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AUSTRALIAN INSTITUTE OF NUCLEAR SCIENCE
AND ENGINEERING

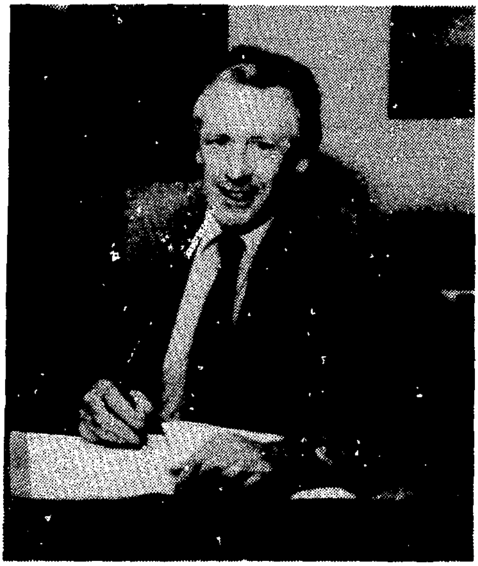
13 AINSE RADIATION CHEMISTRY CONFERENCE

12-14 NOVEMBER 1986

LUCAS HEIGHTS - AINSE THEATRE

In association with the Polymer Division RACI

13th AINSE RADIATION CHEMISTRY CONFERENCE, 1986



1929 — 1986

The Don Stranks Memorial Conference

AUSTRALIAN INSTITUTE OF NUCLEAR SCIENCE AND ENGINEERING
13TH AINSE RADIATION CHEMISTRY CONFERENCE, 1986

THE DON STRANKS MEMORIAL CONFERENCE

LUCAS HEIGHTS N.S.W.

In Association with the Polymer Division
Royal Australian Chemical Institute

Wednesday 12th November, 1986	Commencing	10.30 a.m.
	Conference Luncheon	12.40 - 1.40 p.m.
	Discussion	7.30 p.m.
Thursday 13th November, 1986	Commencing	9.00 a.m.
	Concluding	6.15 p.m.
	Conference Dinner	6.15 p.m.
Friday 14th November, 1986	Commencing	9.00 a.m.
	Concluding	4.00 p.m.

Conference President

Prof. J.H. O'Donnell	University of Queensland

Conference Committee

Prof. J.H. O'Donnell	University of Queensland
Dr. R. Cooper	University of Melbourne
Dr. G.S. Laurence	University of Adelaide
Assoc. Prof. D.H. Napper	University of Sydney
Mr. D.F. Sangster	C.S.I.R.O.
Prof. A. Sargeson	Australian National University
Mr. E.A. Palmer	A.I.N.S.E.
Dr. D.D. Cohen	"

Conference Secretary

Mrs. Joan Watson	A.I.N.S.E.

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Friday 14th November, 1986 - Lucas Heights

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ABSTRACTS

Structure of the Hydrated Electron

G. W. Robinson
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Abstract

Radiolytic processes have been the most popular source of solvated electrons for study. However, if threshold photoionization is used, a much greater specificity can be achieved with respect to interactions of the detached electron with the surrounding medium. Experiments have shown, for example, that the rate of threshold electron solvation in water is at least two orders of magnitude faster than that in the simple alcohols, while radiolytic sources of electrons produce each species equally well. These experiments furthermore have demonstrated that special solvent structural considerations are important in liquid water. Hydration of the electron requires exactly four water molecules.

This 4-water cluster is examined in light of past kinetic, thermodynamic and spectroscopic measurements. Up to now, there have been no experimental data on isolated, negatively charged water clusters that particularly favor the $H_8O_4^-$ form. In fact, this is one of the prominent clusters never observed by Haberland et al. These facts have kept deliberations about specific structural aspects of $H_8O_4^-$ to a minimum. Of course, in bulk liquid water, conditions for stability are undoubtably far different than they are in an isolated cluster.

Based on the threshold ionization experiments, it is concluded that the equilibrium state of the hydrated electron may actually be a hydrated semi-ionic pair $(OH^- \cdots H_3O)(aq)$. A structure for the hydrated dielectron is also suggested. In these structures, thermodynamic stability is gained through hydration of the hydroxyl ion, while spectroscopic properties arise from the oxonium radical.

In order to examine these novel structures more extensively, quantum theoretical computations (with H. F. Hameka) using Gaussian 82 have been carried out. The computations confirm the presence of one highly distorted OH bond when a localized excess electron is present. They therefore have relevance, not only to the hydrated electron problem in bulk liquid water, but also to experimentally important metastable states of small negatively charged water clusters, including the monomer.

Session I Wednesday 10.40 - 11.20 a.m.

INTRA AND INTER ELECTRON TRANSFER WITH MOLECULES CONTAINING METAL IONS, IN SOLUTION

by

A.M. Sargeson

Research School of Chemistry
Australian National University

Abstract

This talk will cover a review of aspects of electron transfer between metal ion complexes and from ligand radicals bound to a metal ion. The degree of non-adiabaticity of such processes and the orbital symmetry demands of the reactions will be addressed. The transfer of electrons intro molecularly through saturated organic frame-works will also be considered and some experiments which bear on this issue will be outlined.

Session I Wednesday 11.20 - 12.00 noon

REACTIONS OF SUPEROXIDE ANION WITH SOME METAL COMPLEXES OF BIOLOGICAL INTEREST

by

S.M. Trotman, J. Webb, and D.F. Sangster†

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

†CSIRO Division of Chemical Physics
Lucas Heights Research Laboratories
Sutherland, New South Wales

Abstract

The superoxide driven Fenton reaction (sometimes called the iron-catalysed Haber-Weiss reaction) has been widely accepted as a major factor contributing to the toxicity of the superoxide anion in biological systems. It is usually suggested that low molecular weight iron complexes catalyse the *in vivo* reaction of O_2^- with H_2O_2 in a two step process which produces reactive OH radicals.

$$O_2^- + \text{Fe(III)complex} \rightarrow O_2 + \text{Fe(II)complex} \qquad [1]$$

$$H_2O_2 + \text{Fe(II)complex} \rightarrow OH + OH^- + \text{Fe(III)complex} \qquad [2]$$

There is little doubt that *in vitro* mixtures of O_2^-, H_2O_2 and 'biological' iron complexes can certainly produce detectable quantities of OH. However, if reaction [1] is too slow to compete effectively with other concurrent *in vivo* reactions of O_2^- and iron(III) complexes, then its relevance to *in vivo* superoxide toxicity is questionable.

The uncatalysed dismutation of superoxide,

$$O_2^- + O_2^- \xrightarrow{2H^+} O_2 + H_2O_2 \qquad [3]$$

occurs with a rate constant of 8×10^4 L mol^{-1} s^{-1} at pH 7.8. Widespread investigation has so far revealed only one 'biological' iron complex, iron(III) picolinate (pyridine-2-carboxylate), which reacts with superoxide with a rate constant (9.3×10^4 L mol^{-1} s^{-1}) comparable with that for the uncatalysed dismutation (1). We have recently commenced a systematic study of the rates of reaction of O_2^- with a range of metal complexes containing both naturally occurring and pharmaceutical chelators. Re-investigation of the reactivity of iron(III) picolinate gave a rate constant of only $(8.1 \pm 2.2) \times 10^3$ L mol^{-1} s^{-1} for its reaction with O_2^- at pH 9, which is an order of magnitude smaller than that determined by Bannister *et al.* (1). In the light of these results the role of ion-picolinate complexes as potential catalysts for the *in vivo* Haber-Weiss reaction may have to be re-considered.

Reference

1. W.H. Bannister *et al.*, *Inorg. Chim. Acta*, 78, 139 (1983).

Session I Wednesday 12.00 noon - 12.20p.m.

14

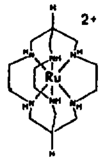
OXIDATION OF ENCAPSULATED RUTHENIUM COMPLEXES

P. Bernhard, and A. M. Sargeson
Australian National University

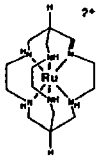
Abstract

A newly developed synthetic route[1] led to the isolation of the first encapsulated Ru(II) and Ru(III) complexes, e.g.

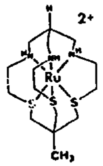
$Ru(sar)^{2+}$



$Ru(imsar)^{2+}$



$Ru(Mesar\text{-}S_3)^{2+}$



An interesting aspect is the facile oxidation of the macrobicyclic ligand, promoted by the metal center:

$$Ru(sar)^{2+} \quad + \quad oxidant \xrightarrow{k_1} Ru(sar)^{3+} \qquad (1)$$

$$2\ Ru(sar)^{3+} \xrightarrow{k_2} Ru(sar)^{2+} \quad + \quad Ru(imsar)^{2+} \qquad (2)$$

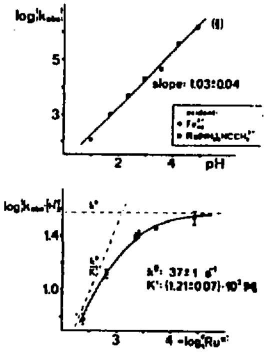


Fig.

For the disproportionation (2) a rate law:

$$k_2 = \frac{k^o}{(1 + K'[Ru(II)])\ [H^+]}$$

(cf. Fig.) has been established using stopped flow techniques.

In order to extend the measurements above pH 5 it is necessary to increase the rate of the initial oxidation (1) by using powerful one - electron oxidants, e.g. radicals.
Recent experiments have shown that the Ru - complexes react with various inorganic radicals, generated by using the electron accelerator at Lucas Heights, at nearly diffusion controlled rates: $k(OH\cdot)$: 7.5 10^9 $M^{-1}s^{-1}$; $k((NCS)_2^-\cdot)$: 2.5 10^9 $M^{-1}s^{-1}$; $k(Br_2^-\cdot)$: 2.9 10^9 $M^{-1}s^{-1}$.

(1) P. Bernhard and A.M. Sargeson, J. Chem. Soc. Chem. Commun. 1985, 1516.

Session I Wednesday 12.20 - 12.40 p.m.

RADIOLYSIS AND PHOTOLYSIS OF SOLID, LIQUID AND GASEOUS WATER

by

T.I. Quickenden and D.F. Sangster
University of Western Australia & C.S.I.R.O.

Abstract

The radiation chemistry and photochemistry of water impinge on many areas of fundamental and applied importance. It is thus perhaps surprising that the optical peoperties of water have not been fully explored. Until recently, the ultraviolet absorption spectrum of liquid water had not been reliably determined and even at the present time, the visible absorption spectrum of liquid water possesses considerable uncertainty. The absorption spectrum of ice is even less well defined.

The emission spectroscopy of water in the gas phase is mainly that of water fragments and good definition of most of the observed emission lines is now available. The emission spectra of solid water differ substantially from the spectra of gaseous water insofar as broad bands dominate and these are difficult to assign to particular electronic transitions. However, there are good reasons to believe that the ubiquitous $A^2\Sigma^+ \rightarrow X^2\pi$ transition of OH plays an important role in ice emission spectroscopy.

This review will consider the results of over ten years' study of the above spectroscopic areas using electron, U.V. and thermal excitation of the various states and polymorphs of H_2O water and its isotopic variants. The radiation chemical and photochemical processes which produce excited states in water will be discussed. The kinetic and other techniques which have led to the identification of light emitting species will be considered and the future directions of this series of investigations will be described.

Session II Wednesday - 12.40 - 1.20 p.m.

5R

LUMINESCENCE FROM PULSE IRRADIATED, CRYSTALLINE, D_2O ICE

by

T.I. Quickenden and C.F. Vernon

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

D.F. Sangster

CSIRO Division of Chemical Physics, Lucas Heights Research
Laboratories, Private Mail Bag 7, Sutherland, N.S.W., 2232,
Australia.

Abstract

Following previous work on the pulse radiolysis of D_2O vapour (1) we have determined the spectral distribution of the luminescence emitted by pulse irradiated, crystalline samples of D_2O ice. The prominent U.V./visible emission band observed around 385 nm in H_2O ice (2,3) was also observed in D_2O ice. However, the visible region in D_2O ice was of higher intensity than in H_2O ice and showed a distinct emission peak whereas the visible emission from H_2O ice appeared only as a "tail" on the 385 nm peak.

Previous investigations of luminescence from D_2O ice have raised the possibility that its distinctive visible region emission peak might arise from the excitation of trace organic impurities which are not commonly removed from isotopically purified D_2O. However, the results of the present study, which used oxidatively purified D_2O samples, indicate that this is not the case.

Radiolytic photon yields and luminescence lifetimes have also been determined as a function of wavelength for D_2O ice samples irradiated with a pulsed electron beam. These values will be compared with the corresponding data for H_2O ice.

(1) T.I. Quickenden, C.F. Vernon, R.A.J. Litjens, C.G. Freeman and D.F. Sangster, "Time resolved study of the luminescence produced by the pulse radiolysis of D_2O vapor." J. Chem. Phys. 85, 80-85 (1986).

(2) T.I. Quickenden, S.M. Trotman and D.F. Sangster, "Pulse radiolytic studies of the ultraviolet and visible emissions from purified H_2O ice." J. Chem. Phys. 77, 3790-3802 (1982).

(3) T.I. Quickenden, S.M. Trotman and D.F. Sangster, "Subdivision of the luminescence spectrum of irradiated crystalline H_2O ice." Radiat. Res. 101, 407-411 (1985).

Session II Wednesday 2.20 - 2.40 p.m.

THE EFFECT OF CRYSTALLITE SIZE ON THE LUMINESCENCE FROM PULSE IRRADIATED H_2O ICE

by

M.G. Bakker, T.I. Quickenden and C.F. Vernon

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C.G. Freeman

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D.F. Sangster

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Abstract

The spectral and kinetic characteristics of the luminescences emitted by pulse irradiated H_2O ice samples were examined as a function of various preparation conditions which produced a variety of crystallite sizes. Some ice samples were formed by very slow growth and contained only several separate crystals per sample. Other samples were grown more rapidly and contained several hundred distinguishable crystallites. Polycrystalline samples which contained crystallites of sub-microscopic size were grown by H_2O vapour deposition in a vacuum.

The results of these investigations indicated that with one possible exception, the processes which lead to the emission of luminescence from electron pulse irradiated ice arise from reaction regions which are very small and which are probably less than ca. 40 nm in linear dimension.

Session II Wednesday 2.40 - 3.00 p.m.

STUDIES OF THE QUENCHING OF THE LUMINESCENCES EMITTED BY ELECTRON PULSE IRRADIATED AND U.V. EXCITED H_2O ICES

by

M.G. Bakker, T.A. Green and T.I. Quickenden

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Australia.

Abstract

The reduction of luminescence intensity by quenching gases such as O_2 provides a convenient means to ascertain whether solid state luminescences arise from the surface of the solid or from within the material.

In the present investigation, O_2 gas was used to quench the luminescences emitted by U.V. excited (1) and electron excited (2) H_2O ice. In the latter case, the O_2 produced negligible reduction in luminescence intensity, while in the former case, substantial decreases in intensity were produced. It appears that the emissions produced by the high energy (0.53 MeV) electron beam mainly arise from deep within the ice lattice, whereas the U.V. light produces excited species close to the ice surface. However, the reduction in luminescence intensity produced in the U.V. excited ice exhibited considerable hysteresis when the O_2 was added and removed. The extent to which the reduction in intensity is due to Stern-Volmer quenching and the extent to which it arises from the scavenging of emission precursors, will be discussed in this paper. A value for the diffusion coefficient of O_2 in ice has been obtained from this study and will also be presented.

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(2) T.I. Quickenden, S.M. Trotman and D.F. Sangster, "Pulse radiolytic studies of the ultraviolet and visible emissions from purified H_2O ice." J. Chem. Phys. 77, 3790-3802 (1982).

Session II Wednesday - 3.00 - 3.20 p.m.

ELECTRIC CHARGE FORMATION IN IRRADIATED DIELECTRICS AND RELATED PHENOMENA

by

V. Gromov
Academy of Sciences of the USSR
Institute of Physical Chemistry, Moscow

Abstract

unavailable at time or printing

Session III   Wednesday 3.40 - 4.20 p.m.

REACTION OF INERT METAL(III) COMPLEXES WITH THE PULSE RADIOLYTICALLY GENERATED AQUATED ELECTRON, HYDROXYL RADICAL OR METAL(I) IONS

by

Geoffrey A. Lawrance

Department of Chemistry,
The University of Newcastle,
Newcastle, N.S.W., 2308, Australia.

Abstract

Pulse radiolysis frequently permits definitive one electron addition to or subtraction from transition metal complexes in aqueous solution. Rates of formation, electronic spectra, and rates of decay of transient complexes in unusual or normally labile oxidation states can be determined readily. Analysis of voltammetry of the complexes may be tied to the pulse radiolysis studies. Reactions of inert complexes with radiolytically-generated metal(I) ions are also readily followed. In this paper, two separate studies which illustrate these techniques are discussed.

Oxidation (with OH) of several *dichloromanganese*(III) complexes of saturated tetraazamacrocycles is observed with rate constants for formation of transients $(k_f) > 10^9$ M^{-1} s^{-1}. Apparently d^3 manganese(IV) monomers with electronic spectra qualitatively similar to d^3 chromium(III) complexes are formed. First-order decay of these intermediates is observed, with rate constants for decay of transients $(k_d) > 5 \times 10^3$ s^{-1}. Alkyl substitution on the macrocyclic ring increases the kinetic stability of the intermediate.

The chromium(III) complexes $Cr(aa)_3^{3+}$, $Cr(aa)_2(ox)^+$ and $Cr(aa)(ox)_2^-$ (aa = 1,10-phenanthrolines or 2,2'-bipyridyl; ox^{2-} = oxalate dianion) react rapidly with e_{aq} in aqueous solution. All k_f are $> 10^{10}$ M^{-1} s^{-1}, and are diffusion-controlled, varying with complex charge and size. Electronic spectra of the transients have been determined. All complexes with ox^{2-} ligands decompose rapidly with first-order rate constants $k_d > 8 \times 10^3$ s^{-1}, and are up to 10^6 times less stable than $Cr(aa)_3^{2+}$ ions. This behaviour parallels voltammetric behaviour at a glassy carbon electrode. Electron transfer reactions between chromium(III) complexes and zinc(I) or cadmium(I) are apparently diffusion-limited, with all rate constants near 2×10^9 M^{-1} s^{-1}.

Session III   Wednesday 4.20 - 4.40 p.m.

Primary Process in Radiation Chemistry of Condensed Phases

by

J F Boas

Australian Radiation Laboratory
Lower Plenty Road
Yallambie Victoria 3085

Abstract

The exposure of solids to electromagnetic radiation (eg. ultraviolet, X or γ rays) or to particle irradiation (eg. electrons, neutrons or ions) results in complex structural and chemical changes. These changes have a dramatic effect on the properties of the materials concerned and are critical in many applications eg. memory devices and radioactive waste storage. This paper reviews the primary processes which occur as a result of irradiation, with an emphasis on those occurring in crystalline inorganic insulators.

Session III Wednesday 4.40 - 5.20 p.m.

Kinetic Models For Luminescence Decay In Pulsed Electron Irradiated Calcium Oxide Crystals

by

J F Boas

Australian Radiation Laboratory
Lower Plenty Road
Yallambie Victoria 3085

and

R Cooper and J L Grant

Department of Physical Chemistry
University of Melbourne
Parkville Victoria 3052

Abstract

The time dependence of the luminescence emission at 375 nm from pulsed-electron irradiated CaO crystals has been studied over the range of 100 no to 50 ms. The results cannot be explained using conventional kinetic models. A model which is capable of simulating the experimental results is one in which direct electron-vacancy recombination occurs at first, but is then followed by electron-vacancy recombination where the electrons originate from the thermal activation of shallow traps.

Session III Wednesday 5.20 - 5.40 p.m.

PHOTOCHEMISTRY WITH LASERS

L.F. Phillips

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

In recent years the field of experimental photochemistry has come to be dominated by the laser. Properties of laser radiation which are widely and routinely exploited include high intensity (tens of megawatts or more), narrow bandwidth (10^{-4} cm^{-1} in the infrared), and short time resolution (picoseconds to femtoseconds). Not all of these desirable characteristics are obtainable in the output from a single laser, so multiple-laser experiments are commonplace. Recent work in some important areas of gas-phase photochemistry will be reviewed, including high-resolution infrared spectroscopy of radicals and ions (Hirota, Saykally), picosecond and sub-picosecond studies of intramolecular processes in large molecules (Zewail), spectroscopic excitation of transition states (Brooks), and pump-and-probe kinetic studies (various laboratories, including our own).

Session V Thursday 9.00 - 9.40 a.m.

THERMALIZATION OF ELECTRONS BY SIMPLE MOLECULAR GASES ADDED TO HELIUM

by

Kevin Caulfied & Ron Cooper
Dept. of Physical Chemistry
University of Melbourne

When small amounts of simple molecular gases such as methane are added to a larger pressure of helium, the rate of electron thermalization, relative to that in pure helium, is increased. The increase in rate is due to electron thermalization by the additive gas.

In this experiment, helium gas (typically 100 to 760 torr) plus an additive gas (0.1 to 10 torr) was ionized by a short intense pulse of high energy electrons. Thermalization of low energy electrons (1eV to 0.04eV) within the gas was monitored by a microwave conductivity technique.

Session V Thursday 9.40 - 10.00 a.m.

APPLICATIONS OF MICROWAVE CONDUCTIVITY TO FAST PROCESSES IN IONIZED GASES.

Michael Scales and Ron Cooper
Dept. of Physical Chemistry
University of Melbourne

It is possible to probe the electrons within an ionized gas sample by microwave conductivity. A low power microwave field propagating through an inoized medium will be attenuated by the free electrons present. The degree of attenuation is proportional to the product of the number and energy of electrons present.

This paper focuses on the application of microwave conductivity to the observation of some fast processes in ionized gases. Processes such as electron thermalization, recombination which are often inaccessible by conventional light absorption emission techniques.

In the context of experiments done over a wide range of pressures, in both pure rare gas, and in systems containing small amount of an additive gas, some of the advantages, and limitations of the technique are discussed.

Session V Thursday 10.00 - 10.20 a.m.

MAGNETIC RESONANCE STUDIES ON RADIATION INDUCED CROSS-LINKING IN POLYMER AND MODEL COMPOUND

by

J. Sohma

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Analysis of ESR spectra obtained by the spin-trapping method indicated a difference in local mobility between cross-links produced by γ-irradiation and those by neutron irradiation in n-eicosane, which is a model compound of polyethylene. The molecular mobility in n-eicosane irradiated by the very weak neutron beam corresponding to 10^{-2} Mrad was nearly as small as in n-eicosane irradiated by heavy γ-irradiation of 86 Mrad.

Three kinds of cross-linked n-eicosane were found after the heavy γ-irradiation; a saturated cross-linked dimer, cross-linked dimers having either one double bond or two. Similar dimers were also detected after the neutron-irradiation, but the relative concentrations of these dimers were different from those of the γ-irradiated one.

^{13}C-NMR spectrum was observed from the cross-linked n-eicosane. The observed spectrum was so complicated that unambiguous assignments of all peaks were actually impossible. By using the INEPT method, the CH_2 peaks were clearly distinguished from other peaks of both CH and CH_3. The relative intensities of peaks were determined by the gated dcoupling method. Analysis of the observed NMR spectra suggested strongly that the cross-links were formed in the central part of the n-eicosane molecules and the majority of cross-linking forms were neither the Y type nor long branches but the H-type. ^{13}C-NMR from the highly cross-linked polyethylene was observed by the CP-MAS method and analysis of the spectrum will be discussed.

The author should like to express his acknowledgement to Dr. M. Tabata, Hokkaido University, Drs. H. Yamaoka and T. Matsuyama, Kyoto University for their collaboration.

Session VI Thursday 10.40 - 11.20 a.m.

16R

PROTECTIVE EFFECTS IN RADIATION

by

D.J.T. Hill

Polymer and Radiation Group
Department of Chemistry
University of Queensland

Abstract

One of the main interests of the Polymer and Radiation Group at the University of Queensland has been the study of the effects of ionizing radiation on synthetic polymers, copolymers and model compounds. The objective of the studies undertaken has been to identify the mechanisms of the important reaction pathways, based upon the identification of the major radical intermediates and low molar mass products and the measurement of their yields.

Over a period, many different polymer systems have been investigated including the polyolefins, polymethacrylates, polysulfones, polyacids and polypeptides. In all cases, it has been shown that incorporation of aromatic groups into the polymer chain has had the effect of protecting the polymer chain against radiation damage. Similar observations have been made for low molar mass, model compounds.

In this paper some of our recent work will be reviewed with particular emphasis being placed on our studies of the amino acids, carboxylic acids and acrylates.

Session VI **Thursday 11.20 - 11.40 a.m.**

RADIOLYSIS OF CARBOXYLIC ACIDS

by

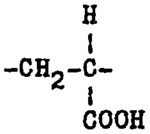
D.J.T. Hill, J.H. O'Donnell, P.J. Pomery and C.L. Winzor

Polymer and Radiation Group
Department of Chemistry
University of Queensland

Abstract

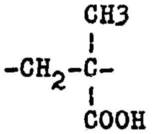
The effect of gamma-radiation on two water-soluble polymers, poly(acrylic acid) and poly(methacrylic acid) has been studied. The carboxylic acid group (-COOH) was found to be very sensitive to high energy radiation, with the ratio of carbon monoxide to carbon dioxide formed (measured by analysis of volatile products) being several times that found for simple aliphatic monocarboxylic acids used as model compounds.

Electron Spin Resonance studies have identified some of the major free radicals produced on irradiation at 77 K and at ambient temperature, in support of a proposed mechanism of degradation. Molecular weight studies have also been undertaken to determine the extent of cross-linking and scission.



$-CH_2-C(H)(COOH)-$

Poly(acrylic acid)



$-CH_2-C(CH_3)(COOH)-$

Poly(methacrylic acid)

Session VI Thursday 11.40 - 12 noon

A ^{13}C NMR STUDY OF RADIATION INDUCED CHANGES IN STEREOREGULARITY IN POLYPROPYLENE

by

John Hanna, W. Ken Busfield, James H .O'Donnell and Andrew K Whittaker

School of Science, Griffith University, Nathan, Qld. 4111
and Dept.of Chemistry, University of Queensland, St. Lucia, Qld. 4067.

Abstract

Previous studies of the effect of high energy irradiation on polypropylene have revealed that hydrogen is the main chemical product with a G value of about 2 and that both chain scission and crosslinking occur with G values in the range 0.1 to 0.9 (1). The extent of chemical change is dependent on sample morphology (1,2). Although radiation induced racemization was first reported by Thompson (3) in 1965 for poly(methylmethacrylate), there has been no previous report of the effect of irradiation on the stereoregularity in polypropylene. Our investigation of the ^{13}C NMR spectrum of polypropylene after various doses of gamma irradiation at room temperature in vacuo has indicated significant changes in the backbone stereoregularity.

The fine structure of the methyl resonance in a high resolution spectrum of a solution of polypropylene in 1,2-dicholorobenzene reveals both triad and pentad sequences of backbone monomer units; these have been previously assigned (4,5). Following doses up to and just beyond the gel dose, the loss of mm triads and the gain of mr and rr triads show that racemization occurs with a remarkably high G value. Assuming racemization occurs in single isolated events the observed triad changes correspond with G (racemization) = 21 ± 3. If further racemization occurs in nearby units, and a preliminary analysis of the pentad sequences supports this possibility, then G (racemization) is considerably greater than 21. Racemization presumably results from chain scission followed by bond rotation and recombination.

References

(1) W.K. Busfield and J.H. O'Donnell, Europ. Polym. J., 15, 379 (1979), and references therein.

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(3) E. Thompson, J. Poly. Sci., Polym. Letters Ed., 3, 675 (1965).

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(5) H.N. Cheng and G.H. Lee, Polym. Bull., 13, 549 (1985).

Session VI   Thursday 12 - 12.20 p.m.

UNIMOLECULAR AND COLLISION-INDUCED FRAGMENTATION PATHWAYS OF POLYPROPYLENE GLYCOL-1000 ADDUCT IONS

by

Muljadji Agma, Peter J. Derrick and Gary D. Willett

School of Chemistry
University of New South Wales
Kensington, NSW 2033, Australia

Abstract

The structure and mechanism of fragmentation of polypropylene glycol-1000 adduct ions $(M + X)^+$(X=H, Li, Na, K or Cs) formed by field desorption have been studied using collision-induced decomposition (CID) and mass-analysed ion kinetic (MIKE) techniques in a large reverse geometry double focussing mass spectrometer.

There are 4 groups of fragment ions observed in the CID spectra; M/Z=58n + 1 + X and 58n + 17 + X, resulting from C-O chain scission of the polymer backbone and 58n + 31 + X and 58n + 45 + X resulting from C-C chain scission. The signal intensity of ions formed from the C-O scission is greater than that from the C-C scission. The collision induced dissociation of protonated polymer oligomers predominantly leads to low molecular weight fragments, whereas that of the alkali metal adducts is to high mass fragments.

The alkali metal oligomer adducts show little spontaneous unimolecular dissociation in the second field free region in contrast to that observed from the protonated polypropylene glycol adduct.

Session VI **Thursday 12.20 - 12.40 p.m.**

RECENT DEVELOPMENTS IN ELECTRON BEAM ACCELERATORS

by

E.A. Abramyan
Academy of Sciences, Moscow
Electro Physics Department

Abstract

unavailable at time of printing

Session VII Thursday 1.40 - 2.20 p.m.

APPLIED RADIATION, POLYMERISATION AND GRAFTING

by

M. Markus
I.C.I. Australia

Abstract

Unavailable at time of printing

Session VII Thursday 2.20 - 2.40 p.m.

FUTURE DEVELOPMENT IN ELECTRON BEAM CURING

by

S. Bett

Polycure Pty. Ltd.

Since rapid radiation processing first emerged in the late fifties as an industrial tool, a number of changes have occurred in the types of chemistry utilized and in electron accelerator design appropriate to curing that chemistry. In particular, the developments in acrylate chemistry and low energy self-shielded "curtain" processors has ushered in a new era of RRP distinguished by EB processing speeds an order of magnitude faster than those possible with UV ionising radiation.

This paper considers the "state of the art" in EB curing in respect of:-

* Applications
* "Inert gas" and "in air" systems
* Electron "curtain" design
* Manifolds and shielding
* Computer interfaces and controls
* Toxicity and irritancy of Chemistry
* Properties of the cured coatings

The limitations of the presently used systems will also be discussed in relation to the above considerations and some future developments will be considered in light of these limitations.

Session VII   Thursday 2.40 - 3.00 p.m.

ELECTRON CURING & VACUUM METALLIZATION OF PAPER

by

John R. O'Neill

Vacuflex Pty. Ltd.
Marayong, N.S.W.
Australia

Abstract

Evaluation of the functional and aesthetic benefits of electron curing applications to vacuum metallization of paper has resulted in the development of two process routes.

DIRECT metallization utilising electron curing is practised by Vacuflex Pty. Ltd., Sydney, Australia, employing its proprietary chemistry for coatings formulations. TRANSFER metallization by the electron curing route is also solely practised world-wide by Hallmark Cards Inc., Kansas City, U.S.A. Hallmark uses proprietary technology with patent protection and purchases chemistry under this protection.

The two processes are reviewed and the benefits and advantages of each are compared in terms of quality and cost.

Future developments of electron curing in paper metallization processes are discussed.

Session VIII Thursday 3.20 - 3.40 p.m.

MATERIALS SCIENCE AND SHAPE MEMORY - A MEMORY OF THE FUTURE

by

Francis M. FitzGerald

BSc (Hons.)
Technical Director
Memorytech
(Formerly Raychem Australia - Marketing Manager)

Abstract

Raychem derives its very name from B-Ray Chemistry. In their 29 years of existence, Raychem have been well known to pioneer many developments in electron-beam radiation leading to so many products we see today in the engineering and even consumer world.

With a worldwide market well in excess of $1 billion today this comes second probably only to computers for the short growth period involved. Engineering products cover a wide range of specially developed Polymers which offer certain design attributes such as:-

Conductivity - PTC for current regulation in heaters and protection devices.

- Known ratios to metallic resistance for sensors.

Shape-memory - The most popular branch of heat shrinkable tubings for environmental, voltage and other protection systems.

But this most interesting facet of shape memory has been extended into other fields such as glass, ceramic and even metals. Shape Memory Alloys show how creative thought is predicting a similar mushroom growth to that of twenty years ago when we wondered what use might anyone possibly ever find for shape memory polymers.

References

(1) Use of Shape Memory Alloys as Engineering Material - R. Yaeger Raychem.
(2) Review of Heat Shrinkable Materials Technology - R.J. Clabburn Raychem.

Session VIII Thursday 3.40 - 4.00 p.m.

INDUSTRIAL APPLICATIONS OF LASER TECHNOLOGY

by

J. A. O'Neill

Centre for Industrial Laser Applications
University of New South Wales

Abstract

Since the invention of the laser 25 years ago, laser sources have been developed which give output in spectral regions ranging from the vacuum ultraviolet to the far infrared. As well as being powerful tools in fundamental scientific investigations, lasers have found a number of industrial applications. In this review the requirements for successful development of laser based industrial processes will be outlined. The breadth of possible industrial applications will then be illustrated by discussion of a number of examples of processes which are either currently in use in industry or which show promise for eventual commercialization. Processes discussed will include laser isotope separation, laser synthesis of pharmaceuticals, laser production of metal and ceramic powders, laser polymerization, laser induced radical chain reactions, laser production of short lived but highly active homogeneous catalysts, laser chemical vapour deposition, laser cutting and welding, and the use of lasers in the heat treatment of metal surfaces.

Session VIII Thursday 4.00 - 4.40 p.m.

THE KINETICS OF THE EMULSION POLYMERIZATION OF BUTYL ACRYLATE

by

I. A. Maxwell, R. G. Gilbert and D. H. Napper

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The University of Sydney, NSW 2000, Australia

Abstract

Butyl acrylate is a monomer of considerable importance in the surface coatings and adhesives industries. Despite this importance, there have been few studies of its emulsion polymerization, probably because of the complexity of its kinetics. Chemically initiated studies alone provide insufficient information to allow the kinetic parameters to be extracted uniqely.

If, however, chemically initiated studies are performed in conjunction with relaxation studies, using γ-radiolysis as the initiating source, sufficient data become available to allow the relevant rate parameters to be evaluated unambiguously.

Butyl acrylate at $50^{\circ}C$ is found by this method to be a system for which the average number of free radicals ($\bar{n}$) per particle is relatively high (1-10) and for which the termination rate coefficient (k_t) is unusually low (8×10^{2} dm^{3} mol^{-1} s^{-1} at a weight fraction of polymer of 0.58). The efficiency of capture of free radicals generated in the aqueous phase by the latex particles is relatively high but still significantly less than 100%. The value (450 dm^{3} mol^{-1} s^{-1}) of the propagation rate constant (k_p) is typical for acrylate monomers of this type.

LASER DESORPTION FOURIER TRANSFORM MASS SPECTROMETRY OF ORGANIC POLYMERS

by

M. Guilhaws, H. Nguyen, J. O'Neill,
G. Paul, G. Willett, P. Derrick
University of New South Wales

Abstract

Session IX **Thursday 4.40 - 6.15 p.m.**

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (H.P.L.C.) AND FIELD DESORPTION MASS SPECTROMETRY (F.D.M.S.) OF LOW MOLECULAR WEIGHT POLY(METHYL METHACRYLATE).

by

Wilbert W. Hope, Peter J. Derrick and Gary D. Willett

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Azio Rizzardo and David H. Solomon

C.S.I.R.O., Division of Applied Organic Chemistry,
506 Lorimer Street, Fisherman's Bend, Victoria 3001, Australia

Low Molecular weight poly(methyl methacrylate) has been synthesized using cobalt tetraphenyl porphyrin (Co-TPP) as the catalyst for chain transfer to monomer. Unsaturated end-group oligomers were produced exclusively. Subsequent hydrogenation provided saturated end group oligomers.

H.P.L.C. has been employed to separate and isolate oligomers for F.D.M.S. studies, including Collision Induced Dissociation (CID). Both unsaturated and saturated end group oligomers have been examined in this manner.

A comparison of the CID spectra of the two types of methyl methacrylate oligomers has supported the view that the unsaturated end-group oligomers are thermally less stable than those with saturated chain-ends. Some light has also been thrown on the chemistry of the double bond in thermal degradation of the polymer.

CID spectra of the tetramer up to the decamer show the effect of molecular weight on fragment intensities and kinetic energy release.

Session IX   Thursday 4.40 - 6.15 p.m.

PHOTOCHEMISTRY OF SULPHAMIC ACID TREATED WOOL

by

B.A. Cameron and M.T.Pailthorpe

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University of New South Wales
Kensington, Australia

Abstract

The photoyellowing and phototendering of sulphamic acid treated wool has been investigated. Sulphamic acid introduces sulphonate and sulphamate groups into wools' structure. Studies of photoyellowing have indicated that initially there is a 'photobleaching' effect followed by a reduced rate of yellowing. Studies of the tryptophan phosphorescence indicate that the tryptophan is masked in some way and that this could lead to the reduced rate of yellowing observed.

Measurements of phototendering indicate that the treatment of wool with sulphamic acid has no significant effect on the strength loss observed during exposure to simulated sunlight.

When dyed with basic dyes, sulphamic acid treated wool has an increased dye uptake compared with untreated wool. Measurements of the light fastness of basic dyes have indicated that the fastness of these dyes have significantly increased and have values comparable to those achieved on acrylics. The increase in light fastness is attributed to the introduction of sulphonate groups, and has been further studied using model PVA films.

Session IX Thursday 4.40 - 6.15 p.m.

HETEROGENEOUS AND HOMOGENEOUS METAL CATALYSED TRITIATION OF NITROBENZENE

by

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University of New South Wales
Kensington, Australia

Abstract

Nitrobenzene has been used in the past to distinguish between heterogeneous metal catalysis and homogeneous metal ion catalysis of hydrogen isotope exchange. It appeared that heterogeneous metal exchange was poisoned by the presence of nitrobenzene, while homogeneous exchange was not so affected.

We have been studying this phenomenon in more detail, particularly with respect to exchange with tritium gas as isotope source rather than tritiated water. Heterogeneous metal exchange with elemental tritium can proceed efficiently under appropriate experimental conditions with the production of only small traces of aniline as by-product. Tritium NMR studies of the product nitrobenzene show that the isotope distribution is dependent on the particular metal chosen. The results can be interpreted in terms of accepted π-complex isotope exchange theories.

Session IX Thursday 4.40 - 6.15 p.m.

ISOTOPIC STUDIES OF METHANOL CONVERSION AND RELATED REACTIONS OVER ZEOLITES

by

E. Kennedy
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University of NSW
Kensington Australia

Isotopic Hydrogen exchange reactions over H-ZSM-5 and other zeolites, between labelled benzene and toluene, were performed at different LHSV's. The relative abundance of isotope in the meta position of toluene is accounted for on the basis of a steric effect, imposed by the zeolite channel. The channel restricts formation of the transition state associated with para-exchange. A π-dissociative mechanism is proposed for these zeolite isotope exchange reactions, consistent with the data obtained.

These isotope exchange studies are being extended to a study of the mechanism of conversion of methane and methanol to gasoline over the same zeolites.

Session IX Thursday 4.40 - 6.15 p.m.

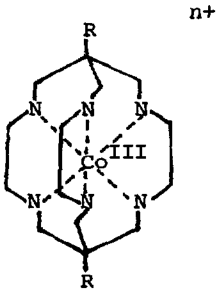
INTRA- AND INTERMOLECULAR ELECTRON TRANSFER IN CAGE COMPLEXES: A PULSE RADIOLYTIC STUDY

by

*G.A. Lawrance, E.A. Miles, and A.M. Sargeson
University of Newcastle & Australian National University.

Abstract

Divalent zinc, cadmium and nickel ions are rapidly reduced by the aquated electron to yield the corresponding monovalent species. These hyperreduced M^+ ions, which are unstable in aqueous solution, are characterised by an intense UV absorption band which allows their rapid reoxidation, by a series of Co^{III} cage complexes (see Figure), to be readily monitored. As these reactions are necessarily outer-sphere,[1] the Marcus-Hush relationships can be applied to estimate unknown self-exchange rates from the experimental cross-reaction rates and known E^0 values.



R	name	n
H	sar	3
NH_3	diamsar	5
Cl	diCLsar	3

Despite the encapsulation of the metal ion in a saturated and insulating organic coat, cage complexes undergo relatively rapid electron transfer.[2] The coupling of two cages via their bridgeheads makes the electron transfer process intramolecular, thereby allowing a more basic appraisal of the factors influencing the electron transfer to be undertaken.

Provided the dimer is unsymmetric, pulse radiolysis can be implemented to determine the rates of such intramolecular electron transfer (I.E.T.). By employing the non-discriminate reductant e_{aq}^-, a sufficient quantity of the thermodynamically unstable mixed valence dimer is generated, thus enabling the ensuing I.E.T. rate to be measured spectrophotometrically.

References

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(2) A.M. Sargeson, Pure & Appl. Chem., 56, 1603 (1984).

Session IX Thursday 4.40 - 6.15 p.m.

MONTE-CARLO SIMULATION OF EXCITATION RATES OF NITROGEN AND RARE GASES BY SUBEXCITATION ELECTRONS

Ian Porter, Ronald Cooper and Derek Chan
Dept. of Physical Chemistry
University of Melbourne

Given cross-section data for elastic collisions of a solvent gas and individual inelastic processes for the solute gas, the decay of energy of subexcitation electrons in a rare gas system containing a trace of a fluorescent probe (eg N_2) can be modelled. This theoretical approach can be compared with experiment by considering the excitation of an emitting state (eg. the $C^3\Pi\mu$ state of N_2 which emits light at 379mm)

Session IX Thursday 4.40 - 6.15 p.m.

DETERMINATION OF ION RECOMBINATION RATE PARAMETERS FOR RARE GAS CATIONS WITH HALIDE IONS

S. Mezyk & R. Cooper,
Dept. of Physical Chemistry,
University of Melbourne,
Parkville, Victoria.

The pulse radiolysis of rare gas-halogen source mixtures yield intense emissions in the Ultra-Violet region of the spectrum due to rare gas-monohalide exiplexes (KrF*, XeF* etc.).

Previous studies have shown that the exiplexes are formed by two distinct and kinetically resolvable processes. The faster process has been shown to be due to rare gas excited states reacting with halogen source molecules, while the slower process is due to ion recombination between rare gas cations and halide source anions.

By using the photon emission rates of the slower process we have been able to determine the first experimental rate constants (α values) for many of these systems over a wide pressure range. For example, for the reaction : $Kr^{+} + SF_6^{-} \longrightarrow KrF^{*} + SF_5$,the α values have been determined from 10 to 3000 torr.

The results of these experiments will be presented and compared with the current theories of ion recombination.

Session IX **Thursday 4.40 - 6.15 p.m.**

ELECTRON IRRADIATION OF ADAMANTINE

by

G.S. Laurence,[1] D. Sangster,[2] R. Cooper[3] and A. Campbell-Ling[4]

[1] Department of Physical & Inorganic Chemistry, University of Adelaide
[2] Division of Chemical Physics, CSIRO
[3] Department of Physical Chemistry, University of Melbourne
[4] Department of Chemistry, San Jose State University

Abstract

Adamantane has been used as a matrix for the study of organic radicals. In the course of work with non-aqueous solvents the opportunity arose to examine the use of adamantine as a solid solvent in the irradiation of organometallic compounds such as ferrocene.

Adamantine did not prove a satisfactory solvent phase for pulse radiolysis using spectrophotometric detection but gamma irradiation of ferrocene-adamantine solids leads to oxidation-reduction reactions of ferrocene and ferrocinium.

The behaviour of free electrons produced in solid adamantine by an electron pulse is being investigated using the microwave conductivity technique. Initial results indicate that the electrons have a very short lifetime in adamantine.

Session IX Thursday 4.40 - 6.15 p.m.

RADIATION CHEMISTRY OF COPPER COMPLEXES IN NON-AQUEOUS SOLVENTS

by

G.S. Laurence,[1] D.F. Sangster,[2] A. Campbell-Ling[3] and A. Bond[4]

[1] Department of Physical and Inorganic Chemistry, University of Adelaide
[2] Division of Chemical Physics, CSIRO
[3] Department of Chemistry, San Jose State University
[4] Department of Chemistry, Deakin University

Abstract

The pulse and gamma radiolysis of copper dithiocarbamates has been studied in a variety of non-aqueous solvents using spectrophotometric detection. Recently trials have been made of the use of electrochemical techniques to follow radiation chemistry in non-aqueous solvents.

The oxidation-reduction of copper-dithiocarbamates in non-aqueous solvents has been studied by electrochemical techniques but the rate constants for electron transfer are unknown. Pulse radiolysis of copper(II) and copper(III) diethyldithiocarbamates in a large number of solvents indicates that the reactions proceed by complex mechanisms and that radical attack on the ligands accompanies the change in oxidation state of the metal. Dithiocarbamates are themselves easily reduced to form radical species and the difference between the electrochemical and radiation chemical behaviour may be due to the more extreme reducting conditions produced by solvated electrons.

Cyclic voltammetry is being tested as an alternative detection technique in the pulse radiolysis studies.

Session IX Thursday 4.40 - 6.15 p.m.

48

THE EFFECT OF DEPOSITION RATE AND SAMPLE THICKNESS ON THE LUMINESCENCE FROM PULSE IRRADIATED, POLYCRYSTALLINE, H_2O ICE

by

R.A.J. Litjens and T.I. Quickenden

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

D.F. Sangster

CSIRO Division of Chemical Physics, Lucas Heights Research Laboratories, Private Mail Bag 7, Sutherland, N.S.W., 2232, Australia.

Abstract

Previous investigations (1) have shown that electron irradiated polycrystalline and amorphous H_2O ices emit luminescences which differ spectrally and kinetically from the emissions produced similarly from crystalline ice. It is not clear from these previous investigations whether the observed differences are caused by differences in sample thickness or arise from differences in the ice structure.

In an attempt to disentangle these two effects, the present investigation examines the spectral and kinetic properties of the luminescences emitted by polycrystalline ice formed at a variety of deposition rates and ranging in thickness by ca. six orders of magnitude.

(1) C.G. Freeman, T.I. Quickenden, R.A.J. Litjens and D.F. Sangster, "Visible and ultraviolet emission from pulse irradiated amorphous and polycrystalline H_2O ice." J. Chem. Phys. 81, 5252-5254 (1984).

Session IX Thursday 4.40 - 6.15 p.m.

THE EFFECT OF DOPANTS ON THE LUMINESCENCE FROM PULSE IRRADIATED CRYSTALLINE H_2O ICE

by

M.G. Bakker, T.I. Quickenden and S.M. Trotman*

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

D.F. Sangster

CSIRO Division of Chemical Physics, Lucas Heights Research Laboratories, Private Mail Bag 7, Sutherland, N.S.W., 2232, Australia.

Abstract

The model proposed by Trotman (1) for the processes which lead to the emission of luminescence from irradiated ice makes a number of predictions about the effects of dopants on the luminescence. By examining the effects of selected dopants on the intensity, spectral distribution, decay kinetics and temperature dependence of the luminescence, the predictions of the model have been tested.

(1) S.M. Trotman, "Ultraviolet and visible luminescence from H_2O ice irradiated by pulsed electrons." PhD Thesis, University of Western Australia (1983).

*Present address: School of Mathematical and Physical Sciences, Murdoch University, Murdoch, W.A., 6150, Australia.

Session IX Thursday 4.40 - 6.15 p.m.

THE EMISSION OF LUMINESCENCE FROM COMETARY ICE AND WATER VAPOUR - SOME REFLECTIONS ON HALLEY'S COMET

by

M.G. Bakker and T.I. Quickenden

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

D.F. Sangster

CSIRO Division of Chemical Physics, Lucas Heights Research Laboratories, Private Mail Bag 7, Sutherland, N.S.W., 2232, Australia.

Abstract

The radiolytic and photochemical processes occurring in electron irradiated (1,2) and U.V. photolysed ice (3) may be similar to the processes which occur when a comet approaches the sun. Calculations have been carried out to ascertain whether the luminescences induced in crystalline, polycrystalline and amorphous ices contribute significantly to cometary emissions compared with water vapour luminescences and reflected light from the sun.

(1) T.I. Quickenden, S.M. Trotman and D.F. Sangster, "Pulse radiolytic studies of the ultraviolet and visible emissions from purified H_2O ice." J. Chem. Phys. 77, 3790-3802 (1982).

(2) C.G. Freeman, T.I. Quickenden, R.A.J. Litjens and D.F. Sangster, "Visible and ultraviolet emission from pulse irradiated amorphous and polycrystalline H_2O ice." J. Chem. Phys. 81, 5252-5254 (1984).

(3) T.I. Quickenden, R.A.J. Litjens, C.G. Freeman and S.M. Trotman, "UV excited luminescence from crystalline H_2O ice." Chem. Phys. Lett. 114, 164-167 (1985).

Session IX   Thursday 4.40 - 6.15 p.m.

FLUORESCENCE YIELD MEASUREMENTS - A VALUABLE ADDITION TO KINETIC MEASUREMENTS.

by

J G Young
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Lower Plenty Road
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and

R Cooper
Department of Physical Chemistry
Melbourne University
Parkville Vic. 3052

Abstract

G-values for KrF*, XeF*, XeCl*, XeBr* and XeI* have been determined for several rare gas/halogen gas mixtures irradiated with a pulse (3ns FWHM) of high energy electrons. The variation in G-value for each exciplex molecule has been measured as a function of rare gas pressure and halogen source gas pressure. In all these exciplex systems the detailed kinetic analysis of the processes responsible for the formation of the exciplex molecule is available. The yields of the various exciplex molecules will be discussed in terms of these processes.

Session IX Thursday 4.40 - 6.15 p.m.

LASER INDUCED FLUORESCENCE OF RADICALS USED IN PLASMA ETCHING

Horatio Rodrigo
Dept. of Physical Chemistry
University of Melbourne

The purpose of the study was to determine the lifetimes rate coefficients of recombination, and the concentration gradients of the radicals within the volume of the plasma.

The gases under investigation were CF_4 and CCl_4, and the radicals such as CF_3 and F were produced by subjecting the gas to a pulse of RF power. The RF pulse lasted for approximately 50 µs and the peak voltage was 10 ku.

The laser was tuned to the absorption frequency of the particular radical under investigation, and pulsed after a finite delay from the start of the RF pulse. The emission from this excited radical was then monitored by the monochromator and gated amplifier. Attempts were made to eliminate emission from the plasma itself by suitably gating the amplifier.

Session IX Thursday 4.40 - 6.15 p.m.

CROSS-LINKING MECHANISM IN PLASMA POLYMERIZED METHYL METHACRYLATE

by

Junkichi Sohma, Mikio Ohno and Keiichi Ohno

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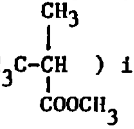
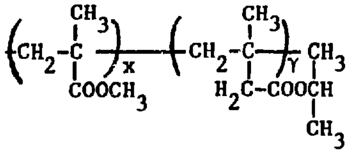
Sapporo, 060, Japan

Plasma-polymerized methyl methacrylate (PPMMA) film was produced by a radio-frequency glow discharge of methyl-methacrylate (MMA) gas with argon. PPMMA deposited under a plasma of mild energy was separated into a soluble fraction (sol-PPMMA) and insoluble matrix (insol-PPMMA), which is highly cross-linked, by solvent extraction and filtering. The chemical structure of sol-PPMMA was determined on the basis of information collected by pyrolysis/gaschromatography, IR spectroscopy, ^{1}H-NMR and ^{13}C-NMR and elemental analysis techniques. The most reasonable structure for the majority components in the sol-PPMMA was a random copolymer of MMA and isobutyric acid methallyl ester. Mechanism for formation of sol-PPMMA is assumed in a following way:

1) Methyl isobutyric ( $H_3C\text{-}\underset{COOCH_3}{\overset{CH_3}{CH}}$) is formed in a gas phase,

2) PMMA is formed by a chain transfer mechanism of MMA. 3) Ester side chains are lost from some monomers in PMMA to leave free radical sites in PMMA chains. 4) Methyl isobutyrate radicals couple with these radical sites to form random copolymer of MMA and isobutyric acid methallyl ester, that is



5) Free radical sites recombine each other to form cross-links. Density of cross-linking points is rather low in the sol-PPMMA but very high in the insol-PPMMA.

Session X Friday 9.00 - 9.20 a.m.

MECHANICAL PROPERTY/STRUCTURE RELATIONSHIPS IN POLYOLEFINS CROSSLINKED BY SENSITIZED IRRADIATION.

by

R.W.Appleby and W.K.Busfield.

School of Science, Griffith University, Nathan, 4111, Australia.

Abstract

The use of irradiation to improve the mechanical properties of polyethylene film is a well known commercial process being used in a wide range of applications. Drawn polyethylene on the other hand is more prone to chain scission when irradiated; consequently a deterioration in mechanical properties is observed. More recently however, the presence of acetylene during irradiation has shown that under the correct conditions an improvement, particularly in creep properties [1], can be achieved.

The irradiation of polypropylene on the other hand generally causes a deterioration of mechanical properties due to significantly greater scission. We have shown that crosslink enhancing agents, such as acetylene, can produce improvements in the creep properties of both polypropylene film [2] and drawn polypropylene tapes [3], particularly at 100°C where the effect of crystallites in the prevention of creep become less important, and crosslinks predominate. Property improvement is optimum with doses of about 100 kGy and irradiation temperatures of about 0°C. Below T_g a significant decrease in the rate of diffusion of acetylene is probably a major factor.

A detailed description of structure-property relationships of selected polyolefin samples will be presented at the symposium.

References

[1] Woods,D.W., Busfield,W.K., Ward,I.M., *Plastics and Rubber Processing Applications*, 5, (1985), p.157.

[2] W.K.Busfield and R.W.Appleby, *British Polymer Journal*, in press.

[3] R.W.Appleby and W.K.Busfield, *Polymer Communications*, 27, (1986), p.45.

Session X Friday 9.20 - 9.40 a.m.

EFFECT OF ZINC CHLORIDE AND CADMIUM IODIDE ON THE POLYMERISATION OF VINYL PYRROLIDONE

by

E. Senogles

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Abstract

The polymerisation of vinyl pyrrolidone (VP) has been shown to be influenced by the hydrogen bonding properties of the polymerisation solvent [1]. Thus in aqueous solution, for example, polymerisation rates and polymer (PVP) molecular weights are significantly higher than with bulk polymerisation or polymerisations conducted in ethyl acetate or dimethyl sulphoxide. The tacticity of the PVP is also affected. Although evidence obtained to date suggests that hydrogen bonding solvents promote the formation of a more syndiotactic polymer, an unambiguous assignment of monomer sequences to peaks in the ^{13}C NMR spectrum of PVP has not yet been made. In an attempt to obtain further information towards solving this problem, the effect of zinc chloride and related compounds on the polymerisation of VP and in particular the tacticity of the PVP formed has been investigated. Polymerisations, induced by γ-radiation, have been conducted in both methanol and acetone. The results obtained to date will be reported and discussed.

Reference

[1] J. R. Ebdon, T. N. Huckerby and E. Senogles, Polymer 23 (3), 339-43 (1983).

Session X Friday - 9.40 - 10.00 a.m.

FUTHER DIRECTIONS IN THE USE OF RADIATION IN THE STUDY OF THE MECHANISM OF FREE RADICAL LATEX POLYMERIZATION

by

I.R. McKinnon, I.R. Wilson, B.A.W. Coller

Department of Chemistry,
Monash University

Most models for the processes of polymerization of latex from emulsions and from solution have developed from those associated with the names of Smith and Ewart[1]. Notable among such models is that due to Gilbert, Napper and their co-workers[2]. These models treat the polymerization process as occuring within the particles of the polymer whereas experimental studies have shown[3] that a highly significant role is played outside the polymer particle by various "precursor" species.

Stable nitroxide radicals have been shown[4] to differentiate between some oxygen radicals and carbon radicals in favour of the latter. Different members of this series through their different surface and solubility behaviour, have the potential of differentiating between different sites of polymerization.

Whilst most attention has been focused on polymerization within the polymer particle the formation of low molecular weight species in the early stages of polymerization has been described only by simple models. Recent results[3] indicate that the simple models are in conflict with the actual range of products formed.

To date the lack of suitable experimental techniques has been a major handicap to following the polymerization process in the early stages. The development of isothermal heat flow calorimetry offers the possibility of observing polymerization rates of less than 10^{-9} mol s^{-1} which should allow observatiion of the early stages of the polymerization process.

These two new experimental techniques when combined with γ-radiation for the precise control of the initiation process should provide the experimental basis for significant advances in our understanding of this class of heterogeneous polymerization processes.

References

1. SMITH W.V., EWART R.M., J.Chem.Phys., 1948, **16**, 592.
2. GILBERT R.G., NAPPER D.H. J.Macromol.Sci., Rev.Macromol.Chem., 1983, **C23**, 27.
3. FEENEY P.J., NAPPER D.H., GILBERT R.G., Macromolecules, 1984, **17** 2520
4. BUSFIELD W.K., JENKINS I.D. THANG S.H. RIZZARDO E., SOLOMON D.H., Aust.J.Chem., 1985, **38**, 689.

Session X Friday 10.00 - 10.20 a.m.

DETERMINATION OF DIFFUSION CONTROLLED TERMINATION RATE COEFFICIENTS

by

M. E. Adams, D. H. Napper, R. G. Gilbert and D. F. Sangster*

School of Chemistry, University of Sydney, NSW, 2006

*CSIRO Division of Chemical Physics,
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Abstract

The conventional text-book analysis of the kinetics of free radical chain-growth polymerization in bulk or in solution is applicable to only the first percent conversion. The reason for this lies in the influence that the polymer generated by the polymerization exerts on the microscopic kinetic events governing polymerization, especially termination. The nature of this influence is as yet poorly understood.

Seeded emulsion polymerization studies that are initiated by γ-irradiation possess the distinct advantage that the initiating source can be switched off rapidly so that the subsequent fate of the free radicals trapped within the polymerizing particles can be followed. For styrene polymerization in small latex particles, the process of radical exit ("desorption") is the rate determining radical removal process. But for larger seed latex particles, bimolecular termination events are responsible primarily for the radical annihilation events. Studies of the relaxation kinetics in large particle systems thus permit the bimolecular termination rate constant to be measured as a function of the weight fraction of polymer, the matrix polymer molecular weight and the molecular weight of the growing chains. This paper will present data on how some of these factors influence termination and discuss the reasons for the observed effects.

Session X Friday 10.20 - 10.40 a.m.

PHOTOCHEMISTRY AND PHOTOPHYSICS OF SOLID POLYMERS

by

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Abstract

Luminescence spectroscopy is a versatile tool for the study of the photophysics and photochemistry of solid polymers. The excitation process may involve the absorption of high energy radiation, UV-visible radiation or the excess energy of chemical reaction (such as the photochemical oxidation of the polymer). Emission may occur from either the singlet or triplet state, but because of the high efficiency of energy transfer in the solid polymer, the emitting species is generally not the chromophore that was originally excited. For example the fluorescence spectrum from solid vinyl aromatic polymers is dominated by excimer fluorescence. The dependence of the efficiency of excimer formation of the conformation of the polymer has been used to study interpenetration polymer networks and phase separation. Intermolecular energy transfer to probe molecules in the solid has been used to study relaxation and transport properties up to the glass transition temperature.

When a solid polymer is irradiated in air then, in addition to photoluminescence, a weak long-lived chemiluminescence is often observed. This arises from the trace photo-oxidation of the polymer leading to alkyl peroxy radials, which, on termination, produce emission from the triplet state. This provides a method for studying free radical reactions such as stabilization processes and of particular interest is the effect of an externally applied stress on the rate of these reactions.

Session XI **Friday 11.00 - 11.40 a.m.**

48R

SOME REACTIVE INTERMEDIATES FORMED BY THERMAL, PHOTOCHEMICAL, AND RADIOLYTIC PROCESSES

by

Curt Wentrup

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Abstract

The purpose of this lecture is to demonstrate that "ordinary" organic chemistry can be of relevance for an understanding of radiolytic processes, and vice versa. For example, Wolf *et al* [1] in 1961 reported the formation of toluene labelled in all positions as the product of the reaction of benzene and ^{14}C recoil atoms. The reaction can be explained in terms of the aromatic carbene-carbene rearrangement subsequently studied under thermal and photochemical conditions by us and others [2], [3].

Recoil atom chemistry can also help explain the formation of some reactive molecules observed in interstellar space, e.g. methanimine, $CH_2{=}NH$. This molecule can be prepared *inter alia* by reaction between recoil ^{14}C atoms and ammonia [4]. Its identification in the gas-phase pyrolysis of methyl azide will also be described [5].

References

[1] R. Visser, C.R. Redvanly, F.L.J. Sixma, and A.P. Wolf, *Rec. Trav. Chim.* 80, 533 (1961).
[2] C. Wentrup, Tracer Methods, in Investigations of Rates and Mechanisms of Reactions, Techniques of Chemistry, Vol. 6, Pt 1, 4/e, Chapter IX, Wiley, N.Y., 1986, pp. 613-661.
[3] K.A. Biesiada, C.T. Koch, and P.B. Shevlin, *J. Am. Chem. Soc.* 102, 2098-2100 (1980).
[4] R.D. Finn, H.J. Ache, and A.P. Wolf, *J. Phys. Chem.*, 73, 3928 (1969).
[5] C. Wentrup, Gas-Phase and Matrix Studies, in Azides and Nitrenes, E.F.V. Scrieven, Ed., Academic Press, N.Y., 1984, pp. 395-433.

Session XI Friday 11.40 - 12.20 p.m.

RECENT DEVELOPMENTS - ELECTRON BEAM ACCELERATORS

by

E.A. Abramyan
Academy of Sciences, Moscow
Electro Physics Department

Abstract

Unavailable at time of printing

Session XII Friday 1.20 - 2.00 p.m.

50R

RADIATION AS A TOOL FOR WATER PURIFICATION: A COMPARISON BETWEEN HIGH ENERGY IONIZING AND LOW ENERGY ULTRAVIOLET

by

Ralph W. Matthews

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Abstract

Pure water is one of the earth's diminishing resources. More than half of the population of the United States derive their drinking water supplies from the ground. A similar dependence on groundwater occurs in other countries. Hence the concern over the increasing contamination of this resource.

The long established methods of water purification using chlorination, ozonation, and UV disinfection have shortcomings and other methods are being used or are under consideration. High energy ionizing radiation is among the latter.

It has recently been shown that titanium dioxide and other semiconductors when suspended in water, and illuminated with bandgap light photocatalytically oxidize organic solutes present in the water[1]. Among these solutes trihalomethanes are common, but highly undesirable. Trihalomethanes are formed during the chlorination of water. In addition, more refractory aromatic compounds[2] are also oxidized completely to carbon dioxide[3] by the powerful oxidization reactions that occur at the surface of near U.V. illuminated TiO_2.

The TiO_2 process is much more effective in destroying organic matter than U.V. light alone and bears some resemblance to the high energy radiation process ; hydroxyl radicals are believed to be key oxidizing radicals in both. A direct comparison between the effectiveness of ^{60}Co gamma photons with 366 nm photons in destroying the fluorescein molecule has been made. On an absorbed energy basis ^{60}Co gamma rays are approximately 33 times more destructive than 366 nm photons.

1. D.F. Ollis, Envion. Sci. Technol. 19, 480 (1985).
2. R.W. Matthews, Water Res. 20, 569 (1986).
3. R.W. Matthews, J. Catal. 97, 565 (1986).

Session XII Friday 2.00 - 2.20 p.m.

62

THE DISSOLUTION OF URANIUM OXIDES IN THE GAMMA RADIATION FIELD

by

V. Gromov
Academy of Sciences of the USSR
Institute of Physical Chemistry, Moscow

Abstract

Unavailable at time of printing

Session XII Friday 2.20 - 2.40 p.m.

FREE RADICAL REACTIONS WITH COLLOIDAL METAL OXIDES

P. Mulvaney, L. Denison, F. Grieser, R. Cooper

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University of Melbourne
PARKVILLE VIC 3052

and

D. Meisel

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The crystal structure of metal oxides is known to play an important role in the reactivity of the oxide to various redox processes in solution. Studies of the role of the crystal structure have, however been complicated by the effects of reactant adsorption, surface area, hydration, lattice impurities or because of the inadequate control of solution conditions.

In this study we have investigated the dissolution of several colloidal manganese oxides of different crystal structure, using the isopropyl alcohol radical and a methylviolorgen derivative (ZMV) as reducing agents. γ-irradiation of colloidal MnO_2 (α, β, γ and a new form with a crystal structure similar to psuedo rutile) in the presence of acetone/isoproyl alcohol or isopropyl alcohol (ZMV) produces Mn^{2+} at pH= 3 with G values in the range of 3.7 to 5.4, which is consistant with the mechanism,

$$MnO_x + 2xH^+ + 2R. \longrightarrow Mn^{2+} + xH_2O + 2R$$

$$MnO_x + H_2O_2 + 2xH^+ \longrightarrow Mn^{2+} + (x+1)H_2O + 1/2\ O_2$$

The work to date has shown that the crystal composition of the oxides of manganes can be readily identified from the G values of Mn^{2+} produced.

We have also instigated the kinetics of dissolution using pulse radiolysis coupled with a transient conductivity detector. The results from this work shown that 3 time domains are involved in the proton up-take leading to Mn^{2+} release from the colloid, ranging from 10 µsec to 100 sec. The temperol characteristics for the dissolution process is virtually the same for all crystal structures examined. The influence of Mn^{2+} on rate of proton up-take in the short time domain < 100 µsec, is crucial. The more Mn^{2+} present in the sample the faster the initial proton consumption. We believe this to be due to the formation of Mn^{3+} centres on the surface due to the step.

$$Mn^{IV}{}_{surface} + Mn^{II}{}_{surface} \longrightarrow 2Mn^{III}{}_{surface}$$

This reaction is known for higher pH systems, but not previous identified at pH=3. More details of the kinetic results will be presented at the conference.

Session XII Friday 2.40 - 3.00 p.m.

CURRENT IDEAS AND DEVELOPMENTS IN RADIATION CHEMISTRY

Ronald Cooper

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University of Melbourne
PARKVILLE VIC 3052

Since the 1984 AINSE conference, several international meetings have been held at which innovations, significant old problems and overlapping photochemical systems or processes have been discussed.

These conferences have brought about several new–look attacks on certain areas of radiation and photochemistry. The inevitable outcome of these studies is (more or less) conflict.

Areas of activity/conflict/agreement are:

(1) Distribution of ions – geminate recombination observed in Radiolystic <u>and</u> Photolytic systems. Experimental <u>and</u> theoretical studies.

(2) Production of excited states in liquids.
Direct effects: Cerenkov radiation excitation: ion recombination excitation transfer; sub–excitation electrons.
Magnetic field effects on excitation yeilds and kinetics.

(3) Anomalous conductivities in irradiated hydrocarbon liquids.

(4) Theory of interaction of low energy electrons with simple atoms and molecules: Thermalisation in liquids and gases. Comparison of theory <u>and</u> experiment.

(5) Oxygenated, alkaline water – what species are present?

(6) Charge separation but no ionisation – ginat dipoles.
A review of the status of these areas will be given.

Session XII Friday 3.00 - 3.40 p.m.

RADIATION TECHNIQUES IN THE STUDY OF EMULSION POLYMERISATION

by

D. Napper

Department of Chemistry
University of Sydney

Abstract

Emulsion polymerisation is used to produce some 5-10% of polymer manufactured in the world to-day. The end product, in the form of latex, is widely used in the surface coatings and adhesives industry; in addition the polymers can be harvested for use in the synthetic rubber and plastics industries.

Our fundamental understanding of the microscopic kinetic processes that underpin emulsion polymerisation is still insecure. Part of the reason for this lies in the complexity of the processes involved; these heterogeneous systems are formed and grow as a result of the complex interplay of a wide range of colloidal and polymeric phenomena.

Radiation initiation of emulsion polymerisation has the virtue that it can be "switched off" rapidly, unlike chemical initiation. This allows the relaxation of the systems to be followed and provides direct information about radical annihilation processes. The Lucas Heights facilities has thus been able to provide unique information about the exit of free radical latex particles and about bi-molecular termination events. The latter has important implications for all bulk or solution free radical polymerisation.

GENERAL INFORMATION

GENERAL INFORMATION

CONFERENCE VENUE

The Conference will be held in the AINSE Theatre, Lucas Heights (Institute Building) - see map page 69
Wednesday 12th, Thursday 13th and Friday 14th November, 1986

DISCUSSION

Wednesday 13th November, 1986
7.30 p.m. (AINSE Theatre)
"Radiation Chemistry & Food Irradiation"
Speaker:- Dr. T. McEwan,
Animal Research Institute,
Qld. Dept. of Primary Industry

PAPERS

Timing	Green light shows for presentation of paper - Warning light shows when 5 and 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 35mm 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.

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, Lucas Heights Research Laboratories) - or at the Sapphire Motel, 408 Princes Highway, Sylvania Heights - see map back cover. The Institute will make payment directly to the management 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, keys to be left in room door.

MEALS

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

Conference Luncheon - Wednesday 12th November, 1986

A luncheon for all participants will be held in the Stevens Hall Dining-room and Ante-room during the scheduled lunch periods on Wednesday 12th November.

Thursday & Friday 13th & 14th November, 1986

Lunches may be purchased from the AAEC Canteen.

Evening Meals

Tuesday & Wednesday 11th & 12th November, 1986

Please advise the conference secretary, if you require an evening meal on these evenings.

Conference Dinner - Thursday 13th November, 1986

5.30 p.m.	Pre-dinner drinks	Stevens Hall Lounge (included with Poster Session)
6.15 p.m.	Buffet Dinner	Bamboo Room, AAEC Canteen
7.45 p.m.	Conference Address	Prof. J.H. O'Donnell (Uni. of Qld)

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

TRANSPORT

Transport from Sydney Airport - Wednesday 12th November, 1986

An AAEC bus ('Z' number plate) will leave Australian Airlines Terminal (Sydney Airport) for Lucas Heights, at 9.25 a.m. 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 AAEC bus from Airport

As time will be limited, participants are asked to proceed 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 Wednesday 12th)

Taxis are available from the airport to -
Lucas Heights
Sydenham Railway Station - thence train to Sutherland Station.
Sutherland Railway Station - thence bus to Lucas Hts. or taxi (ref. bus timetable below).

NOTE: Bookings must be made for all transport listed below - through AINSE - as transport only operates on demand.

Monday - Friday

Depart Lucas Heights for Sutherland	**Depart Sutherland for Lucas Heights**
7.35 am	8.00 am
8.30 "	8.20 "
9.35 "	9.05 "
10.35 "	10.05 "
11.30 "	11.10 "
12.30 pm	12.00 pm
1.00 "	1.10 "
2.15 "	1.25 "
3.35 "	2.50 "
	4.00 "
* 8.20 "	8.40 "
* 9.20 "	9.40 "
*10.25 "	11.00 "
11.35 "	12.05 am

Buses from Lucas Hts. leave from outside AAEC Main Gate.

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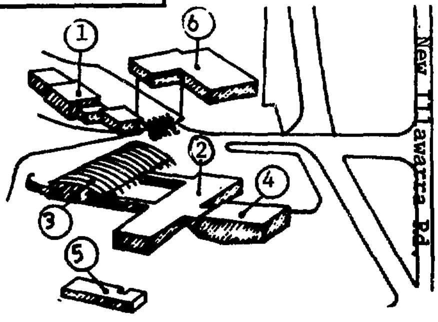
Buses from Sutherland leave from outside Post Office - Flora Street

\- - - - -

*Upon request these buses will transport participants 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

Transport from Sapphire Motel to Lucas Heights

Transport will be arranged for participants on Wednesday, Thursday and Friday mornings. Please wait outside the motel reception office for transport leaving at 8.30 a.m. (approx). It would be appreciated if participants with their own transport could drive to Lucas Heights, and assist others if possible.

Transport from Lucas Heights to Sapphire Motel

Buses leaving Lucas Heights at the following times will transport participants to the Sapphire Motel - 8.20 p.m., 9.20 p.m., and 10.25 p.m. (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 14th November, 1986

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 14th November, 1986

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 or room door.

TELEPHONE MESSAGES

Telephone messages will be taken for conference participants on -

543-3411	543-3436	543-3111
(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
SUTHERLAND. 2232

Phone: 543-3411 or 543-3111

PARTICIPANTS

LIST OF PARTICIPANTS

OVERSEAS VISITORS		PAPER NO.
Professor G.W. Robinson	Texas Tech University, USA	1R
Professor V. Gromov	Academy of Sciences, Moscow, USSR	9R,52
Professor E.A. Abramyan	Academy of Sciences, Moscow, USSR	21R,50R
Professor J. Sohma	Hokkaido University, Japan	16R,43
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Mrs. D. Freeman	
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C.S.I.R.O.	
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