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AUSTRALIAN INSTITUTE OF NUCLEAR SCIENCE AND ENGINEERING
11TH AINSE RADIATION CHEMISTRY CONFERENCE, 1982
LUCAS HEIGHTS N.S.W.

IN ASSOCIATION WITH THE POLYMER DIVISION
ROYAL AUSTRALIAN CHEMICAL INSTITUTE

Wednesday 10th November, 1982	Commencing	10.30 a.m.
	<u>Conference Luncheon</u>	12.40 p.m.
	Concluding	5.30 p.m.
Thursday 11th November, 1982	Commencing	9.00 a.m.
	Concluding	6.15 p.m.
	<u>Conference Dinner</u>	6.15 p.m.
Friday 12th November, 1982	Commencing	9.00 a.m.
	Concluding	4.30 p.m.

Conference President

Dr. G.S. Laurence University of Adelaide

Planning Committee

Dr. G.S. Laurence	University of Adelaide
Professor A.L.J. Beckwith	Australian National University
Assoc. Professor J.H. Hawke	Macquarie University
Dr. K.H. Lokan	Australian Radiation Laboratory
Dr. J.H. O'Donnell	University of Queensland
Mr. D.F. Sangster	C.S.I.R.O.
Mr. E.A. Palmer	A.I.N.S.E.

Programme Committee

Dr. G.S. Laurence	University of Adelaide
Professor A.L.J. Beckwith	Australian National University
Dr. J. Boas	Australian Radiation Laboratory
Dr. R. Cooper	University of Melbourne
Dr. J.H. O'Donnell	University of Queensland
Mr. D.F. Sangster	C.S.I.R.O.
Mr. E.A. Palmer	A.I.N.S.E.

Conference Secretary

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

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GENERAL INFORMATION

S U M M A R YWednesday 10th November, 1982 - Lucas Heights

10.30 - 10.40 a.m. Opening Remarks Dr.G.S. Laurence
Conference President. Uni. of Adelaide

SESSION I

10.40 - 12.40 p.m. RADICAL OXIDATION - REDUCTION PROCESSES
Chairman: Professor A.L.J. Beckwith (ANU)

12.40 - 1.40 p.m.

C O N F E R E N C E L U N C H (STEVENS HALL)

SESSION II

1.40 - 3.20 p.m. ATOMIC & RADICAL PROCESSES IN GASES
Chairman: Dr.J.F. Boas, (A.R.L.)

3.20 - 3.40 p.m.

A F T E R N O O N T E A

SESSION III

3.40 - 5.30 p.m. FREE RADICALS IN ENERGY CONVERSION
Chairman: Dr. P.G. Alfredson (CSIRO)

Thursday 11th November, 1982 - Lucas Heights

SESSION IV

9.00 - 10.20 a.m. RADIATION POLYMERISATION & DEGRADATION I
Chairman: Assoc. Professor D.H. Napper (Uni. of Sydney)

10.20 - 10.40 a.m.

M O R N I N G T E A

SESSION V

10.40 - 12.30 p.m. RADIATION POLYMERISATION & DEGRADATION II
Chairman: Dr. E. Senogles. (James Cook Uni.)

12.30 - 1.30 p.m.

L U N C H

SESSION VI(a)

1.30 - 3.00 pm. SYMPOSIUM - RADICALS, RADICAL IONS & EXCITED SPECIES
Chairman: Mr. D.F. Sangster (CSIRO)

3.00 - 3.20 p.m.

A F T E R N O O N T E A

SESSION VI(b)

3.20 - 4.40 p.m. Chairman: Dr. J.H. O'Donnell (Uni. of Queensland)

SESSION VII

4.40 - 6.15 p.m. POSTER SESSION (Includes Pre-dinner drinks)

6.15 onwards

C O N F E R E N C E D I N N E R

Friday 12th November, 1982 - Lucas Heights

SESSION VIII

9.00 - 10.20 a.m. POLYMER MODEL COMPOUNDS
Chairman: Assoc. Professor J.G. Hawke (Macquarie Uni.)

10.20 - 10.40 a.m.

M O R N I N G T E A

SESSION IX

10.40 - 12.20 p.m. EXCITATION IN GASES.
Chairman: Professor P.J. Derrick (Uni. of N.S.W.)

12.20 - 1.30 p.m.

L U N C H

SESSION X

1.30 - 3.20 p.m. EXCITATION IN SOLIDS
Chairman: Dr. R. Cooper (Uni. of Melbourne)

3.20 - 3.40 p.m.

A F T E R N O O N T E A

SESSION XI

3.40 - 4.20 p.m. STATE OF THE ART
Chairman: Dr. G.S. Laurence (Uni. of Adelaide)

CLOSING DISCUSSIONS

4.20 - 4.30 p.m.

Dr. G.S. Laurence - Conference President.

CONFERENCE SESSIONSWEDNESDAY 10TH NOVEMBER, 1982 - LUCAS HEIGHTS

<u>TIME.</u>	<u>PAPER NO.</u>	
10.30 - 10.40		<u>Opening Remarks - Conference President</u> Dr. G.S. Laurence - (University of Adelaide)
<u>SESSION I</u>		
<u>RADICAL OXIDATION - REDUCTION PROCESSES</u>		
<u>Chairman: Professor A.L.J. Beckwith (ANU)</u>		
10.40 - 11.20	1R Review	<u>Radiation Chemistry in Non-Aqueous Solvents.</u> G.S. Laurence (Uni. of Adelaide).
11.20 - 11.40	2	<u>Pulse Radiolysis Studies of Sulphur-Containing Radicals - Wu Zhennan (Uni. of Science & Technology of China), R. Ahmad, D.A. Armstrong (Uni. of Calgary)</u>
11.40 - 12.00	3	<u>γ-Radiolysis and U.V. Photolysis of Alkylthio- and Alkylseleno-Derivatives of Mercury : An E.S.R. Study.</u> P.J. Barker (ANU), M.C.R. Symons (Uni. of Leicester).
12.00 - 12.20	4	<u>Mechanistic Studies of the Role of the Metal in Coordinated Amine Oxidative Dehydrogenation Using Flash Photolysis Techniques.</u> F.R. Keene, M.J. Ridd, (James Cook University of North Queensland).
12.20 - 12.40	5	<u>Pulse Radiolysis Study of Pentaamminecobalt(III) Complexes: Ligand to Metal Electron Transfer Reactions.</u> P. Comba, G.A. Lawrance, A.M. Sargeson (ANU), D.F. Sangster (CSIRO)
12.40 - 1.40		C O N F E R E N C E L U N C H (Stevens Hall)
<u>SESSION II</u>		
<u>ATOMIC & RADICAL PROCESSES IN GASES</u>		
<u>Chairman: Dr.J.F. Boas (Australian Radiation Laboratory).</u>		
1.40 - 2.20	6R Review	<u>Chemistry of Gaseous Radical Ions.</u> P.J. Derrick (Uni. of N.S.W.)
2.20 - 2.40	7	<u>Inside the Mass Spectrometer - A Radiation Chemist's Perspective.</u> S. Bett (Uni. of N.S.W.)
2.40 - 3.00	8	<u>The Kinetics of the Reaction of Atomic Bromine with HO₂ and H₂O₂.</u> J. Sherwell (Uni. of Melbourne).
3.00 - 3.20	9	<u>Nuclear Spin Directed Tritium Recoil Reactions with Isotopic Hydrogens.</u> J.G. Hawke, A.A.A. Suweda, (Macquarie Uni.)
3.20 - 3.40		A F T E R N O O N T E A

<u>TIME</u>	<u>PAPER NO.</u>	
<u>SESSION III</u>		
<u>FREE RADICALS IN ENERGY CONVERSION</u>		
Chairman: Dr. P.G. Alfredson (CSIRO)		
3.40 - 4.10	1GR Review	Rates and Yields of Cage Escape in Model Systems for the Photolysis of Water. A.W.H. Mau, W.H.F. Sasse (CSIRO)
4.10 - 4.30	11	Oxidising Radical Reactions Induced by Light on Heterogeneous Aqueous Suspensions of Titanium Dioxide. R.W. Matthews (CSIRO)
4.30 - 4.50	12	Pulse Radiolysis Study of the Reactions of Hydrogen Atoms and Hydroxyl Radicals with Methyl Viologen. N.A. McAskill (CSIRO)
4.50 - 5.30	13 Review	The Scope of Electron Spin Resonance Spectroscopy as an Alternative Dating Technique. D.S. Hunter, P.J. Pomery. (Uni. of Queensland).

THURSDAY 11TH NOVEMBER, 1982 - LUCAS HEIGHTS

<u>SESSION IV</u>	<u>RADIATION POLYMERISATION & DEGRADATION I</u>
Chairman: Assoc. Professor D.H. Napper (Uni. of Sydney)	
9.00 - 9.20	14 Pulse Radiolysis of Aqueous Solutions of N-Vinylpyrrolidin-2-One and Poly(N-Vinylpyrrolidin-2-One). J.E. Davis, E. Senogles (James Cook Uni. of North Queensland) D.F. Sangster (CSIRO)
9.20 - 9.40	15 The Photolysis of N-Acetyl Amino Acids in the Solid State. D.J.T. Hill, J.H. O'Donnell, A.K. Whittaker (Uni. of Queensland)
9.40 - 10.00	16 An Investigation of Acid Effects in Radiation Induced Grafting of Monomers to Polymer Substrates. S.V. Jankiewicz (Uni. of N.S.W.)
10.00 - 10.20	17 The Influence of Thermal History on the Nature and Activity of Active Sites in Gamma-Irradiated Polypropylene. W.K. Busfield, T.Morley-Buchanan (Griffith Uni.).
10.20 - 10.40	M O R N I N G T E A

<u>TIME</u>	<u>PAPER</u> <u>NO.</u>	
<u>SESSION V</u>		
<u>RADIATION POLYMERISATION & DEGRADATION II</u>		
Chairman: Dr.E. Senogles (James Cook University of North Queensland)		
10.40 - 11.00	18	Kinetics of Styrene Emulsion Polymerisation: The use of Gamma Irradiation. G.Lichti(ICI).D.F.Sangster(CSIRO)
11.00 - 11.20	19	The Effects of Chain Transfer Agents on the Kinetics of the Seeded Emulsion Polymerization of Styrene. G. Lichti (ICI), D.F. Sangster (CSIRO), B.C.Y.Whang, D.H. Napper, R.G. Gilbert (Uni. of Sydney)
11.20 - 11.40	20	The Radiolysis Technique for Determination of Short Chain Branching in Polymers. T.N. Bowmer, S.Y.Ho J.H. O'Donnell. (Uni. of Queensland)
11.40 - 12.00	21	The Effects of Ultraviolet Radiation on the CR-39 and Lexan Plastic Nuclear Track Detectors. C.F. Wong, P. Hoberg (Queensland Institute of Technology).
12.00 - 12.30	22R Review	Review of 4th International Meeting on Radiation Processing to be held in Dubrovnic Yugoslavia. J.L. Garnett (Uni. of N.S.W.)
12.30 - 1.30		L U N C H
<u>SESSION VI(a)</u>		
<u>SYMPOSIUM</u>		
<u>RADICALS, RADICAL IONS & EXCITED SPECIES</u>		
Chairman: Mr.D.F. Sangster (CSIRO)		
1.30 - 2.20	23R Review	The Reaction of Hydroxyl Radicals with Aromatics. C. Walling (Uni. of Utah)
2.20 - 3.00	24R Review	Some Characteristic Reactions of Organic Free Radicals. A.L.J. Beckwith (ANU)
3.00 - 3.20		A F T E R N O O N T E A
<u>SESSION VI(b)</u>		
Chairman: Dr.J.H. O'Donnell (Uni. of Queensland)		
3.20 - 4.00	25R Review	The Determination of the Mechanisms of Gas Phase Ionic Rearrangements by the Application of ^2H and Heavy Atom Isotope Effects. The McLafferty Rearrangement. D.J. Underwood, D.J.M. Stone, J.H. Bowie (Uni. Adelaide) D.E. Lewis, A. Fry, L.B. Sims - (Uni. of Arkansas), K. Donch, P.J. Derrick (Uni. N.S.W.)
4.00 - 4.40	26R Review	Energy Transfer Processes in Irradiated Gases. R. Cooper (Uni. of Melbourne)

<u>TIME</u>	<u>PAPER NO.</u>	<u>POSTER SESSION</u> (Includes Pre-dinner drinks)
<u>SESSION VII</u>		
4.40 - 6.15	27	An ESR Study of the Radiation Degradation of Poly(Olefin Sulphone)s. <u>T.N. Bowmer, E. Grespos, J.H. O'Donnell, P.J. Pomery.</u> (Uni. of Queensland)
4.40 - 6.15	28	Electron Spin Resonance as a Probe of Polymer Compatability. <u>R.W. Garrett, J.H. O'Donnell P.J. Pomery.</u> (Uni. of Queensland)
4.40 - 6.15	29	Radiation Sensitivity of Cellulose Polymers. <u>A.C. Ingham, J.H. O'Donnell</u> (Uni. of Queensland)
4.40 - 6.15	30	The Structural Chemistry of Synroc. <u>D.R. Cousens, J. Penrose, R.L. Segall, R.St.C. Smart, P.S. Turner, T.J. White</u> (Griffith Uni.)
4.40 - 6.15	31	Zeolite Catalysis of Hydrogen Isotope Exchange Reactions. <u>P.G. Williams.</u> (Uni. of N.S.W.)
4.40 - 6.15	32	Investigation of Vacuum Ultraviolet Emissions from Electron Irradiated Gases. <u>J. Sherwell, S. Mezyk</u> (Uni. of Melbourne)
4.40 - 6.15	33	Pulse Radiolysis Study of the Reaction $\text{OH} + \text{CO} \rightarrow \text{CO}_2$ <u>C.D. Johan</u> (Argonne National Laboratory). <u>P. Zeglinski</u> (Uni. of Melbourne).
4.40 - 6.15	34	Mechanisms for Luminescence in Electron Irradiated Alkaline Earth Oxides. <u>J. Boas</u> (Australian Radiation Laboratory). <u>R.Cooper, J.Grant</u> (Uni.Melbournen)
4.40 - 6.15	35	Photochemistry and Radiation Chemistry of Vaska's Compound. <u>G.S. Laurence</u> (Uni. of Adelaide).
4.40 - 6.15	36	A Reference File Search for Radiation Chemistry Literature using a Minicomputer. <u>G.S. Laurence</u> (Uni. of Adelaide).
4.40 - 6.15	37	Reactive and Non Reactive Quenching of $\text{I}_2(\text{D}^1\Sigma^+)$: The Reaction of $\text{I}_2(\text{D}^1\Sigma^+)$ and $\text{I}_2(3\Pi_2g)$ with C_2H_6 <u>B.V. O'Grady</u> (Uni. of Tasmania) <u>R.J. Donovan</u> (Uni. of Edinburgh) <u>L. Lain,</u> (Uni. of Bilboa.)
4.40 - 6.15	38	Red Emission from Ice Excited by Pulsed Electrons. <u>R.A.J. Litjens, T.I. Quickenden, S.M. Trotman,</u> (Uni. of Western Australia) <u>D.F. Sangster</u> (CSIRO)

TIME PAPER
SESSION VII (cont'd)NO.

4.40 - 6.15 39 Time Resolved Luminescence in the 360 - 600 nm
 Region from Water Vapor Irradiated with Pulsed
 Electrons. C.G. Freeman, (Uni. of Canterbury)
T.I. Quickenden (Uni. of Western Australia)
D.F. Sangster (CSIRO)

6.15 onwards C O N F E R E N C E D I N N E R

FRIDAY 12TH NOVEMBER, 1982 - LUCAS HEIGHTS

SESSION VIII

POLYMER MODEL COMPOUNDS

Chairman: Assoc. Professor J.G. Hawke
 (Macquarie Uni.)

9.00 - 9.20 40 The Radiation Degradation of N-Acetyl Amino Acids.
D.J.T. Hill, S.Y. Ho, J.H. O'Donnell, P.W. O'Sullivan
P.J. Pomery (Uni. of Queensland)

9.20 - 9.40 41 Radiolysis of Aromatic Acids : The effect of
 Heteroatom. D.J.T. Hill, D.A. Lewis, J.H. O'Donnell
P.J. Pomery. (Uni. of Queensland)

9.40 - 10.20 42R The Transport and Recombination of Clustered Ions.
 Review D.A. Armstrong (Uni. of Calgary).

10.20 - 10.40 M O R N I N G T E A

SESSION IX

EXCITATION IN GASES

Chairman: Professor P.J. Derrick (Uni. of N.S.W.)

10.40 - 11.00 43 Excitation Processes in Rare Gas-Additive Mixtures
R. Cooper, L.S. Denison (Uni. of Melbourne) M.C. Sauer Jr.
 (Argonne National Laboratory).

11.00 - 11.20 44 Formation of Rare-Gas Halogen Atom Exciplexes in
 Electron Beam Irradiated Gases. R. Cooper,
L.S. Denison, S. Mezyk, P. Zeglinski. (Uni. of
 Melbourne) C.R. Roy (Australian Radiation Laboratory)
H. Gillis (National Research Council of Canada).

11.20 - 11.40 45 Absolute Photon Yields in Electron Irradiated Gases.
J.G. Young (Australian Radiation Laboratory)
R. Cooper (Uni. of Melbourne).

11.40 - 12.20 46R Photochemical Processes in Irradiated Micellar Systems.
 Review K. Thomas (Notre Dame Uni. Indiana, U.S.A.).

12.20 - 1.30 L U N C H

<u>TIME</u>	<u>PAPER NO.</u>	
<u>SESSION X</u>		
<u>EXCITATION IN SOLIDS</u>		
<u>Chairman: Dr. R. Cooper (Uni. of Melbourne)</u>		
1.30 - 2.00	47R Review	Glass as a High Level Waste Matrix: A Review of the Variables. <u>R.A. Lewis</u> , S. Myhra, R.L. Segall, R.St.C. Smart, P.S. Turner (Griffith Uni.)
2.00 - 2.20	48	Pulse Radiolytic Studies of the 200 - 600 nm Emissions from Low Temperature H ₂ O Ice. T.I. Quickenden, <u>S.M. Trotman</u> (Uni. W.A.) D.F. Sangster (CSIRO)
2.20 - 2.40	49	The Visible Absorption Spectrum of Liquid Water. <u>R.A.J. Litiens</u> , T.I. Quickenden (Uni. of Western Australia).
2.40 - 3.00	50	ESR and Optical Studies of Rare Earth Doped CaSO ₄ . <u>R.L. Calvert</u> , R.J. Danby (Australian Radiation Laboratory).
3.00 - 3.20	51	Luminescence Studies of Electron Irradiated Calcium Oxide. J.L. Grant, R. Cooper, (Uni. of Melbourne) <u>J.F. Boas</u> (Australian Radiation Laboratory)
3.20 - 3.40		A F T E R N O O N T E A
<u>SESSION XI</u>		
<u>STATE OF THE ART.</u>		
<u>Chairman: Dr. G.S. Laurence (Uni. of Adelaide)</u>		
3.40 - 4.20	52 R Review	Current Frontiers of Radiation Chemistry. <u>R. Cooper</u> (Uni. of Melbourne)
<u>CLOSING DISCUSSIONS</u>		
4.20 - 4.30		Dr. G.S. Laurence - Conference President.

ABSTRACTS

RADIATION CHEMISTRY IN NON-AQUEOUS SOLVENTS

by

G.S. Laurence

Department of Physical and Inorganic Chemistry
University of Adelaide
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Abstract

Radiation chemistry and pulse radiolysis have been powerful techniques for the study of a variety of reactions of metal complexes in aqueous solutions. Unstable oxidation states, electron transfer processes and substitution reactions have been extensively studied, but the large area of organometallic chemistry has remained outside the technique chiefly because most organometallic compounds are insoluble or unstable in water. The primary radiation produced species in water are well understood and their reactions well characterised but this is not the case for many organic solvents.

Apart from the variety of primary solvent products, the most elementary properties of the organic radicals or radical ions, such as the reduction potentials, are often unknown, while their reactivity towards organometallic compounds has never been explored. Pulse radiolysis would be a most valuable technique in exploring the mechanisms of many organometallic reactions but for the lack of primary data on the radiolysis of useful solvents. The radiation chemistry of alcohols has been extensively studied, but even for these the reactivity of the radicals towards organometallic compounds is hardly known.

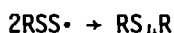
The current data on non-aqueous solvents is reviewed and some indication of reactions which could be studied by pulse radiolysis in solvents such as acetonitrile, benzene, dichloromethane and alcohols is given. The extensive electrochemical data for organometallic species in non-aqueous solvents is useful in providing a possible tool for exploring the reactions of radiation produced species with the metal compounds. It is desirable to establish base-line data for some representative solvents in order to strike out for the unexplored summit peaks of organometallic chemistry.

PULSE RADIOLYSIS STUDIES OF
SULPHUR-CONTAINING RADICALS

Wu Zhennan*, Rizwan Ahmad and David A. Armstrong

Chemistry Department
The University of Calgary
Calgary, Alberta T2N 1N4

A variety of sulphur-containing radicals have been produced and studied by pulse radiolysis methods. It has been found that each of the reducing radicals $e^-_{(aq)}$, $\cdot CO_2^-$ and $(CH_3)_2\dot{C}OH$ cleaves bis-(2-hydroxyethyl) trisulfide in aqueous solution to produce 2-hydroxyethyl perthiyl (RSS \cdot) radicals and 2-hydroxyethane thiol. The RSS \cdot radical has $\lambda_{max} = 374$ nm, $\epsilon_{max} = 1630 \pm 50$ M $^{-1}$ cm $^{-1}$ and a second order rate constant for dimerisation $2k_1 = 1.4(\pm 0.3) \times 10^9$ M $^{-1}$ s $^{-1}$.



It is able to abstract H atoms from dihydroflavin adenine dinucleotide, but not from formate. Thus in aqueous solution D_{RSS-H} must be greater than 60 kcal per mole, but probably not by more than a few kcal. The perthiyl radical is also produced in the oxidation of amino-containing disulphides. The reaction of the cyclic disulphide lipoamide $S-S-CH_2-CH_2-CH-(CH_2)_4CONH_2$ with $\cdot CO_2^-$ produces a cyclic negatively charged ion-radical which decays by disproportionation to the disulphide and disulphydryl, as does the related lipoate anion. Reactions of alcohol radicals with lipoamide are complex and proceed via addition, followed by unimolecular decomposition or reaction with additional lipoamide to give the same anion radical as $\cdot CO_2^-$. It seems probable that the intermediate formed by addition is the sulphuranyl radical $R-S-S-CH_2-CH_2-CH-(CH_2)_4CONH_2$.

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γ -RADIOLYSIS AND U.V. PHOTOLYSIS OF ALKYLTHIO-
AND ALKYLSELENO-DERIVATIVES OF MERCURY : AN E.S.R. STUDY

by

*Philip J. Barker and **Martyn C.R. Symons

* Research School of Chemistry,
Australian National University, and
Canberra, A.C.T. Australia

** Department of Chemistry,
The University,
Leicester, LE1 7RH, England

Abstract

There has been increasing interest over the past few years in the use of organomercury compounds as precursors to novel organic free-radicals. When subjected to u.v.-photolysis or thermolysis in solution such compounds afford convenient first-order routes, via equation (1) to free-radicals, the reactions of which may be studied by e.s.r. spectroscopy or gas-phase kinetic methods.



Presence of mercury(I) intermediates in reaction (1) is suggested by kinetic and thermochemical data. Although they have not been detected in fluid solution, γ -radiolysis provides a convenient route to such species which may be studied by e.s.r. in frozen solution or in the solid phase at 77K.

The aims of this work have been twofold. Firstly, we have studied the photochemical decomposition of the title compounds in solution. When the photolysis was carried out in 1,1-di-tert-butylethylene as solvent, e.s.r. spectra corresponding to the adducts of trifluoromethylthiyl- and -selenyl- radicals were observed. The e.s.r. spectra are discussed in terms of the decreasing electronegativity and increasing spin-orbit coupling effects encountered upon descending group VI of the periodic table.

Secondly, the γ -radiolysis results yield information on the novel intermediates produced, particularly interesting being those results involving Hg(I) species. These species are characterised by large mercury hyperfine coupling constants which when evaluated with the isotropic hyperfine coupling constant of mercury yield the orbital contributions at the metal centre. When radiolysis is effected in suitable solvents, ionic species may be produced. The results are discussed in terms of the variation of e.s.r. parameters with substituent at mercury.

In conclusion, this work demonstrates the potential of the title compounds as easily handled sources of, particularly, thiyl-radicals. Previously, these radicals have been accessible only from bis-trifluoromethyldisulphide. In addition γ -radiolysis gives a useful insight to the nature and structures of intermediates in decompositions of bis-organomercury derivatives.

MECHANISTIC STUDIES OF THE ROLE OF THE METAL IN COORDINATED AMINE
OXIDATIVE DEHYDROGENATION USING FLASH PHOTOLYSIS TECHNIQUES

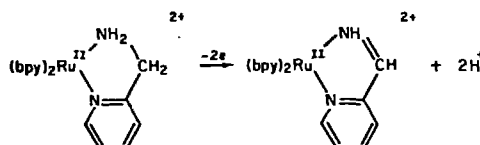
by

F.R. Keene and M.J. Ridd

Department of Chemistry and Biochemistry
James Cook University of North Queensland
Townsville Queensland 4811

Abstract

The oxidative dehydrogenation of amines to imines or nitriles is catalyzed by their coordination to metal centres.¹ A detailed mechanistic investigation¹ of the oxidation of 2-(aminomethyl)pyridine (ampy) coordinated to ruthenium(II)



reveals that the particular efficacy of ruthenium in the promotion of ligand oxidation is related to its ability to attain an oxidation state (Ru(IV)) two units greater than the final state, allowing a low energy pathway for the even-electron process required in these dehydrogenation reactions.

The initial step in these metal-promoted ligand oxidation reactions is the rapid oxidation of the metal centre. Using conventional flash photolysis techniques, the MLCT excited state of the complex was quenched rapidly by Fe(III) producing the Ru(III) species. The subsequent intramolecular redox process resulting in ligand dehydrogenation was followed spectrophotometrically.

Similar kinetic studies of analogues of 2-(aminomethyl)pyridine (with the aliphatic carbon (i) deuterated and (ii) with a single methyl substituent) reveal that both dehydrogenation from the carbon atom and the intramolecular transfer of two electrons from ligand to metal are achieved in a synchronous process via a Ru(IV)-hydride transition state. Furthermore, within the ampy ring system, it is specifically the axial C-H bond which is broken.

The paper will report details of the use of flash photolysis techniques in the study of ligand oxidation reactions, and of the elucidation of the mechanism the oxidative dehydrogenation process.

Reference

1. M.J. Ridd and F.R. Keene, *J. Am. Chem. Soc.*, **103**, 5733-5740.

PULSE RADIOLYSIS STUDY OF PENTAAMMINECOBALT(III) COMPLEXES:
LIGAND TO METAL ELECTRON TRANSFER REACTIONS

by

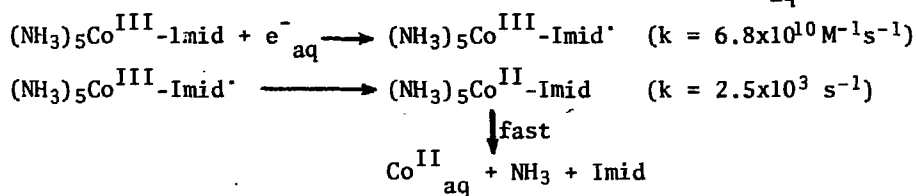
P. Comba,¹ G.A. Lawrance,¹ D.F. Sangster² and A.M. Sargeson¹

¹ Research School of Chemistry, The Australian National University,
P.O. Box 4, Canberra, A.C.T. 2600

² CSIRO Chemical Physics, AAEC Research Establishment,
Private Mailbag, Sutherland, N.S.W. 2232.

Abstract

A range of pentaamminecobalt(III) complexes with coordinated imidazole, carboxylates, nitriles or halides have been subjected to pulse radiolysis study in aqueous solution. Reaction with OH⁻ or e⁻_{aq} frequently leads to formation of coordinated ligand radical intermediates which decay relatively slowly ($t_{1/2}$ in the millisecond range) by ligand to metal electron transfer, with reduction of the inert cobalt(III) centre to a labile cobalt(II) complex. For example, with coordinated imidazole and e⁻_{aq}:



Ligands with aromatic substituents, such as cinnamate, apparently stabilize the radical intermediate, and the observed rate of decay is even slower (~ 10 -fold). Implications of these observations for inner-sphere electron transfer reactions between two metal ions will be discussed.

CHEMISTRY OF GASEOUS RADICAL IONS

by

Peter J. Derrick
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University of New South Wales
Kensington, N.S.W. 2033

Abstract

Structure in the context of gaseous organic ions is a qualitative term. The usual spectroscopic methods used to determine molecular geometries have not been applied extensively to ions, and the accepted qualitative structures of most gaseous ions have for the most part been inferred from the nature of their reactions as studied by mass spectrometry. Gaseous organic ions may have very short lifetimes with respect to unimolecular isomerization and decomposition, however even at picoseconds fragmentation is essentially chemical in nature. The apparent "scrambling" of atoms following ionization can be attributed to series of rapid discrete chemical reactions. The distribution of internal energy among different degrees of freedom of the products of ionic reactions is sensitive to whether in the transition state the energy is present as potential (chemical) energy or vibrational energy. Vibrational energy is distributed randomly (statistically); potential energy can be distributed in a specific fashion. The established ionization techniques have in recent years been augmented by sputtering and field desorption techniques, which bring involatile thermally sensitive samples within the scope of study by mass spectrometry. These questions of structure determination, reactivity and ionization are discussed in this paper.

INSIDE THE MASS SPECTROMETER - A RADIATION CHEMIST'S PERSPECTIVE

by

S. Bett

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Abstract

Negative ion mass spectrometric studies of transition metal β -diketone complexes have shown them to be particularly sensitive to electron capture and the minimal resulting fragmentation makes them ideal for use in trace metal analysis.

In order to gain more insight into the processes which occur in the short period of time following electron capture (i.e. in the time of flight of ions in the mass spectrometer) some liquid and gas phase pulse radiolysis studies of transition metal β -diketonates have been undertaken. The results of these studies are discussed in terms of their relevance to mass spectrometry.

THE KINETICS OF THE REACTION OF ATOMIC BROMINE
WITH HO₂ AND H₂O₂

by

J. Sherwell

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Abstract

Although considerable publicity has been given to the possible destruction of the stratospheric ozone layer by chlorine - containing compounds such as chlorofluoromethanes, much less attention has been paid to the analogous problem resulting from bromine containing compounds.

In modelling stratospheric chemistry rate constants are required for many elementary reactions. As the experimental data for ClO_x is more complete than for BrO_x rate constant have often been estimated from the analogous ClO_x reactions.

This study measures the rate of reaction between Br and HO₂ and Br and H₂O₂ both important in stratospheric modelling since they are considered to be the prime route for the conversion of BrO_x to HBr which is catalytically inactive in the destruction of stratospheric ozone.

The reactions were studied at room temperature using a fast flow reactor coupled to a molecular beam mass spectrometer. It was found that

$$k \text{ Br} + \text{H}_2\text{O}_2 \leq 1.2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

$$k \text{ Br} + \text{HO}_2 = 1.26 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

which are considerably slower than the values previously estimated.

On the basis of these values the ratio [BrO_x]/[HBr] will be higher than previously considered and hence predict a more important role for BrO_x than presently thought.

NUCLEAR SPIN DIRECTED TRITIUM RECOIL REACTIONS
WITH ISOTOPIC HYDROGENS

BY

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ABSTRACT

The HT/DT yield ratio from the tritium atoms produced by the $\text{He}^3(n,p)\text{T}$ reaction, reacting with scavenged mixtures of gaseous H_2 and D_2 studied previously in these laboratories⁺ is almost independent of the nuclear spin of the reactants. However in the absence of scavengers we have found that the tritium atoms react preferentially with the ortho-isomer over the para which provides further support for the conventional distinctions between hot and thermal reactions. The enhanced yields of HT, DT may be related to the CIDNP effect in NMR.

References

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1974

RATES AND YIELDS OF CAGE ESCAPE IN MODEL SYSTEMS
FOR THE PHOTOLYSIS OF WATER

by

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Abstract

Interest in the photochemical conversion of solar energy has led to the discovery of many systems for the photoreduction of water. Generally such systems operate by way of several coupled electron-transfer reactions between sensitizers, electron-transfer agents and catalysts, and sacrificial electron donors.

In many cases the first step involves the oxidative quenching of an excited sensitizer by a ground state electron acceptor. The efficiency of this step depends on the quantum yield of formation of the excited sensitizer, the efficiency of bimolecular quenching and the yield of separated redox products.

Until recently the problem of the rates and yields of cage escape has received little attention and more experimental and theoretical studies are needed.

The present paper will present data on the oxidative quenching of the anion of 9-anthracenecarboxylic acid by methylviologen and compare them with the quenching of the tris(2,2'-bipyridine)ruthenium (II) dication.

OXIDISING RADICAL REACTIONS INDUCED BY LIGHT ON
HETEROGENEOUS AQUEOUS SUSPENSIONS OF TITANIUM DIOXIDE

by

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2232

Abstract

A marked increase in the photoreduction rate of ceric ions in ceric/thallos ion solutions occurs when titanium dioxide is present. The photoreduction rate was studied as a function of thallos ion concentration both in the homogeneous system (no TiO_2) and in the heterogeneous system (TiO_2). Analysis of the kinetic data provided evidence that, even though there is a markedly increased reduction yield in the presence of TiO_2 , the same oxidising radical intermediate is involved in both systems. In addition, significant oxidising radical reactions can occur in aqueous titanium dioxide slurries without the need for the formation of hydrogen peroxide as an intermediate.

Aqueous suspensions of TiO_2 in benzoic acid and sodium benzoate solutions containing known hydroxyl radical scavengers were also photolysed. The yield of salicylate species is inhibited by these solutes in accordance with that expected for a simple competition between the solute and benzoate species for hydroxyl radicals. In the absence of added solute, the isomer distribution ortho:meta:para hydroxybenzoic acids is, within experimental error, in agreement with that found from radiation studies for hydroxyl radical attack on benzoic acid.

PULSE RADIOLYSIS STUDY OF THE REACTIONS OF HYDROGEN
ATOMS AND HYDROXYL RADICALS WITH METHYL VIOLOGEN

by

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Abstract

Methyl viologen is often used as an electron relay in photochemical schemes for the production of hydrogen gas from water in the presence of platinum. However, the efficiency of hydrogen production is decreased by the loss of methyl viologen (mv^{2+}) due to a platinum-catalysed hydrogenation reaction¹. Pulse radiolysis of acid aqueous solutions is a useful source of hydrogen atoms and in this work the uncatalysed reactions of hydrogen atoms with mv^{2+} have been studied together with those of the $\cdot OH$ radical since the latter is also a likely product in any water-splitting process.

The absorption spectra caused by the reaction of hydrogen atoms with mv^{2+} show the well known spectrum of the methyl viologen radical cation ($mv^{+\cdot}$) together with additional absorptions at 345 nm and 470 nm. It is concluded that 0.4 of the hydrogen atoms undergo an electron transfer reaction to form $mv^{+\cdot}$ whilst 0.3 add to the ring to form $CH_3-^+Py-Py(H)^{+\cdot}-CH_3$ (absorbing at 470 nm) and 0.3 react by a hydrogen abstraction reaction to form $CH_3-^+Py-Py^+-CH_2\cdot$ (absorbing at 345 nm).

It was found in deaerated neutral solutions that hydroxyl radicals added rapidly to the ring to form $CH_3-^+Py-Py(OH)^{+\cdot}-CH_3$ (absorbing at 470 nm). This is in contrast to the slower formation and larger extinction coefficient in air saturated solutions² and provides evidence for the secondary formation of $\cdot OH$ in the latter work, presumably by a reaction involving $mv^{+\cdot}$ and oxygen. In acid solution the $\cdot OH$ adduct at 470 nm undergoes a water-elimination reaction to form the hydrogen deficient radical absorbing at 345 nm.

References

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THE SCOPE OF ELECTRON SPIN RESONANCE SPECTROSCOPY AS AN
ALTERNATIVE DATING TECHNIQUE

by

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Abstract

Many methods of dating archaeological and geological materials have been introduced and developed in the last twenty years. The techniques can be broadly divided into two main categories -

A) those involving changes in the chemical nature of the sample with time, e.g. amino acid assay or the measurement directly or indirectly of the amount of active isotopes contained in the sample from which the age of the specimen can be calculated, providing the isotope stability is known,

and B) methods involving the detection of defects occurring in the sample material, the number of defects being proportional to the age of the sample. The defects are believed to be the result of radiation damage caused by naturally occurring isotopes within or in close proximity to the material.

In this latter area one such technique which has been developed is that of Thermoluminescence (TL) dating, which has mainly been applied to studies of archaeological ceramic materials. In this technique the sample is crushed and then heated, when the trapped electron associated with the defect recombines with positive hole traps with the emission of light, the intensity of the light being proportional to the amount of electrons in the sample. A more direct method of observing the number of defects (electrons) is by use of Electron Spin Resonance Spectroscopy. The technique has been used for some years for the dating of geological samples but has recently been adapted to study archaeological materials such as bone and teeth, the dating of which are difficult by other methods.

In this talk some of the advantages, difficulties and limitations associated with this new technique will be discussed, with particular reference to the problems being investigated at the University of Queensland.

PULSE RADIOLYSIS OF AQUEOUS SOLUTIONS OF N-VINYLPYRROLIDIN-2-ONE
AND POLY(N-VINYLPYRROLIDIN-2-ONE)

by

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^ADepartment of Chemistry and Biochemistry
James Cook University of North Queensland

^BCSIRO Division of Chemical Physics

Abstract

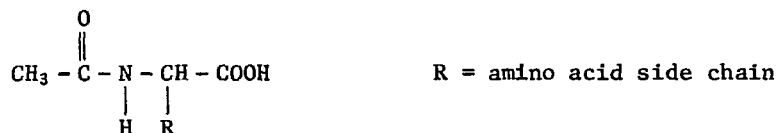
The absorption spectra of transient species produced when dilute aqueous solutions of N-vinylpyrrolidin-2-one (VP) and poly(N-vinylpyrrolidin-2-one) (PVP) are subjected to pulse radiolysis in the presence and absence of radical scavengers have been obtained and compared with those obtained from analogous compounds. The precise structure of the transients has not been established. Rate constants for the reaction of the hydroxyl radical with VP and PVP have been evaluated both by a competition kinetic method and by direct observation of the build-up of transient species: $k(\text{VP} + \cdot\text{OH}) = (6.4-8.1) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k(\text{PVP} + \cdot\text{OH}) = (1.5-2.3) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C. The rate constant for the reaction of the hydrated electron with VP has been determined as $(1.6 \pm 0.3) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C. Rate constants for decay of the transient species have also been evaluated at 25°C: $2k(\text{VP} - \text{OH}^\cdot) = (8.1 \pm 1.0) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $2k(\text{VP} - e^-) = (1.7 \pm 0.2) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $2k(\text{PVP} - \text{OH}^\cdot) = (1.5 \pm 0.2) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

THE PHOTOLYSIS OF N-ACETYL AMINO ACIDS IN THE SOLID STATE

by

D.J.T. Hill, J.H. O'Donnell, P.J. Pomery and A.K. WhittakerPolymer and Radiation Group, Department of Chemistry,
University of Queensland, Brisbane, Australia 4067Abstract

N-acetyl amino acids have been used extensively as model compounds for the study of the radiation sensitivity of polypeptides and proteins.



Generally, studies of this type have concentrated on gamma radiolysis of solid or aqueous solutions of the amino acid [1]; this paper considers the photolysis of the model compounds in the solid state with ultraviolet light, and will compare the effects of radiation of differing energies on this system. This has important applications in many biologically oriented sciences.

Five N-acetyl amino acids were studied after photolysis at low temperatures by electron spin resonance spectroscopy (ESR). Reactions on photolysis were found to occur mainly at the main chromophores of the molecule - the carboxylic acid group and the peptide linkage. Absorption of UV radiation by the peptide group resulted in cleavage of the C-C bond α to the carbonyl group giving an ESR spectrum consistent with the formation of methyl and acetyl radicals. The decarboxylation reaction however proceeded by a non-radical intramolecular reaction and had to be confirmed by volatile product analysis. The effect of the structure of the amino acid side chain on these reactions will also be discussed.

References

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AN INVESTIGATION OF ACID EFFECTS IN RADIATION INDUCED GRAFTING
OF MONOMERS TO POLYMER SUBSTRATES

by

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Abstract

The addition of mineral acid to grafting systems initiated by ionising radiation has been shown to markedly enhance grafting efficiency. The current study has been the investigation of the mechanism of this enhancement. Approaches taken include GPC examination and NAA analysis of solution polymers produced under grafting conditions in the presence of mineral acid. Evidence so far indicates enhancement is due to a combination of radiolysis product interactions and increased partitioning of monomer into the graft region.

THE INFLUENCE OF THERMAL HISTORY ON THE NATURE AND ACTIVITY OF
ACTIVE SITES IN GAMMA-IRRADIATED POLYPROPYLENE

by

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Abstract

Electron Spin Resonance Spectroscopy (ESR) has been used to investigate the stability and chemical nature of active radical sites produced in commercial isotactic polypropylene film by gamma-irradiation at low temperature as a function of the morphological structure and temperature of the sample.

Below the glass transition the total radical concentration is approximately independent of sample morphology and directly proportional to sample dose. The rate of radical decay is low showing that radical termination is slow due no doubt to the low mobility of backbone molecules in this temperature range. There are radical conversion reactions taking place however; the eight line alkyl radical signal is to some extent converted to the seventeen line allyl radical signal over a period of time. Radical decay accelerates in all samples as the temperature is raised above T_g . However rates are very much lower in the case of highly annealed samples. Total radical concentration has been followed with time at fixed temperatures; the results show that in annealed samples, rates of decay decrease steadily to a very low value after a few days at intermediate temperatures, e.g. 45°C , leaving a reasonable concentration of very stable radicals, i.e. having very long lifetimes. In unannealed samples on the other hand, the total radical concentration decreases to much lower concentrations at these temperatures. Detailed kinetics of these decay processes will be discussed further at the Symposium.

The reactivity of active sites with monomers have been studied by ESR for the purpose of understanding the mechanism of post irradiation grafting. The addition of butadiene to irradiated annealed polypropylene at 45°C causes a dramatic drop in radical concentration indicating addition to the active sites, probably propagation followed by a termination process which is more rapid than that occurring in the absence of butadiene. At this stage the chemical nature of the reacting radicals has not been identified; we are currently tackling this problem by computer simulation of the observed spectra.

KINETICS OF STYRENE EMULSION POLYMERISATION:
THE USE OF GRAMMA IRRADIATION

by

G. Lichti, ICI Ascot Vale, Melbourne

R. G. Gilbert, D.H. Napper, School of Chemistry, Sydney University

and

D. F. Sangster, CSIRO Divn Chemical Physics, Lucas Heights

Abstract

Monomer-swollen latex particles are the main locus of polymer growth in styrene emulsion polymerisation systems. Accordingly, the reaction kinetics are strongly influenced by the rate at which free radicals enter ($\rho \text{ s}^{-1}$) and exit from ($k \text{ s}^{-1}$) the latex particles. Previous attempts to obtain estimates of ρ and k from experiment have concentrated on the steady-state regime of the polymerisation reaction.⁽¹⁾ Since the magnitude of the steady-state rate depends on at least five independent variables, the values of ρ and k so obtained were ambiguous in the extreme.

It is possible to remove all these ambiguities by measuring and interpreting transient kinetic behaviour in the system. The most convenient experiment involving transient behaviour is the measurement of the relaxation of the polymerisation rate which occurs when gamma rays are used to initiate the reaction, and the system is subsequently withdrawn from the radiation.

Techniques for measuring and interpreting the transient kinetics will be discussed. For polystyrene latex particles of size 50 nm, the entry rate depends on the initiation conditions, but the rate of free radical exit is of the order of 10^{-2} s^{-1} .

Reference

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THE EFFECTS OF CHAIN TRANSFER AGENTS ON THE KINETICS
OF THE SEEDED EMULSION POLYMERIZATION OF STYRENE

by

G. Lichti and D. F. Sangster, AINSE and AAERE (now CSIRO)
and B. C. Y. Whang, D. H. Napper and R. G. Gilbert

Departments of Physical and Theoretical Chemistry,
The University of Sydney,
N. S. W. 2006

Abstract

The kinetics of the seeded emulsion polymerization of styrene have been studied in the presence and absence of the chain-transfer agents carbon tetrachloride and carbon tetrabromide. Initiation was achieved by both a chemical initiator (potassium peroxydisulphate) and irradiation with γ -rays. The latter permitted relaxation studies to be performed.

A combination of γ -ray initiation, relaxation and particle size distribution studies allowed the fate of the exited free radicals generated in the presence of carbon tetrabromide to be determined. Cross-termination in the aqueous phase was found to be operative in γ -ray initiated systems when the free radical concentration in the aqueous phase was relatively high. In contrast, re-entry of the exited free radicals into the latex particles was found to be important in relaxation studies when the free radical concentration in the aqueous phase was comparatively low. These results show that the exited free radical fate parameter can vary between -1 and +1.

The exit rate coefficient was found from relaxation measurements to increase linearly with increasing concentration of chain-transfer agent; this result is consistent with a diffusion-transfer mechanism for exit. The increase in the exit rate coefficient paralleled the increase in the chain-transfer constant for the additives: $\text{CBr}_4 > \text{CCl}_4 > \text{styrene}$. On the other hand, the efficiency of exit from the latex particles of free radicals formed by chain transfer follows the inverse order: $\text{CBr}_4 < \text{CCl}_4 < \text{styrene}$. This order may well reflect the relative reactivities with monomer of the low-molecular-weight free radicals formed by atom abstraction.

THE RADIOLYSIS TECHNIQUE FOR DETERMINATION OF
SHORT CHAIN BRANCHING IN POLYMERS

by

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Abstract

Several methods are available to characterize the short chain branches in polyolefins. These include ^{13}C NMR, IR and γ -radiolysis [1]. The γ -radiolysis method involves analysis of the volatile radiolysis products from the polymer and probably provides the most sensitive technique that is available.

Experiments on ethylene- α -olefin copolymers have shown that the short side chains attached to the main polymer chain at a tertiary carbon are removed selectively on γ -irradiation. Radiolysis yields after correction for chain-end fragmentation have been compared with ^{13}C NMR determinations of short branch frequencies for the same copolymers to give branch detection efficiencies, which could then be used in determinations of branch frequencies in other polyolefins using the radiolysis yields. The effect of irradiation temperature on the alkane and alkene yields has been examined from 25°C to 175°C (a temperature range including T_m).

The radiolysis technique has also been used to determine the short chain branching in poly(vinyl chloride) (PVC). The PVC is reduced to polyethylene by trialkyl tin hydride.

The alkane radiolysis products from a variety of reduced PVC samples indicated that the main branch type was methyl. There was also evidence for butyl and ethyl branches. However, the method was very sensitive to small amounts of occluded trialkyl tin hydride reductant and residual chlorine. The products also depend on factors such as chain-ends, polymer morphology and irradiation temperature.

References

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THE EFFECTS OF ULTRAVIOLET RADIATION ON THE
CR-39 AND LEXAN PLASTIC NUCLEAR TRACK DETECTORS

by

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Brisbane, Australia.

Abstract

Lexan and CR-39 plastics have been used as nuclear track detectors for measuring charged particles. The CR-39 plastics have been found to be a detector superior to the lexan plastics in terms of sensitivity and optical quality(1). In some cases, the detectors may be exposed to certain environmental conditions which may affect the etching rates and hence the registration properties. A study of these effects could be useful for the interpretation of the results in these experiments.

A study of the effects of ultraviolet radiation on the tracks caused by alpha particles and fission fragments in CR-39 and lexan plastic nuclear track detectors is reported in this paper. While the track diameter in CR-39 plastics could be enhanced by 100%, the increase in the lexan was found to be no more than 40%.

The effects tend to saturate after the detectors were exposed to a carbon arc source for three hours or to sunlight for five days approximately. The increase in the track density caused by ultraviolet exposure was found to be less than 30% in CR-39 plastic and less than 40% in lexan plastics. This latter effect implies that the ultraviolet radiation would not affect the count rates measured with these detectors significantly, although its effects on the track-size are very important.

Based on the large increase in track-size, an application to measure personal doses of ultraviolet radiation using CR-39 track detectors is proposed.

Reference

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REVIEW OF 4TH INTERNATIONAL MEETING ON RADIATION PROCESSING
TO BE HELD IN DUBROVNIC YUGOSLAVIA
4TH - 10TH OCTOBER, 1982

by

J.L.Garnett
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University of New South Wales

Abstract

Review of 4th International Meeting on Radiation
Processing to be held in Dubrovnic, Yugoslavia,
from 4th - 10th October, 1982.

THE REACTION OF HYDROXYL RADICALS WITH AROMATICS

Cheves Walling
University of Utah

Hydroxyl radicals are major reactive intermediates in aqueous radiation chemistry, and also in a variety of metal ion-peroxide reactions. They react rapidly with most aromatic molecules (k 's $> 10^9 \text{ M}^{-1} \text{ sec}^{-1}$).

The initial step is generally addition to yield hydroxycyclohexadienyl radicals, which then react further to yield final products. Major reaction paths are dimerization, oxidation to phenols, and acid catalyzed loss of water to yield radical cations. These, in turn may undergo sidechain fragmentation, and this provides the major path to the oxidation of aromatic sidechains. The result of these complex competing paths is that the final products observed depend strikingly on experimental conditions - pH, the presence of oxidizing and reducing transition metal ions, etc., and this dependence is illustrated for a number of specific cases.

SOME CHARACTERISTIC REACTIONS OF ORGANIC FREE RADICALS

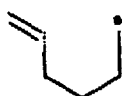
by

A.L.J. Beckwith

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 Canberra, A.C.T. Australia.

Abstract

Certain organic free radicals, e.g. hexenyl (1), hexynyl (2), cyclopropylmethyl (3), 2-but-3-enylvinyl (4), *o*-butenylaryl (5), and related radicals undergo characteristic rearrangements which allow reactions of such species to be distinguished from those of ionic intermediates. The first-order rate constants for many of these rearrangements have been determined by kinetic ESR spectroscopy and other methods. They provide kinetic standards against which the rates of competing second order processes can be measured.



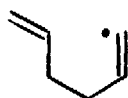
(1)



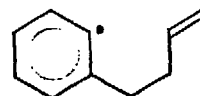
(2)



(3)



(4)



(5)

The application of free-radical rearrangements as kinetic and mechanistic probes will be illustrated by reference to copper-ion catalysed reactions, transformations of diazonium salts, reactions of molecular oxygen, etc.

THE DETERMINATION OF THE MECHANISMS OF GAS PHASE IONIC
REARRANGEMENTS BY THE APPLICATION OF ^2H AND HEAVY ATOM
ISOTOPE EFFECTS. THE McLAFFERTY REARRANGEMENT

by

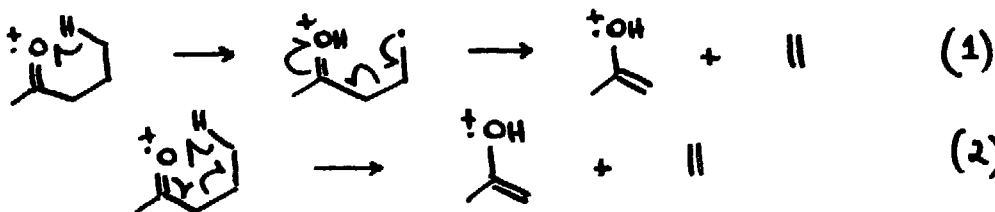
D.J. Underwood, D.J.M. Stone and J.H. Bowie
(Department of Organic Chemistry, University of Adelaide)

D.E. Lewis, A. Fry and L.B. Sims
(Department of Chemistry, University of Arkansas)

K. Donchi and P.J. Derrick
(Department of Chemistry, University of N.S.W.)

ABSTRACT

McLafferty and related rearrangements are the most studied of all gas phase ionic rearrangements.¹ Whether such rearrangements occur by stepwise (1) or concerted (2) mechanisms is a matter of debate.² McLafferty²



considers the reaction to be stepwise and a specific example of a stepwise reaction has been reported.³



We will present evidence that the McLafferty rearrangement of butyrophenones is *concerted* (see 3); this conclusion is based upon studies of substituent effects together with ^2H and ^{13}C kinetic isotope effect investigations. Similarly, the six-membered hydrogen transfer of benzyl ethyl ethers is also *concerted* as evidenced by substituent effects, and ^2H and ^{18}O kinetic isotope effects. This constitutes the first report of the application of heavy atom isotope effects to systems of this type.

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ENERGY TRANSFER PROCESSES IN
IRRADIATED GASES.

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University of Melbourne.

ABSTRACT

The interaction of ionising radiation with gases produces a wide range of excited species from excited ions; electronic excited states of neutral atoms and molecules; thermal ions; and a spectrum of energetic electrons. All these species can be observed in irradiated systems either directly or indirectly by the observation of products of relaxation or collisional processes.

Observation of emission spectra in irradiated gaseous systems can aid identification of species present and the kinetics of formation and decay of these states enables one to identify the precursors (if any) of those states.

This presentation will examine available data from pulse radiolysis studies of pure rare gases and rare gas-additive systems to show how the electronic excited states may be formed.

The principal processes available are

- (1) Direct optical excitation by an electron beam.
- (2) Relaxation from states created directly.
- (3) Ion recombination processes.
- (4) Sub-excitation electrons.
- (5) Collisional energy transfer processes.

AN ESR STUDY OF THE RADIATION DEGRADATION OF
POLY(OLEFIN SULPHONE)S

by

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Polymer and Radiation Group, Department of Chemistry
University of Queensland, Brisbane, Australia 4067

Abstract

This paper reports a comparative study of the radiation degradation of poly(olefin sulfone)s utilizing electron spin resonance (ESR) spectroscopy. The objectives were to (1) measure G(radical) values after irradiation at 77 K, (2) identify the radicals present at 77 K, (3) determine the proportions of the different radicals by simulation, (4) measure changes in the concentrations of radicals as a function of temperature, (5) relate the ESR studies to the mechanism of radiation degradation.

Nine poly(olefin sulfone)s, prepared by free radical copolymerization of the olefin with sulfur dioxide, were irradiated with ^{60}Co γ -rays at 77 K. The ESR spectra were measured at 77 K, 100 K and on progressive warming to 350 K. For each polymer, the ESR spectra showed evidence of one or more alkyl radicals and a singlet, which was assigned to a sulfonyl radical. The total radical concentration was obtained by double integration of the observed spectrum and comparison with pitch and DPPH standards. The temperature dependence of the total radical concentration showed that radical decay commenced at about 200 K and was essentially complete by 350 K.

The proportions of the component radicals were obtained by computer simulation of the ESR spectra of the individual radical and their summation, utilizing the observed hyperfine splittings and deduction of the radical identities from the volatile radiolysis products. It was clearly indicated that transformation of alkyl to sulfonyl radicals occurred concurrently with decay of alkyl radicals during warming.

References

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ELECTRON SPIN RESONANCE AS A PROBE OF POLYMER COMPATIBILITY

by

R.W. Garrett, J.H. O'Donnell and P.J. PomeryPolymer and Radiation Group, Department of Chemistry
University of Queensland, Brisbane, Australia 4067Abstract

An electron spin resonance study has been made on the effect of gamma-irradiation at 77 K on blends of polystyrene (PSTY) and poly(methyl methacrylate) (PMMA) using a range of molecular weights for the polystyrene component. The range of molecular weights was 900-250,000 using mostly monodisperse polymer. The poly(methyl methacrylate) component was a high M.Wt. polydispersed material [$\bar{M}_w = 2 \times 10^6$, $\bar{M}_w/\bar{M}_n = 4$].

The protection effect of styrene units in random copolymers of styrene and methyl methacrylate is now well established in this laboratory. We have previously seen no such effect in high molecular weight blends of PSTY with PMMA due to the incompatibility of the two homopolymers in the mix regardless of the method of preparation of the blend. However, reduction of the molecular weight of the PSTY component leads to improvement in compatibility and this is reflected in the ESR spectra of the gamma irradiated blends. The onset of protection of the styrene unit as the molecular weight is reduced can be used as a novel method of probing for the transition from complete compatibility to incompatibility.

RADIATION SENSITIVITY OF CELLULOSE POLYMERS

by

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Hydroxypropyl cellulose (HPC) has recently become an industrial polymer. It is produced by a base-catalysed reaction of propylene oxide with cellulose. HPC is soluble in water and many organic solvents. It is a thermoplastic which undergoes orientation during processing to give a high degree of longitudinal order, but poor lateral order. Under suitable conditions, particularly in solution, liquid crystalline behaviour is observed.

The interaction of high-energy radiation with cellulose initiates dehydrogenation, main-chain scission and depolymerization reactions of the cellulose molecules. Free radicals are trapped in the crystalline regions and these long-lived radicals cause post-irradiation effects and may be used to initiate grafting of different monomers.

The hydroxypropyl branches of HPC would be expected to provide sites for radical formation which could lead to radiation crosslinking.

The proportion of insoluble polymer (gel fraction) after irradiation to various doses in vacuum at 25°C was measured by multiple and long-term extractions, with water at 20°C (the polymer shows an upper critical solution temperature of 38°C in water). These measurements should enable determination of (i) gel doses, (ii) limiting scission/crosslinking ratio, and (iii) the individual G values for scission and crosslinking. The results of these measurements will be presented. Preliminary studies with radical scavengers have shown little effect on the crosslinking.

Electron spin resonance (ESR) studies of HPC after irradiation at 77 K and subsequent warming, and comparison with cellulose, indicate that radicals are produced on the cellulose rings and in the hydroxypropyl substituents.

THE STRUCTURAL CHEMISTRY OF SYNROC

by

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ABSTRACT

The capacity of Synroc to be an effective matrix for the immobilisation of high level waste (HLW) products has largely been discussed on the premise that it consists entirely of hollandite (~40%), zirconolite (~30%) and perovskite (~25%). This description is now recognised as an oversimplification as other Synroc phases have been identified. Even the three major constituents are not the basic structures originally proposed.

In hollandite [$AB_8X_{16} = BaAl_2Ti_6O_{16}$] the radwaste elements (principally Cs) fill eight coordinate cubic sites constructed from TiO_6/AlO_6 octahedra. Ordering of empty and filled A polyhedra lead to commensurate and incommensurate superstructures which exist as microdomains in a larger matrix. The ability of hollandite to accommodate a large proportion of vacancies suggests that Cs may not enter the structure as easily and effectively as first thought.

Zirconolite [$A_2B_2X_7 = (Ca, Zr)Ti_2O_7$] appears to exist in only one form, but the addition of radwaste elements causes multiple twinning on a unit cell scale (and perhaps some degree of superstructuring).

Only preliminary work has been carried out on perovskite, [$ABX_3 = CaTiO_3$] however initial studies show that it is often twinned and that the addition simulated HLW often leads to the formation of polytypes.

It is quite likely that many of the microstructural modifications outlined above will have a minimal effect upon the performance of Synroc as a wasteform. However, a recognition of Synroc's complexity and a fuller understanding of all its constituents will be essential if the properties of commercially produced Synroc are to be optimised.

ZEOLITE CATALYSIS OF HYDROGEN ISOTOPE
EXCHANGE REACTIONS

by

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The application of shape selective zeolites to the problems of non-synthetic procedures for labelling with tritium and deuterium is an important recent development. In preliminary exchange studies with HY, ZSMS and H- mordenite we have demonstrated that a wide range of aromatic compounds may be labelled with these catalysts where either high specific activity H₂O, benzene, or tritium gas may be used as isotope source. The onset of exchange occurs at temperatures considerably below that at which hydrocarbon conversion processes become apparent. The tritium is incorporated with high efficiency (typically greater than 90%) and the compounds are largely free of labelled byproduct formation. The distribution of the label in the early stages of the exchange cycle is typically that representative of electrophilic substitution reactions. The relative reactivity of various aromatics appears to differ for various zeolites. Current work involves the extension of these catalysts to metal loaded zeolites. Results reveal that the metal loaded zeolites will activate elemental tritium and saturated alkanes with high efficiency thus opening up a new area of zeolite catalysis. It is possible to combine the selectivity typical of transition metal catalysts with the shape selectivity of zeolites.

Tritium n.m.r. is being used to study the details of tritium exchange within various components, as well as the influence of zeolite properties and the nature of the isotope source on the character of the exchange.

INVESTIGATION OF VACUUM ULTRAVIOLET EMISSIONS
FROM ELECTRON IRRADIATED GASES

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ABSTRACT

The study of selected emissions from the radiolysis of rare gas-additive mixtures is a well established method of investigating molecular dynamics, however, there is little experimental data on the fate of species that give rise to emissions in the vacuum ultraviolet. It has been suggested that in the irradiation of rare gases with high energy (~ 0.5 MeV) electrons, high Rydberg levels are the most probable states initially produced. It is of some interest to investigate the possible involvement of these levels in energy transfers to additives in the rare gas and also their relationship to the occurrence of rare gas metastables. These metastables are thought to be produced by the decay of more highly excited states and not by direct excitation due to the electrons.

An experimental technique is being developed to investigate these primary energy transfer processes. Rare gas-additive mixtures are pushed with 0.5 MeV electrons from a Febetron 706. Light, of wavelength longer than 105 nm (the cut off of the lithium fluoride optics), emitted perpendicular to the electron beam is collected, and analysed on a McPherson 0.3m Monochrometer. The signal from the Schlumberger 541F-08.18 photomultiplier tube is recorded on a high speed CRO and is subsequently digitised and stored on floppy disk for subsequent analysis.

PULSE RADIOLYSIS STUDY OF THE REACTION $\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$

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ABSTRACT

The reaction of OH radicals with CO is of considerable importance in both atmospheric and combustion chemistry. However, this reaction has not been studied over a wide temperature range by a single technique and this has led to uncertainties.

Pulse radiolysis techniques offer a convenient method of generating and assaying OH radicals over a wide temperature range. Electron pulse radiolysis of argon/water vapour mixtures using $3\mu\text{sec}$, 19MeV , pulses from a LINAC was used to generate OH radicals in a flow system over the temperature range $300\text{K} - 1250\text{K}$. The OH radicals were detected using an OH resonance lamp, a narrow band pass filter (308nm) and a P.M. tube. The resultant signal was digitised using a Biomation 8100 waveform digitiser interfaced with a Xerox Sigma 5 computer. Signal averaging for up to 200 pulses was undertaken to improve the signal to noise ratio.

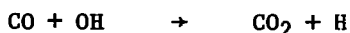
In $\text{H}_2\text{O}/\text{argon}$ mixtures, the OH radical was found to decay with mixed first/second order kinetics over many milliseconds. The predominant reaction is $\text{OH} + \text{OH} \rightarrow \text{Products}$. When CO is introduced into the system a much faster first order decay was observed which was CO pressure dependent. In addition, the OH absorption decayed to a non-zero plateau region: this plateau increased with increasing temperature.

Over the temperature range $300\text{K} \rightarrow 700\text{K}$ the rate of OH decay decreased with increasing temperature implying a negative activation energy of $\sim 2\text{K.J.mol}^{-1}$. Above 700K the rate of OH decay was found to increase markedly with increasing temperature.

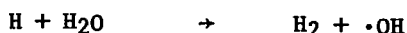
A mechanism consistent with the results below 700K is



whilst above 700K the mechanism is believed to be



In the plateau region for OH absorption is believed to be due to the contribution from a reaction -



reaching a steady state with the $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$ reaction.

MECHANISMS FOR LUMINESCENCE IN ELECTRON IRRADIATED
ALKALINE EARTH OXIDES.

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and

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ABSTRACT

The emission wavelengths from irradiation at 0.5MeV (see poster of Grant et al.) are characteristic of the luminescence emission of the F^+ center (375nm) and F_A^+ center (410nm) (Henderson 1980). The F^+ center is a single electron trapped in an oxygen vacancy and the F_A^+ center is a single electron trapped in an oxygen vacancy with one nearest neighbour calcium cation replaced by magnesium. Since the incident electron energy required to displace an oxygen anion is around 330 KeV (Chen et al, 1970), we may conclude that the emissions arise from centers created by irradiation.

The kinetics of luminescence decay over the time range 10^{-8} s to 10^{-1} s clearly show that at least 3 processes are involved. These processes may be i) spontaneous radiative decay of the excited state of a centre formed directly by electron bombardment.

- ii) recombination of geminate electron - anion vacancy pairs,
- iii) recombination of randomly distributed electrons with anion vacancies and
- iv) thermally induced recombination of electrons from shallow traps.

At high energies, more species are created and these decay at different rates. An energy threshold in the range 0.5 to 1.0 MeV is indicated, which would be consistent with the production of cation vacancies. The mechanisms of luminescence in these circumstances are complex and probably involve interactions between the various species created.

PHOTOCHEMISTRY AND RADIATION CHEMISTRY OF VASKA'S COMPOUND

by

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Abstract

Vaska's compound, $\text{Ir(I)Cl(CO)(PPh}_3)_2$, and other square planar iridium(I) compounds photochemically catalyse the hydrogenation of alkenes in reactions with high quantum yields. The reactive intermediates which act as chain carriers have been investigated by flash photolysis and pulse radiolysis in toluene and dichloromethane.

Photolysis of the octahedral iridium(III) adduct compounds, $\text{cis-Ir(III)Cl(CO)(PPh}_3)_2\text{(X}_2\text{)}$, where $\text{X} = \text{H}_2$ or O_2 , results in the loss of H_2 or O_2 via an intermediate which is apparently the catalytically active species. The intermediate can react with alkenes, O_2 , CO and phosphenes. Competition studies have established the relative rates and equilibrium constants for reactions of the intermediate. The square-planar Ir(I) compounds are not themselves effective hydrogenation catalysts and the active species may be an Ir(II) compound or a four or five coordinate compound which has a favourable configuration for binding the alkene and so catalysing the hydrogenation.

The analogous Ir(I)(dppe)_2 compound (dppe = bis-diphenylphosphinoethane), also forms Ir(III) adducts with H_2 and O_2 , and photolysis of these produces an intermediate with a longer lifetime than that from Vaska's compound.

Pulse radiolysis showed no evidence of possible iridium(II) species and the catalytically active species produced by photolysis of the iridium(III) compounds is probably a four coordinate species with a tetragonally distorted configuration in which relaxation to the stable planar form is so slow that alkenes and other substrates can bind to it in competition with the relaxation.

A REFERENCE FILE SEARCH FOR RADIATION CHEMISTRY
LITERATURE USING A MINICOMPUTER

by

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Abstract

References in radiation chemistry obtained from the Radiation Chemistry Data Centre (Notre Dame) files are the basis of a personal literature filing system based on a minicomputer. Titles of papers and added enriching key-words may be searched for a match with terms in a simple logic search which allows up to five terms to be logically "AND" and four to be logically "NOT".

The system operates in real time on a DEC PDP 11/10 or 11/03 (or equivalent) computer. The output is displayed on the terminal during the search and may be output to a printer at the end of the search. It is adaptable for operation via a terminal to a larger DEC machine. The search program is written for TECO, the DEC editing and text manipulation language.

Documentation is provided and it is expected that a demonstration will be available using the AINSE radiation chemistry PDP 11/03. The files which will be available are a sub-set of the RCDC files which reflect the author's interests. Copies of the software are available from the author on floppy disk.

Reactive and Non Reactive Quenching of $I_2(D^1\Sigma_U^+)$:
The Reaction of $I_2(D^1\Sigma_U^+)$ and $I_2(^3\Pi_{2g})$ with Ethane

by

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Abstract

It has been shown that $I_2(D^1\Sigma_U^+)$ produced by excitation of I_2 at 193 nm (ArF laser) and 185 nm (Hg radiation) reacts with methane and a wide range of halomethanes^{1,2,3}. $I_2(D^1\Sigma_U^+)$ may also be physically quenched through several intermediate states to the lowest ion pair state, $^3\Pi_{2g}$, which has recently been shown to react with CH_4 and CF_3Cl .³

In the present work the reaction of $I_2(D^1\Sigma_U^+)$ and $I_2(^3\Pi_{2g})$ with ethane has been studied by two techniques:-

- (i) I_2/C_2H_6 and $I_2/C_2H_6/SF_6$ mixtures were irradiated by 185 nm radiation (low pressure mercury lamp) and the course of the reaction followed spectrophotometrically at 190-202 nm.
- (ii) I_2/C_2H_6 mixtures were irradiated by an ArF laser (195 nm, 14 n sec pulse) and the iodine fluorescence following a single pulse, recorded in the wavelength range 200-500 nm using a monochromator, optical multichannel analysis (O.M.A.) combination.

In I_2/C_2H_6 mixtures effective quenching of $I_2(D^1\Sigma_U^+)$ occurs ($k = 1.5 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$) with little apparent formation of $I_2(^3\Pi_{2g})$.

The major products from the reaction are C_2H_5I and CH_3I . At low pressures, $<10 \text{ Nm}^{-2}$ of C_2H_6 , extensive fragmentation of C_2H_5I occurs suggesting the formation of excited C_2H_5I . With SF_6 added to quench $I_2(D^1\Sigma_U^+)$ to $I_2(^3\Pi_{2g})$, C_2H_5I and CH_3I are still the major products but there is no fall off in C_2H_5I production at low SF_6 pressures.

References

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- [2] B.V. O'Grady, L. Lain and R.J. Donovan, Chem. Phys. Letters (in press).
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RED EMISSION FROM ICE EXCITED BY PULSED ELECTRONS

by

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Emission in the 600 - 800 nm region was observed from high purity, crystalline H₂O ice irradiated at 88 K with 3 ns pulses of 0.53 MeV electrons produced by a Febetron 706 pulsed electron source. This spectral region was examined in order to search for emission from the well known e_{vis} trap in ice.

The e_{vis} trap in ice absorbs at about 540 nm with a full-width-at-half-maximum of ca. 170 nm, but no emission attributable to electrons in this trap was observed during the present measurements. The long wavelength tail of an emission previously observed by Quickenden, Trotman and Sangster (1) around 550 nm, was however observed. Superimposed on this broad emission at 656.5 nm, was a narrow (< 1 nm) peak, which was attributed to the Balmer α emission of atomic hydrogen. This peak exhibited a decrease in intensity and an apparent broadening as the degree of ice crystallinity was increased.

A weaker and less well resolved emission was found in the vicinity of the $3p^3P \rightarrow 3s^3S^0$ transition of atomic oxygen.

References

1. T.I. Quickenden, S.M. Trotman and D.F. Sangster, J. Chem. Phys. (in press - scheduled for the September 1982 issue).

TIME RESOLVED LUMINESCENCE IN THE 360 - 600 nm REGION FROM WATER
VAPOR IRRADIATED WITH PULSED ELECTRONS

by

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^{*}Department of Chemistry, University of Canterbury, Christchurch,
New Zealand (currently on sabbatical leave at [†] and ^{††}).

Abstract

Quickenden, Irvin and Sangster (1) have previously examined the luminescence emitted in the 210 to 360 nm region from electron pulse irradiated water vapor and Quickenden, Irvin, Trotman and Sangster (2) have carried out a similar study on the 600 to 800 nm region. The purpose of this present work was investigate the emissions produced in the 360 to 600 nm region which has not previously been studied in this manner.

The water vapor was excited by 3 ns pulses of 0.53 MeV electrons from a Febetron 706 pulsed electron source. The β , γ and δ Balmer emission lines from atomic hydrogen were identified at 486.1 nm, 434.0 nm and 410.2 nm, respectively, and a weaker and as yet unidentified band was observed around 465 nm .

Line intensities, lifetimes and the quenching behaviour of water vapor on all the emissions, have been determined.

References

1. T.I. Quickenden, J.A. Irvin and D.F. Sangster, J. Chem. Phys., 69, 4395 (1978).
2. T.I. Quickenden, S.M. Trotman, J.A. Irvin and D.F. Sangster, J. Chem. Phys., 71, 497 (1979).

THE RADIATION DEGRADATION OF N-ACETYL AMINO ACIDS

by

D.J.T. Hill, S.Y. Ho, J.H. O'Donnell, P.W. O'Sullivan and P.J. PomeryPolymer and Radiation Group, Department of Chemistry
University of Queensland, Brisbane, Australia 4067Abstract

Numerous workers have adopted N-acetyl amino acids as model compounds to aid in the study of the effects of ionizing radiation on polypeptides and proteins because they offer the following advantages: (i) they contain a single amino acid residue and a single peptide bond, (ii) they have greater solubility in simple solvents than do the corresponding amino acid homopolymers.

Garison *et al.* [1] investigated the yields of small molecule products for γ -radiolysis of N-acetylalanine at 290 K and reported that the major products were those formed by N-C α bond cleavage. Carbon dioxide was not observed amongst the products, though this is the major product of radiolysis of aliphatic carboxylic acids. ESR studies by several different workers of X- and γ -radiolysis of a number of N-acetyl amino acids in aqueous glasses, in the polycrystalline state and as single crystals have been reported. These studies show the radical intermediates formed depend on the matrix, the nature of the amino acid side chain and the temperature. It has been suggested (e.g. Sevilla *et al.* [2]) that the observed radicals are consistent with a mechanism involving decarboxylation via cation precursors and deamination via anion precursors, with both paths being of approximately equal importance. The dominant stable radicals at room temperature for the N-acetyl amino acids with aliphatic side chains are the α -carbon radicals. No measurements of radical yields have been reported.

We have recently re-examined the small molecule products formed on γ -radiolysis of the N-acetyl derivatives of glycine, alanine, valine, tyrosine and phenylalanine using the technique of gas chromatography. We have shown carbon dioxide to be the major product of radiolysis for all these compounds. We have also examined the radical intermediates and measured the radical yields and have shown that there is an almost linear correlation between the carbon dioxide and radical yields. In this paper we will review this work and point out the mechanistic implications of our observations.

References

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[2] M.D. Sevilla, J.B. D'Arcy, K.M. Morehouse, *J. Phys. Chem.*, 83, 2893 (1979).

RADIOLYSIS OF AROMATIC ACIDS : THE EFFECT OF A HETEROATOM

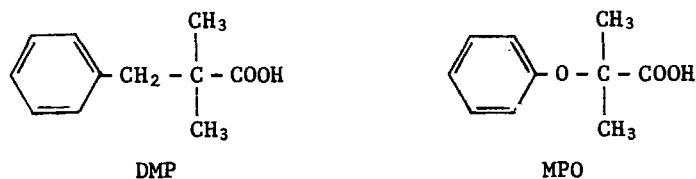
by

D.J.T. Hill, D.A. Lewis, J.H. O'Donnell and P.J. PomeryPolymer and Radiation Group, Department of Chemistry
University of Queensland, Brisbane, Australia 4067Abstract

Although the γ -radiolysis of aliphatic carboxylic acids has been studied extensively, benzoic acid appears to be the only carboxylic acid containing an aromatic group in the molecule for which the radiolysis has been reported.

We are interested in the radiolysis of aromatic carboxylic acids as model compounds for aromatic polymers and particularly in the relationship between molecular structure and radiation sensitivity.

The aromatic acids, 2,2-dimethyl-3-phenylpropanoic acid (DMP) and 2-methyl-2-phenoxypropanoic acid (MPO) are especially interesting because (i) they offer the opportunity to study the difference between $-\text{CH}_2-$ and $-\text{O}-$ as the linking unit between the aromatic ring and the carboxylic acid group, and (ii) they are model compounds for the well-known pesticides 2,4-dichlorophenoxyacetic acid (2,4,D) and 2,4,5-trichlorophenoxyacetic acid (2,5,T).



Electron spin resonance (ESR) spectra after irradiation at 77 K showed the presence of a radical anion, formed by electron addition to the carboxylic acid group, in both compounds. Radical anions were also formed by electron addition to the phenyl rings. In aliphatic carboxylic acids radical anions are formed solely on the carboxylic acid groups. Cyclohexadienyl radicals were observed in DMP, but not in MPO. The radical yields are shown in Table 1. A mechanism for the radiation degradation will be presented.

TABLE 1: Radical yields at 77 K

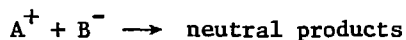
	<u>DMP</u>	<u>MPO</u>
Anions	0.12	0.17
Cyclohexadienyl	0.50	-
Other	0.15	0.18
TOTAL	0.77	0.35

THE TRANSPORT AND RECOMBINATION
OF CLUSTERED IONS

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Studies of ion recombination and ion transport in gases will be reviewed with particular reference to the effects of increasing pressure of neutral molecules present. This acts first to increase the clustering of the ion cores and secondly to enhance the frequency of collisions of the ions with neutrals. Both of these factors can cause profound changes in the rate of transport of ions and the value of α , which is the overall second order rate coefficient for the recombination (or ion neutralization) reaction:



Since the reviews of Mahan, Bates and Flanney progress has been made in number of areas. Firstly, interesting developments have occurred in our understanding of the effects of molecular structure and clustering of ions in two body ion-ion and ion-electron neutralization reactions. Also progress has been made in the study of three body mechanisms, particularly for ion-electron reactions, the rates of which have now been investigated at much higher pressures than previously. Thirdly it will be shown that the pressure dependence of α for ion-ion recombination can be treated rather well by the equations for diffusion-controlled reactions in fluids. Traditionally these have been applied primarily to liquid systems, but it has been found that much information can be gained concerning the accuracy of these theories from their application to gases. New theoretical approaches for incorporating two and three body stabilization coefficients into the overall equation for α have been developed. These provide further insight into the mechanism of diffusion controlled processes, and they will briefly be reviewed.

EXCITATION PROCESSES IN RARE GAS-ADDITIVE MIXTURES

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and

M.C. Sauer Jr.

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Chicago, U.S.A.ABSTRACT

The technique of pulse radiolysis has been used to study the kinetics of formation and decay of excited states in electron-irradiated rare gas/trace additive mixtures.

In mixtures of the aromatic hydrocarbons anthracene, tetracene and terphenyl, with rare gases (Ar, Ne, Kr and Xe) the formation of the S_1 levels can be observed at additive pressures < 1 torr. The rate of formation was found to be dependent on the additive pressure over the pressure range used, and the kinetics could be described by a sequential two-step process. The second-order rate constants obtained were of the order of $1 \times 10^{13} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ for all systems used. It is proposed that the excitation of the hydrocarbons is due to the sub-excitation electrons, i.e., electrons of energy between the lowest rare gas energy level and the energy levels of the additive, since any collisional relaxation process or any atomic or molecular two-body energy transfer process would occur at a rate at least one order of magnitude smaller than that observed.

These results are in agreement with results obtained for mixtures of nitrogen with the rare gases He and Ne. In this case nitrogen pressures less than 0.1 torr were used. Again a first order dependence on the additive pressure was observed, and analysis of the data leads to a second order rate constant of the order of $5 \times 10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, again, too fast to be due to energy transfer on collisional processes. Thus, the sub-excitation electrons are again thought to be responsible for the excitation of the additive.

FORMATION OF RARE-GAS HALOGEN ATOM EXCIPLEXES
IN ELECTRON BEAM IRRADIATED GASES.

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and

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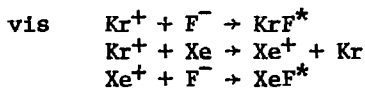
ABSTRACT

The formation of krypton-halide exciplexes in electron beam irradiated mixtures of krypton-halogen source molecules was observed to be formed by two distinct and kinetically resolvable time dependent processes. These processes were investigated using a 10 nsec. pulse of 0.5 MeV electrons, from a Febetron 706, as the excitation source.

The rate of one process was found to be dose/pulse independent, but dependent on the partial pressure of the halogen source. This process was attributed to reactions between electronic excited states of krypton and the halogen source.

The second, slower, process was found to be highly dependent on the dose/pulse and was attributed to ion-recombination processes. The negative ion dependence of this process was investigated by using a variety of halogen source molecules, CF_3Cl , CF_3Br , SF_6 and CF_4 in a krypton background. The Halide negative ions were formed by thermal electron capture of the halogen source molecules.

The positive ion dependence was studied by the introduction of a scavenger, Xe, in the pulsed gas mixture, which set up competitive charge transfer in ion recombination reactions,



Upon increasing the partial pressure of xenon a one-to-one correspondence between the increase in XeF^* yield and the decrease in KrF^* yield was observed. At a constant pressure or xenon, dose/pulse variations showed relative changes in yields of XeF^* and KrF^* ; again consistent with the scheme proposed.

Variations in the total sample pressure showed that the kinetics and yields across the emission spectrum of both XeF^* and KrF^* varied. This is consistent with the ion recombination processes forming exciplexes in high vibrational levels in the upper electronic state.

ABSOLUTE PHOTON YIELDS IN ELECTRON IRRADIATED GASESJ.G. YOUNGAustralian Radiation Laboratory,
Yallambie, Victoria 3085

R. Cooper

Department of Physical Chemistry
University of MelbourneABSTRACT

A technique has been devised for the determination of the absolute photon yields in electron irradiated gases. Appropriate gas samples were irradiated with 6 nsec pulses of 0.5 MeV electrons from a Febetron 706 pulsed electron source.

Visible and U-V emissions were monitored by a calibrated optical system composed of quartz lenses, a 'Spex' Minimate monochromator and appropriate photomultiplier tubes. P.M. tubes were calibrated using microcalorimetry. Emission signals were displayed on a fast storage oscilloscope (Tektronix 7633) digitised by a TV camera "Telescan" system interfaced with an L.S.I. 11 computer.

The systems studied were: pure nitrogen ($N_2^* C^3\Pi_U$ and $N_2^+ B^2\Sigma_U^+$); pure nitrogen (1 torr) with excess helium and neon; the 2p levels of various rare gases and KrF^* and XeF^* in various rare gas halogen source mixtures. In all these systems, detailed kinetic analysis of the processes responsible for the formation of excited states is available. The yields may thus be apportioned between direct energy transfer and ion recombination processes.

A specially designed irradiation cell enabled both emission signals as well as the necessary ozone dosimetry to be performed in the same irradiated volume.

PHOTOCHEMICAL PROCESSES IN IRRADIATED MICELLAR SYSTEMS.

by

K. Thomas

Notre Dame University
Indiana, U.S.A.

Abstract

Abstract to be circulated at the Conference

GLASS AS A HIGH LEVEL WASTE MATRIX:
A REVIEW OF THE VARIABLES

by

R.A. Lewis, S. Myhra, R.L. Segall, R.St.C. Smart, and P.S. Turner

School of Science
Griffith University
Nathan, Qld Australia

Abstract

The paper discusses aspects of glass science which bear on the question of high level radioactive waste disposal. Appropriate illustrations from our work and that of other laboratories are cited.

A review is made of specific factors which determine the stability of a glass waste form, dividing these into those which may be disregarded and those which are significant. In the first category are volatility losses, which remain low except at very high temperatures; pressure, which has little direct influence up to at least 160 MPa; compositional modifications, which are well understood and may be tailored to provide a low-melting temperature, high durability matrix capable of accepting a diversity of types and amounts of waste elements; geological environments, which tend to increase durability compared with attack by pure water; radiation, including radiation damage to the solid, thermal deposition in the solid and radiolysis in the solvent, which have been examined by ion beam and α -emitter implantation simulations and found to have little effect on glass durability. Factors which significantly affect the stability of the waste glass are mechanical stress, producing disintegration; self-heating, the effect of which is exacerbated by the low thermal conductivity of glass and which greatly accelerates glass breakdown in solution above 150°C; scale-up, in that cracking due to thermal shock, macroscopic inhomogeneity and localised devitrification occur in commercial scale production.

The direction of future research is considered. The effects of phase separation, transmutations, density changes and transition and rare earth elements in the glass composition, require study. Most important, a cohesive and predictive theory needs to be formulated which identifies the controlling mechanisms in the attack of glass by a solvent and enables confident extrapolation from the laboratory to the repository.

PULSE RADIOLYTIC STUDIES OF THE 200 - 600 nm
EMISSIONS FROM LOW TEMPERATURE H₂O ICE

by

T.I. Quickenden*, D.F. Sangster†, and S.M. Trotman*

*Department of Physical and Inorganic Chemistry, University of W.A.

†Lucas Heights Research Laboratories, C.S.I.R.O. Division of Chemical Physics.

Abstract

The Febetron 706 pulsed electron source has been used as a source of 0.53 MeV, 3 ns electron pulses in order to excite luminescence from high purity, crystalline H₂O ice held at a temperature of 88 K. The spectral distribution of the luminescence and its radiolytic photon yields (G_p) and decay kinetics, have been determined.

The observed ice luminescence can be analysed into three distinct regions of emission, *viz.* the 280-300 nm region ($G_p = 1 \times 10^{-7}$ photons/100 eV); the 320-550 nm region ($G_p = 2 \times 10^{-4}$ photons/100 eV); and the 500-600 nm region ($G_p = 1 \times 10^{-5}$ photons/100 eV). Experiments in which ice samples have been doped with common impurities show that the luminescence does not arise from impurity centres.

The 320-550 nm emission shows a marked dependence on accumulated dose and largely obeys second order kinetics. The results of the study of this luminescence are consistent with emission from an OH radical produced via a bimolecular recombination of H₃O⁺ or H₂O⁺ with trapped electrons produced during the irradiation. The emission probably arises from the OH transition $A^2\Sigma^+ \rightarrow X^2\Pi$, red shifted by the ice lattice from its gas phase wavelength of 306 nm. This assignment casts considerable doubt upon the suggestion put forward by earlier workers (1,2) that the $A^2\Sigma^+$ state of OH is responsible for the emission at 280 nm.

The results of the study of the 500-600 nm emission are consistent with the recombination by a tunnelling mechanism of geminate electron - positive ion pairs, within a radiation produced spur.

References

1. A. Bernas and T.B. Truong, Chem. Phys. Lett., 29, 585 (1974).
2. P.B. Merkel and W.H. Hamill, J. Chem. Phys., 54, 1695 (1971).

THE VISIBLE ABSORPTION SPECTRUM OF LIQUID WATER

by

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

Department of Physical and Inorganic Chemistry, University of W.A.

Abstract

Ultraviolet and visible absorptivities of liquid water have been measured by a number of workers, using a variety of techniques, but the results vary from worker to worker by up to two orders of magnitude. Quickenden and Irvin (1) have rationalised the 200-320 nm region by obtaining reliable values which are much lower than any previously reported values in this region and which give considerably better agreement with theory and also align well with the edge of vacuum U.V. absorption data.

The present study extends the work of Quickenden and Irvin from 320 nm to 800 nm via the development of a variable pathlength absorption cell which enables measurements to be carried out on columns of water of up to 1.2 m in length. Particular care was taken to remove organic impurities as these are probably responsible for a good deal of the variability in the absorptivities reported in the literature. To this end, the water was subjected to a four stage distillation process, one of the stages involving oxidative distillation from alkaline permanganate and the last stage involving distillation via a furnace at 870 K, in the presence of oxygen in silica apparatus. Care was also taken during the design of the optical arrangement, to ensure that traces of light scattered from various parts of the apparatus did not interfere with the absorption measurements.

The absorptivities obtained in this manner were generally lower than previously reported values for this region and the short wavelength end of the data coincided well with the long wavelength edge of the Quickenden - Irvin spectrum. Overtones of the OH stretch of water could be observed at the long wavelength edge of the spectrum.

References

1. T.I. Quickenden and J.A. Irvin, *J. Chem. Phys.*, **72**, 4416 (1980).

ESR AND OPTICAL STUDIES OF RARE EARTH DOPED CaSO_4

by

R.L. Calvert and R.J. DanbyAustralian Radiation Laboratory
Lower Plenty Road
Yallambie, Vic. 3085

Abstract

CaSO_4 doped with the rare earth dysprosium (Dy) is now used in Australia as a thermoluminescent dosimeter. In order to study the thermoluminescence processes that occur in these phosphors, single crystals and powders of undoped and rare earth doped (Dy, Eu, Gd) CaSO_4 have been grown at the Australian Radiation Laboratory. The results of electron spin resonance, photoluminescence and thermoluminescent glow peak measurements following room temperature X irradiation of these samples appear to support the following model. Incident X rays excite an electron from the lattice and this electron is trapped by a RE^{3+} ion reducing it to RE^{2+} and leaving a hole trapped at a lattice site. When the sample is heated the holes become mobile and recombine with an electron from the RE^{2+} ion converting it to RE^{3+} in an excited state. This then decays to the ground state with the emission of light characteristic of RE^{3+} . The temperature at which the glow peaks appear is thus determined by the CaSO_4 lattice whereas the emission spectra of each glow peak is dependant on the introduced rare earth. A variation from this model is observed in $\text{CaSO}_4:\text{Eu}$ as a strong Eu^{2+} emission is observed only at 100C.

LUMINESCENCE STUDIES OF ELECTRON IRRADIATED
CALCIUM OXIDE.

J.L. Grant and R. Cooper

Department of Physical Chemistry
University of Melbourne.

and

J. F. Boas

Australian Radiation Laboratories
YALLAMBIE, Victoria 3085.

ABSTRACT

High purity crystals of CaO and CaO doped with a nominal 1% MgO show luminescence emission bands at 375 and 410nm after irradiation at room temperature with 6ns duration pulses of 500keV electrons from a Febetron 706 source. No other emissions are observed over the range 200 to 800nm as a consequence of the electron irradiation. The emission intensity decreases as the electron energy is reduced and is not observed below 300keV. These emissions are consistent with those expected from F^+ and F_A^+ centres.

The emission is fully developed immediately after the electron pulse, and a log-log plot of intensity versus time over the range 10^{-8} s to 10^1 s shows several interesting features. Approximately unimolecular kinetics are followed in 3 distinct time zones: 0-3 μ s; 30 μ s-200 μ s; after 10ms. Higher order kinetics are followed over the time intervals 3 μ s-30 μ s and 200 μ s-10ms.

Using a variable energy (up to 3MeV) electron Van de Graaf delivering 5 nsec pulses, new emissions are observed over the wavelength range 400 + 650nm. Emission bands at 530nm and 600nm are observed as well as the bands at 384 and 410nm. The relative intensity and lifetime of these emissions vary depending on the degree of Mg doping and the presence of pre-formed F centres.

The emissions at 530 and 600nm show an electron energy dependence indicating a threshold for formation in the energy range 0.5 + 1MeV. The kinetics of decay of these species is complex and as yet no positive identification can be made either of the nature of the emitting species nor its mechanism of formation and decay.

CURRENT FRONTIERS OF RADIATION CHEMISTRY

R. CooperDepartment of Physical Chemistry
University of MelbourneABSTRACT

In the twenty years since the first AINSE conference on Radiation Chemistry (Sydney, August 1962) a wide and expanding range of topics have been presented at the conferences. The earliest studies reported were results from continuous irradiation of aqueous, organic and gas phase systems. The accent was on stable products detected by careful analytical methods. Scavenging studies gave hints as to possible precursors of radiolytic products. Later conferences added polymer studies, mass spectrometry and photochemical systems to amplify the range of excited species initiation techniques available, with advantage, to radiation chemistry.

The advent, in 1968, of pulse radiolysis techniques introduced a dramatic tool for the elucidation of radiolytic mechanisms. This technique, coupled with those of flash photolysis and laser photolysis have added much to AINSE workers knowledge of reactive intermediates.

In the last few years the limitations of simple optical absorption detection methods in pulsed experiments has become obvious and new techniques giving structural information about transient species have been evolved. The results of these studies using EPR and NMR techniques have had important consequences in areas of fundamental processes in liquid phase radiolysis. The development of microwave and D.C. conductivity techniques has also enabled the observation of early species in the radiolysis of liquids.

The availability of high powered UV pulsed lasers has enabled photo-ionisation studies to be made in systems identical to one of radiolytic interest. Results indicate that very similar processes are operative - e.g. geminate recombination - and the overlap between these studies is very marked.

GENERAL INFORMATIONCONFERENCE VENUE

The conference will be held in the AINSE Theatre, Lucas Heights (Institute Building) - see map page 62
Wednesday 10th, Thursday 11th and Friday 12th November, 1982

SYMPOSIUM - THURSDAY 11TH NOVEMBER, 1982

1.30 p.m. - 4.40 p.m.

'Radicals, Radical Ions, and Excited Species'

PAPERS

Timing Green light shows for presentation of paper -
Warning light shows 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 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 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 AAEC Gate) - see map page 62 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 10.30 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.

Participants should make arrangements to pay cash for breakfast charges at Lucas Heights or the Sapphire Motel.

CONFERENCE LUNCHEON - WEDNESDAY 10TH NOVEMBER, 1982

A luncheon for all participants will be held in the Stevens Hall Dining-room and Ante-room during the scheduled lunch period (ref. programme). The cost has been included with the conference dinner payment.

THURSDAY 11TH & FRIDAY 12TH NOVEMBER, 1982

Lunches may be purchased from the AAEC Canteen.

EVENING MEALS

TUESDAY 9TH & WEDNESDAY 10TH NOVEMBER, 1982

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

CONFERENCE DINNER - THURSDAY 11TH NOVEMBER, 1982

5.45 p.m. Pre-dinner drinks - Stevens Hall Lounge (included with Poster Session)
 6.15 p.m. Buffet Dinner - Bamboo Room - AAEC Canteen
 After Dinner - Stevens Hall Lounge

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

TRANSPORT

TRANSPORT FROM SYDNEY AIRPORT - WEDNESDAY 10TH NOVEMBER, 1982

An AAEC bus ('Z' number plate) will leave TAA Terminal (Sydney Airport) for Lucas Heights, at 9.25 a.m. If any difficulty is experienced in locating the bus, the TAA Information Desk will advise details of its precise location.

REQUEST TO PARTICIPANTS ARRIVING ON AAEC BUS FROM AIRPORT

Participants are asked to go directly to the AINSE Theatre and not to their rooms at Stevens Hall, as time will be limited. 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.

TRANSPORTTRANSPORT FROM SYDNEY AIRPORT (excluding special arrangements Wednesday 10th)

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 "	1.30 "
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

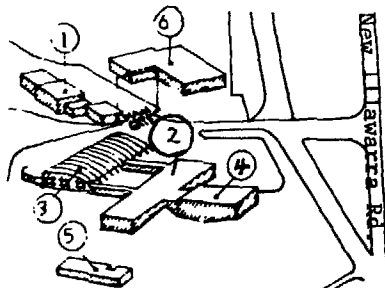
- - -

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 8.20 a.m. (approx). It would be appreciated if participants with their own transport could drive to Lucas Hts and assist by transporting 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 12TH NOVEMBER, 1982

Transport will be arranged to take participants to Sydney airport, after the conference concludes. *Please place your name on the list provided at the conference, on the noticeboard outside the theatre, if you require this service.*

Participants leaving Stevens Hall - Friday 12th November, 1982

Participants are requested to vacate their rooms by 10.30 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
(AINSE)

543 - 3436
(AINSE)

543 - 0111
(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 543-0111

LIST OF PARTICIPANTS

LIST OF PARTICIPANTS

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A.C.I. PLASTICS

Mr. K.M. Dunn

ANSELL INTERNATIONAL

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