as the main factor but even with slow production and extended aging of well formed crystals (5 - 25 μm) the enhancement was not reduced below about 15% [1]. The residual enhancement of solubility appeared to be due to defects and secondary nuclei resulting from internal irradiation during nucleation and growth. Further evidence suggested that well aged barium sulphate crystals (both labelled and unlabelled) have perfected outer layers that dissolve to reveal granular or mosaic internal structures that collapse into particles small enough to show enhancement of solubility according to the Kelvin equation for particles of sub-micrometre dimensions.

Rates of dissolution of barium sulphate and other 2:2 electrolytes of sparing solubility follow second order dependence on distance from equilibrium; a pattern that is peculiar to heterogeneous processes. This was rationalised by Davies and Jones by reference to a saturated stoichiometric boundary layer. In other circumstances, similar second order behaviour has been rationalised in terms of the Burton Cabrera and Frank picture of dissolution at surface kink sites perpetuated by ledges emanating from screw dislocations but studies of silver chromate [2] and of barium iodate [3] have given evidence of higher order dependences on concentrations, consistent with the involvement of more than two ions in the stoichiometry.

Further study of barium sulphate dissolving from a rotated single crystal confirmed the second order dependence on distance from equilibrium. Variation of solubility and apparent activation energy with mode of preparation of polycrystalline BaSO₄ was interpreted in terms of a competition between edges and dislocations (screw, line or plane) as loci for initiation of dissolution processes [4]. Monte Carlo simulations of the dissolusion process have been used to demonstrate the feasibility of this idea.

DIFFICULTIES ASSOCIATED WITH THE ELECTROCHEMICAL DETERMINATION OF RADIOLYTIC PRODUCTS

by

T.A. Green and T.I. Quickenden

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D.F. Sangster

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Abstract

The electrochemical study of the transient radicals generated by pulse radiolysis involves a number of experimental difficulties which are not encountered in spectrophotometric measurements. These problems include the electrical interference produced in the detection circuit by the irradiation pulse; the difficulty of measuring the very small currents produced at the working electrode; and the problems associated with the need for microsecond time resolution. This paper will describe some of the experimental precautions which are necessary to overcome the above difficulties.
A NEW MECHANISM FOR ICE LUMINESCENCE

by

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D.F. Sangster

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Abstract

Isotopic substitution of D for H has provided important new information about the mechanisms involved in producing the various luminescences from electron excited ice. New kinetic analyses combined with information drawn from crystallinity studies and studies of excimer emission from gaseous water vapour now enable a reassessment to be made of the species and mechanisms involved in the production of the ice luminescence.
THE EFFECT OF CRYSTAL FRAGMENTATION ON THE ELECTRON EXCITED LUMINESCENCE FROM ICE

by

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C.G. Freeman
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Abstract

Although the major portion of the luminescence from electron-excited ice is not affected by varying the extent of the ice fragmentation, it was found that the Balmer alpha emission line at 656 nm is reduced in intensity when the extent of ice fragmentation is increased. This effect will be explained in terms of the trapping at dislocations, of either exciton or electron precursors to the Balmer emission.

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FINE STRUCTURE IN THE LUMINESCENCE FROM U.V. EXCITED ICE

by

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C.G. Freeman

Department of Chemistry, University of Canterbury, Christchurch, 1, New Zealand.

Abstract

Previous work (1,2) from this group has established the existence of two luminescence bands from U.V. excited ice, centred around 340 and 420 nm. This paper will present the results of higher resolution work which shows that these bands can be resolved into a series of spectral lines. The effect of isotopic substitution of D for H on the line spacing has been determined and will be discussed. The mechanistic implications of these observations will be considered.


USE OF DNA SEQUENCE TECHNIQUES TO
ANALYSE DNA DAMAGE

by

Roger F. Martin, Glenn D'Cunha and Marshall Pardee

Molecular Science Group
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Abstract

In addition to its central importance in radiobiology as a critical target, DNA has also proved useful in basic radiochemical studies. The general structural features of the DNA double helix are well-established; hydrogen bonded pairs of complementary bases (A-T and G-C) are attached to two antiparallel chains of alternating deoxyribose and phosphate moieties. A major consequence of irradiation of DNA is the induction of strand breaks and the breaks are generally manifestations of fragmentation of the sugar ring. Thus the DNA molecule can be considered as an array of molecular dosimeters (deoxyribose groups) supported on a molecular framework of defined dimensions. Furthermore it is possible to introduce reactive species (e.g. radioactive isotopes) into defined locations within this framework and to record the sites of the induced strand breaks by application of DNA sequencing techniques. This sort of experiment enables assessment of the range of damage associated with the reactive species. We have used this approach to study the consequences of two sorts of events:

(i) decay of $^{125}$I, either covalently incorporated into DNA or associated with DNA as a $^{125}$I-labelled DNA ligand, and

(ii) generation of a free radical species on DNA by photolysis of a bound DNA ligand.
RADIATION INDUCED DISSOLUTION OF COLLOIDAL MANGANESE AND IRON OXIDES:

Paul Mulvaney(a), Franz Grieser(a), Ronald Cooper(a) and Dan Meisel(b)

(a) Department of Physical Chemistry, University of Melbourne, Parkville, Victoria, 3052.
(b) Chemistry Division, Argonne National Laboratory, Argonne, Illinois, 60439, USA.

ABSTRACT:

We have recently studied the reductive dissolution of a variety of colloidal iron and manganese oxides using γ-radiolytically produced radicals.

At pH 3, manganese oxides are quantitatively dissolved by weak reductants such as HO₂, as well as stronger reducing agents like viologen (E°=−0.44V) and 1-hydroxy-1-methylethyl radicals (E°=−1.5V). At low oxide concentrations however, radical-radical reactions compete with dissolution.

The stoichiometry of the dissolution obeys:

\[ \text{MnO}_x + 2x\text{H}^+ + 2(x-1)\text{R}^- \longrightarrow \text{Mn}^{2+} + x\text{H}_2\text{O} + 2(x-1)\text{R}, \]

where x is the oxidation state of the oxide due to the presence of both Mn(III) and Mn(IV) in the lattice, and \( \text{R}^- \) is the reductant. Hydrogen peroxide produced by radiolysis of water is also quantitatively oxidized at high oxide concentrations (>3m²/L).

By contrast, transfer of electrons to colloidal iron oxides at pH 3 does not result in quantitative dissolution. Some Fe\(^{2+}\) is released to the solution, but some electrons remain trapped at the surface as well as within the bulk lattice. Complete dissolution only occurs below pH 2.3. Trapping of electrons in the bulk lattice becomes more important at higher pH, and also dominates as the particle size increases. In alkaline solutions, electron transfer converts colloidal haematite into magnetite, which is even more resistant to dissolution.
Application of Pulse Radiolysis to the Chemistry of Radiobiology

by

E. Martin Fielden

MRC Radiobiology Unit, Chilton, Didcot, Oxon, U.K.

ABSTRACT

There is a large literature on the radiation chemical changes observed when DNA or its constituent moieties are irradiated in aqueous solution. These studies, however, do not identify the biologically significant lesions. Nevertheless, the classification of free radical damage to DNA, according to its oxidising or reducing properties, offers, in principle, a method of characterising such lesions more closely. Thus, hydroxyl radical attack on the nucleotides has been shown to yield a mixture of radicals with oxidising (type O) and reducing (type R) properties. Type O radicals in general will only react with reducing agents, which include most of the radioprotective agents, and will not react with oxygen. The reaction with reducing agents often leads to restoration of the original base moiety. Type R radicals, on the other hand, will react with oxygen and other oxidising agents (e.g. nitro-aromatic radiosensitisers) to yield a chemically modified (damaged) base. Thus, chemical radioprotection and sensitisation appear to operate on separate compartments of DNA base damage. Hydroxyl radical attack on the deoxyribose moiety yields a radical which is susceptible to attack by radiosensitising or protective agents, thus fitting into the competing repair/fixation hypothesis.

Direct ionisation of DNA bases is difficult to study in the solid states, but it has been shown that reaction of the $\text{SO}_4^-$ radical with the bases produces a positive ion by electron abstraction that should be equivalent to that produced by direct ionisation. The result is a series of base radicals with oxidising (type O) properties, but which in general have a different structure to the type O radicals produced by OH addition. With the exception of thymidine these type O radicals do not react with oxygen. However, this does not preclude there being an oxygen effect associated with direct ionisation since, by preventing ion recombination, oxygen can affect the initial yield of radicals. The study of sensitisers and protectors is an important method to probe the different yields and characteristics of DNA damage at its early stages.

While transmission spectroscopy is the most used technique for observing radiation induced changes in pulse radiolytic studies, it is generally applicable only to gas and liquid systems, and its use in the solid state is restricted to materials that have suitable optical properties. By observing spectral changes in the diffuse reflectance from opaque solid materials which have been pulse irradiated, information can be gained on the characteristics and kinetics of reacting species. Apparatus has been developed for studies with biologically-related material where the effects of energy deposited in the target molecules are of particular interest.

The apparatus and technique will be described and results presented following the irradiation of polynucleotides and DNA. These studies are particularly relevant to the understanding of the chemical processes that are fundamental to radiobiology, and complement the parallel studies on the effect of water radicals on DNA described above.

PROTEIN PEROXIDATION BY HYDROXYL RADICALS

by

J.M. Gebicki, G. Van Oorshot and J. Winn

School of Biological Sciences
Macquarie University
Sydney NSW 2109

Abstract

Early studies of the effects of radiation on proteins suggested that oxidized products could form in small yields. However, neither the chemical nature of the products nor their amounts could be determined in the absence of specific assays.

We have now applied a technique developed for measurements of nanomolar amounts of hydroperoxides to a variety of proteins exposed to gamma rays in presence of oxygen. The technique is based on oxidation of iodide in acid solution by the hydroperoxide:

\[ \text{ROOH} + 2\text{I}^- + 2\text{H}^+ \rightarrow \text{ROH} + \text{I}_2 + \text{H}_2\text{O} \]

The iodine complexes with excess \( \text{I}^- \) to give \( \text{I}_3^- \)

\[ \text{I}^- + \text{I}_2 \Leftrightarrow \text{I}_3^- \]

which has absorbance maximum at 358 nm with molar extinction coefficient of 30,000 M\(^{-1}\) cm.

Several proteins tested were capable of oxidizing \( \text{I}^- \) after exposure to <100 k rad of \( ^{60} \text{Co} \) rays. We selected bovine serum albumin and lysozyme for detailed studies. The oxidizing groups on the protein were identified as hydroperoxides, the effective oxidant as the hydroxyl radical and SH groups as effective antioxidants. We have recently begun to study the interaction between peroxidized proteins and other biomolecules.
IRRADIATION OF KIWIFRUIT

by

D.R. Wheeler¹, J.E. Packer¹, A. Stewart², and A.R. Ferguson³

¹Chemistry Department, ²Botany Department, University of Auckland, New Zealand
³Division of Horticulture & Processing, DSIR, Mt Albert, Auckland, New Zealand

Abstract

New Zealand production of kiwifruit [Actinidia deliciosa (A. Chev.) C.F. Liang et A.R. Ferguson 'Hayward'] for 1988 stands at 200,000 tonnes. This is expected to rise to 300,000 tonnes by 1990 and 380,000 tonnes by 1995. Three issues of economic concern to the New Zealand kiwifruit industry are (1) insect disinfestation, (2) control of post-harvest storage diseases, and (3) improved post-harvest storage quality.

The scientific and technological feasibility of using irradiation to provide quarantine security and to reduce post-harvest losses of fruit is well documented. However, differences in the response of organisms to irradiation requires the development of individual treatment protocols for fruit, insect pests and microorganisms.

The tolerance of kiwifruit towards irradiation is not known. There is a need to establish what beneficial effects can be achieved using the 1000 gray limit imposed by the U.S. Food and Drug Administration (FDA). We are also studying the effects of the higher irradiation levels usually considered necessary to control storage diseases. This research project has concentrated upon identifying both the beneficial and detrimental effects of irradiation on the quality and wholesomeness of kiwifruit, the radiation resistance of the fungal storage rot Botrytis cinerea and the possibility of using irradiation to give improved long-term storage and extended shelf-life.
Radical Induced Degradation of Organic Halogen Compounds; Radiation Chemical Model Studies Related to Other Fields

by

K.D. Asmus

Radiation Chemistry Group, Hahn-Meitner Institute, West Berlin, Germany

ABSTRACT

Halogenated organic compounds and their radicals have become an interesting research subject with relevance to various fields. Biochemical and clinical studies, for example, have revealed that the toxicity and cell damaging action of simple halogenated aliphatic compounds are closely related to the metabolic generation of free radicals. Radical species also play a major role in the overall environmental action of halogenated compounds, and this statement refers to atmospheric conditions as well as catalysis by solid state particles.

An excellent and most informative tool for model studies related to these fields is Radiation Chemistry which can provide fundamental kinetic and other physico-chemical information on radicals and short-lived species, in general. Such model investigations are necessary for the understanding of the underlying chemistry of halogenated organic radicals in complex biological and environmental systems and often relate to interesting basic questions in the field of physical organic chemistry.

Our studies are in particular concerned with the generation of primary radicals from halogenated aliphatics via oxidative and reductive initiation, and the formation and properties of halogenated peroxyl radicals generated in oxygen containing environment. This includes the measurement of absolute rate constants for individual radical reactions, the evaluation of redox properties of the radicals (particularly for halogenated peroxyl radicals), product analysis, specific aspects of carbon-carbon and carbon-halogen bond cleavage, halogen migration in radicals, and based on all the establishment of complex reaction mechanisms.
A review of the contributions of radiation chemistry to inorganic systems. It was quickly recognised that the redox properties of OH· and eaq and the time range of pulse radiolysis would allow the exploration of uncommon oxidation states of transition metals. Pulse radiolysis has contributed to the chemistry of intra- and inter-electron transfer reactions, coordinated free radicals, very fast ligand exchange reactions and stereochemical changes, and the reactions of transient metal oxidation states.

The generation of one-electron change intermediates and the direct observation of free radical reactions in model bio-inorganic and protein systems have made important contributions to our understanding of electron-transfer metal proteins.
Free Radicals and their Role in some Aspects of Human Endeavour:
Chemical Evolution of Life on a Planet's Surface and Fire-Control in Aircraft

Alan Campbell Ling
San Jose State University, San Jose, California U.S.A.

Abstract

Free Radicals, and high energy chemistry in general, contribute to many facets of our technological society. I have selected two areas that interest me, and two areas in particular which I hope will arouse interest in non-traditional areas of chemistry research, and that may provoke discussion and even perhaps scepticism or controversy.

With respect to the chemical evolution of life on this planet's surface, the ubiquitous hypothesis of a heavy rich methane/ammonia atmosphere, lightning discharges, and plethora of chemical reactions in a warm primordial soup is not founded in anything other than convenience. Convenience of conventional chemical reactions and processes. In fact, the original planetary atmosphere for Earth was most probably carbon dioxide, carbon monoxide, water vapor and nitrogen. Moreover, it was cold, with only a thin band of liquid water around the equator. Yet, development of life under these conditions is still virtually a certainty given various physical limitations on planetary size, orbital data around a suitable sun, and fundamental laws of physics. We will explore an alternate set of chemical reactions based on the carbon monoxide/carbon dioxide/nitrogen atmosphere that yield two key chemicals, cyanogen and carbon suboxide. This model, developed in conjunction with NASA planetary probes, appears to provide too many fortunate coincidences and interesting correlations to be totally ignored. It also avoids one of the long standing criticisms concerning the development of macromolecules, in that the impossibility of getting all of the necessary monomer units together at a high enough concentration at the same place and the same time is hard to deny.

Turning to a second area of endeavour, consider the problems of fire control in aircraft, particularly, the control of fires in engine nacelles where jet fuel contacting a 900°C surface might be in the presence of 600mph air-flows. Knocking the fire down and keeping the fire extinguished even though fuel, oxident and source of ignition are continuously present is no trivial task, particularly when very high airflow will both disperse the fire fighting agent and assist in vaporizing the fuel! Equally, fire control in the interior of any inhabited cabin poses special problems in fume control, volatility, and after effects. Yet fire is a chemical reaction and should be amenable to control by a chemical reaction. We will examine this problem and the advances made in recent years.

Supported in part by the U.S. National Aeronautics and Space Administration.

49R Session XI Friday 12.00 - 12.40 p.m.
RADIATION STUDIES ON ANTICANCER DRUGS

by

R.F. Anderson¹, J.E. Packer², W.A. Denny³, B.M. Sutton², C.J. O’Connor², and W.R. Wilson⁴

¹Gray Laboratory of the Cancer Research Campaign, Mt Vernon Hospital, Middlesex, United Kingdom

²Chemistry Department, ³Cancer Research Laboratory, ⁴Pathology Department, University of Auckland, New Zealand

Abstract

The one electron redox chemistry of the clinical antileukemia drug amascrine (I) has been studied using steady-state and pulse techniques. One electron reduction of I leads to an intermediate with a reduction potential -803 mV which disproportionates to I and its acridan, a strong reducing agent. One electron oxidation of I and one electron reduction of its quinimine (II) give a common intermediate which disproportionates to I and II, and which has reduction and oxidation potentials of 85 mV and 915 mV respectively at pH 7.4. The reduction of II occurs initially on the acridine ring, followed by intramolecular transfer to the quinimine moiety.

Nitracrine (III) and 2- or 4-substituted derivatives show promise as hypoxia selective cytotoxic agents, and are thought to be activated by enzymatically mediated nitro reduction. We have carried out one-electron reduction titrations of derivatives of III using γ-radiolysis of aqueous formate solutions to compare the products with those obtained from xanthine-oxidase mediated reductions.

\[ \text{CH}_3\text{O} - \text{NH}^\text{SO}_2\text{CH}_3 \]

I

\[ \text{CH}_3\text{O} - \text{NSO}_2\text{CH}_3 \]

II

\[ \text{Me}_2\text{NCH}_3\text{N}^\text{H} \text{NO}_3 \]

III

Session XII Friday 1.40 - 2.00 p.m.
NEW LIGHT ON THE MECHANISMS FOR LUMINESCENCE EMISSION IN ELECTRON-IRRADIATED ICE

by

T.I. Quickenden

Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands, W.A., 6009.

Abstract

Many of the luminescences emitted by irradiated, aqueous systems have been attributed to the $A^2\Sigma^+ \rightarrow X^2\Pi$ transition of OH radicals. In the gas phase, this transition is a dominant feature of emission from irradiated systems containing even a trace of water. It is therefore not surprising that the luminescences emitted by irradiated ice, particularly those in the 300 - 400 nm region, have also tentatively been attributed to this source.

However, a recent study of the laser excited luminescence from water vapour by Engel et al. (1) has led to an interesting new interpretation. These workers found that when water vapour is excited by photons of energy above ca. 10 eV, a broad spectral band of excimer luminescence is produced. The broad bandwidth of this emission is in sharp contrast to the narrow line spectra usually obtained from excited water vapour.

Engel et al. showed that the excimer emission arises from transitions between upper states of the water molecule which are separated by energy gaps appropriate to visible region luminescence.

This review will show the relevance of the work of Engel et al. to the identification of the source of the luminescences emitted by electron-irradiated ice. In addition, the information gleaned from isotopic substitution and crystallinity studies will be combined with these results in order to produce a new mechanism (2) for the production of the ice luminescence.


THE TEMPERATURE DEPENDENCE OF THE LUMINESCENCE FROM ELECTRON PULSE-IRRADIATED H₂O ICE

by

M.G. Bakker, A.J. Matich and T.I. Quickenden

Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands, W.A., 6009.

D.F. Sangster

CSIRO Division of Chemicals and Polymers, Lucas Heights Research Laboratories, Private Mail Bag 7, Menai, N.S.W., 2234.

Abstract

The temperature dependence of the 385 nm luminescence peak from electron pulse-irradiated H₂O ice was determined. The luminescence decay curve was analysed into short-lived and long-lived components and the temperature dependences of the two associated rate constants were determined. These measurements provided mechanistic information about the processes which lead to the production of the excited species in the ice lattice.

*Present address: Chemistry Division, Argonne National Laboratory, Argonne, Illinois, 60439, U.S.A.
ON THE ROLE OF HYDROGEN AND HYDROXYL IONS IN THERMOLUMINESCENCE AND OTHER RADIOLYSIS PROCESSES IN SOLIDS.

J.F. Boas and J.G. Young
Australian Radiation Laboratory
Lower Plenty Road
Yallambie
Victoria, 3085
Australia

Electron spin resonance (e.s.r.) and optical spectroscopic studies have demonstrated that a close relationship exists between substitutional hydrogen ions and the centres responsible for thermoluminescence in the alkaline earth oxides MgO and CaO. There are other reports which link hydroxyl ion impurities with thermoluminescence in LiF and CaSO₄.

However, despite intensive efforts in a number of laboratories, there has to date been only one example where a direct correlation has been shown to exist between the intensity of the e.s.r. signals from centres associated with hydrogen ions and the thermoluminescence glow peak. The paper will discuss some of the experiments and the possible thermoluminescence mechanisms.

References
GENERAL INFORMATION

VENUE

The Conference will be held in the AINSE Theatre (Institute Building) see map page 67, from Wednesday 9th November to Friday 11th November, 1988.

SYMPOSIUM

Wednesday 9th November, 1988
7.30 p.m. AINSE Theatre
"Radiation Chemists and Society"
 Speakers: The Lord Dainton, FRS
 Dr. R. Cooper
 Dr. G.S. Laurence
 Prof. J.H. O'Donnell
 Mr. D.F. Sangster

PAPERS

Timing
Green light shows for presentation of paper,
Warning lights show when 5 & 2 minutes are remaining,
Red light shows when presentation time has expired,
Discussion time of 5 minutes is then allowed by the Chairman.

Slides
Authors using 35 mm slides in conjunction with their talk are requested to place their slides in the projector magazine during the break preceding the session in which the paper is scheduled.

Poster Session
The Poster Session will be held in the ANSTO Amenities Centre adjacent to the Swimming Pool, see map p.67, at the scheduled time. Posters should be set up before the Poster Session commences and removed after the final session that day. Posters should be prepared before arrival at the Conference in accordance with the guidelines previously provided. Authors are expected to be in attendance by their posters throughout the poster session. Materials for setting up posters are available from any member of the AINSE staff.

ACCOMMODATION

For out of Sydney participants whose nominations have been previously accepted, accommodation has been arranged in accordance with advised requirements, at Stevens Hall, Lucas Heights (adjacent to the Institute Building, outside the Main Gate) - see map p.67, or at the Sapphire Motel, 408 Princes Highway, Sylvania Heights. The Institute will make payment directly for room only charges at Stevens Hall or the Sapphire Motel. Participants should make personal arrangements to pay cash for breakfast charges at Lucas Heights and the Sapphire Motel. Participants are requested to vacate Stevens Hall rooms by 10.00 a.m. Friday, and to leave their luggage in the room marked 'luggage' adjacent to the Theatre Foyer. Room keys to be left in the Stevens Hall Reception Office.
MEALS

Breakfast
For Stevens Hall residents, breakfast is served in the ANSTO Canteen from 7.30 a.m.
For Sapphire Motel residents, breakfast time to be advised.
Participants should make arrangements to pay cash for breakfast charges at Lucas Heights and at the Sapphire Motel.

Conference Lunch - Wednesday, 9th November, 1988
Lunch for all participants will be held in the Stevens Hall Dining Room during the scheduled lunch period (ref. programme). The cost has been included with the Conference Dinner payment.

Lunches - Thursday, 10th November and Friday, 11th November, 1988
Lunches may be purchased from the ANSTO Canteen.

Conference Dinner - Thursday, 10th November, 1988
Pre-Dinner Drinks - Amenities Centre with Poster Session
6.15 p.m. Buffet Dinner - Bamboo Room, ANSTO Canteen
7.45 p.m. After dinner speaker - Mr. D.F. Sangster

Note: No other meal service will be available at Lucas Heights on this evening.

Evening meals are provided on any other evening in Stevens Hall Dining Room from 5.30 to 6.00 p.m. for guests of Stevens Hall and the Sapphire Motel. Please advise the Conference Secretary if you require an evening meal on Tuesday, 8th November or Wednesday, 9th November, 1988.

TRANSPORT

Transport from Sydney Airport - Wednesday, 12th November, 1988
An ANSTO bus will leave the Australian Airlines Terminal (Sydney Airport) for Lucas Heights at 9.25 a.m. Kindly give your name to the driver when entering the bus. If any difficulty is experienced in locating the bus, the Australian Airlines Commonwealth Car Desk will advise details of its precise location.

Request to Participants Arriving on ANSTO Bus from Airport
As time will be limited, participants are asked to go directly to the AINSE Theatre and not to their rooms at Stevens Hall. Luggage may be left in a room adjoining the Theatre Foyer marked 'luggage'. Keys may be picked up from Stevens Hall Reception at any time during the day.

Transport from Sydney Airport (excluding Special Arrangements for Wednesday, 12th November, 1988)
Taxis are available from the airport to:
Lucas Heights,
Sydenham Railway Station - then train to Sutherland Station,
Sutherland Railway Station - then bus to Lucas Heights, or taxi (ref. bus timetable below)
Note: Bookings must be made for all transport listed below - through AINSE, as transport is only provided if demand exists.

<table>
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<th>Monday - Friday</th>
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Buses from Lucas Heights leave from outside ANSTO Main Gate

Buses from Sutherland leave from outside Post Office, Flora Street.

* Upon request these buses will transport to the Sapphire Motel

LUCAS HEIGHTS N.S.W.

1. Main Gate
2. AINSE Building
3. Canteen
4. AINSE Theatre
5. Stevens Hall
6. Reception
7. Amenities Centre
TRANSPORT

Transport from Sapphire Motel to Lucas Heights
Transport will be arranged for participants. Please wait outside the Motel Reception Office for pick-up at 8.20 a.m. It would be appreciated if participants with their own transport could drive to Lucas Heights and assist by transporting others if possible.

Transport from Lucas Heights to Sapphire Motel
Buses leaving Lucas Heights will transport participants to the Sapphire Motel (see timetable). It is necessary, however, to book for these services - through AINSE, as transport is only provided if demand exists.

Transport from Lucas Heights to Sydney Airport - Friday, 11th November, 1988
Transport will be arranged to take participants to Sydney Airport after the Conference concludes. Please place your name on the list provided, on the noticeboard outside the Theatre, if you require this service.

Participants leaving Stevens Hall - Friday, 11th November, 1988
Participants are requested to vacate their rooms by 10.00 a.m. Luggage may be left in the room marked 'luggage' adjacent to the AINSE Theatre Foyer. Room keys may be left in the Stevens Hall Reception Office.

TELEPHONE MESSAGES

Telephone messages will be taken for conference participants on:-

543-3411  543-3436  543-311
(AINSE)  (AINSE)  (Switchboard)

All enquiries concerning the Conference arrangements should be directed to:-

Mrs. Joan Watson,
Conference Secretary,
A.I.N.S.E.,
Private Mail Bag 1,
MENAI NSW 2234

Phone: 543-3411 or 543-3436
PARTICIPANTS
### List of Participants

#### Visitors from Overseas

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<td>Professor K.D. Asmus</td>
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<td>Dr. E.M. Fielden</td>
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<td>Professor A.C. Ling</td>
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<td>Dr. S. Okamura</td>
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<td>(Kyoto, Japan)</td>
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<td>Professor W. Schnabel</td>
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<tr>
<td>(Hahn-Meitner Institute, West Germany)</td>
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<td>Professor V.T. Stannett</td>
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#### Visitors from New Zealand

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<tr>
<td>(University of Auckland, N.Z.)</td>
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<tr>
<td>Mrs. D.R. Wheeler</td>
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<tr>
<td>(University of Auckland, N.Z.)</td>
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<tr>
<td>Dr. C.G. Freeman</td>
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<tr>
<td>(University of Canterbury, Christchurch, N.Z.)</td>
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#### James Cook University of North Queensland

(Chemistry and Biochemistry)

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#### University of Queensland

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<td>Dr. D.J.T. Hill</td>
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<td>Dr. H. Berko</td>
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<td>Mr. P. Farrington</td>
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<td>Dr. R. Kellman</td>
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<td>Mr. A. Lang</td>
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<td>Ms. C. Winzor</td>
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GRiffith University
(Science)
Mr. J. Hanna

University of Sydney
(Physical Chemistry)
Professor D. Napper
Assoc. Professor R. Gilbert
Mr. R. Mann
Mr. B. Morrison

(Theoretical Chemistry)
Mr. M. Milis

(Pharmacy)
Dr. D.E. Moore

University of New South Wales
(Chemistry and Industrial Chemistry)
Assoc. Professor J. Garnett
Mr. Dang Hui Phuoc
Mr. P. Dworjanyn
Mr. E. Kennedy
Ms. B. Smith

(Chemical Engineering and Industrial Chemistry)
Dr. R.P. Burford

(Chemistry)
Assoc. Professor M.A. Long
Mr. Chit Than
Mr. A. Watson

(Centre for Industrial Laser Applications)
Dr. G.L. Paul

Macquarie University
(Biological Sciences)
Assoc. Professor J.M. Gebicki

University of Technology, Sydney
(Physical Sciences)
Professor R.J. Breakspere

C.S.I.R.O.
(Chemicals and Polymers)
Mr. D.F. Sangster

Mr. G. Baxter
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