

DEPARTMENT OF CHEMISTRY

ANNUAL REPORT - 1963

STAFF

Professor and Head of Department	A.N. Hambly, M.Sc., Dip. Ed., F.R.A.C.I.
Associate Professor (Organic Chemistry)	W.D. Crow, M.Sc., Ph.D. (Promoted July 1st, 1963) (On leave from 31st October, 1963 - December, 1964)
Senior Lecturers	J.H. Bradbury, M.Sc., Ph.D., F.R.A.C.I. R.F.C. Brown, M.Sc., Ph.D. N.S. Gill, M.Sc., Ph.D.
Lecturers	L.L. Hawes, Jnr., B.Sc., Ph.D. R.C. Irwin, M.Sc., Ph.D. (from February, 1963) R.N. Warrenner, M.Sc., Ph.D.
Senior Demonstrators	G.F. Kolar, B.Sc. M. Sterns, M.Sc. M.L. Tonnet, M.Sc.
Research Assistants	K.H.J. Bryant, B.Sc. (from 11/10/63) G.V. Chapman, A.G.I.T. J.J. Foster, B.Sc. (from 28/5/63) N.L.R. King, B.Sc. (from 9/12/63) B.V. O'Grady, M.Sc. (resigned 9/8/63)
Head Technician	A.T. Miles, A.W.A.S.M. (from 1/12/62)

MAJOR DEVELOPMENTS DURING YEAR

The transfer of the staff from the cramped conditions in the Ellery Circuit building to the new building in University Avenue took place at the end of 1962. The building as a whole was not handed over until March 1st, 1963 but this was in time for the commencement of the undergraduate classes. The building was officially opened by His Excellency the Governor General, the Right Honorable Viscount De L'Isle, on June 7th. This ceremony was followed by an "open night" during which many hundreds of Canberra residents inspected the new building and its facilities. In August the building was used for the Fourth Australian Spectroscopy Conference in which some 300 spectroscopists participated.

In 1963 the first group of students took the fourth (honours) year. The first candidates from the department also completed post-graduate courses. B.V. O'Grady was admitted to the degree of M.Sc. for a thesis entitled "Hydrogen Bonding in Primary Aromatic Amines". L.L. Hawes and J.H. Hodgkin submitted theses on the subjects "Lattices of some Solid Solutions and Compounds of Sulphur", and "The Alkaloids of Halfordia Scleroxyla. F. Muell. Isolation and Studies", respectively and were admitted to the degree of Doctor of Philosophy.

TEACHING PROGRAM

The increase of forty-three percent in the total enrolments was easily handled in the larger laboratories and lecture rooms. Lecture demonstrations were used much more extensively and effectively with first-year classes. A modification in the order of presentation of subjects in the first-year lecture course, to correspond more closely with the laboratory work, gave an improvement in the latter without apparent loss to the former. We were indebted to Dr. S.R. Taylor of the Department of Geophysics (I.A.S.) and Dr. R. Mills of the Department of Particle Physics (I.A.S.) for lecture courses given to senior students. A program of seminars was held fortnightly in the Staff Common Room or the smaller lecture theatre. We are grateful to the following visitors who led one or more seminars:

Professor B. Dempsey (Royal Military College)
 Dr. D. St.C. Black (Cambridge)
 Professor L. Jackman (Melbourne)
 Professor G.W. Stacy (Washington State)
 Dr. W. Taylor (Sydney)
 Dr. M. Venugopalan (Benares)

A seminar on "Examinations: their purpose, design and validity", may have contributed to the improvement in the pass rate in first year chemistry. The following table summarises the enrolments and examination results:

Unit	Chem. I	Chem. II	Chem. IIIA	Chem. IIIB	Chem. IV (Hons.)	M.Sc. Qual.
Enrolment	114	14	6	5	4	2
Examined	101	12	6	5	4	2
Passed	83 5 H.D. 20 D, 17 C	7 1D, 2C	5 3C	3 2C	4 1H1, 2H2A, 1H2B	2

RESEARCH ACTIVITIES

(a) Inorganic Chemistry

Studies of the effect of cations and of solvents on the formation of chloro complexes by divalent manganese have been continued. Absorption and reflectance spectra of these compounds and the effect of U.V. irradiation on them have been investigated. This work has been extended to the bromo complexes of divalent manganese. (Gill and Foster)

Preliminary studies on the formation of chloro complexes by tri-valent chromium have been made. (Gill)

Pure cis and trans isomers of potassium dioxalatodiaquochromium (III) have been prepared and the former resolved into its optical isomers. (Gill, Reid and Sargeson)

Studies on the reaction of amines with coordinated amino acid esters have shown that amides and/or aldimines may be formed depending on the metal present. The part played by the metal in these reactions is being investigated. (Gill, Sargeson and Turnbull)

An optical-mechanical device has been developed for producing gnomonic projections from Laue patterns of crystal structures.

The study of cyclic interchalcogen compounds has been concluded and the determination of the crystal structure of the β form of $\text{SnI}_4 \cdot 2\text{S}_8$ is almost complete. (Hawes)

Intermolecular compounds of sulphur, $\text{C}_2\text{I}_4 \cdot 4\text{S}_8$ and $\text{P}_2\text{I}_4 \cdot 4\text{S}_8$ have been prepared and an investigation of their structures has commenced.

(Hawes and Aggarwal)

The study of the crystal chemistry of the uranates is continuing. A new cadmium uranate Cd_2UO_5 has been isolated and its structure determined. The structure of Pb_3UO_6 is being investigated as part of the general study of the $\text{PbO-UO}_2\text{-UO}_3$ phase system. (Sterns)

(b) Organic Chemistry

A number of rearrangements of the dithiole system in acylamino-dithiolones has been observed during attempts to cyclise such intermediates to pyrrolodithioles. (Brown and Rae)

The synthesis of a substituted α -ketoglutarimide required to complete a proof of structure was achieved via the remarkably stable crystalline ozonide of a diphenylmethyleneglutaramide.

A survey of base catalysed exchange of nitronic hydrogen in aldonitrones was commenced. (Brown)

The investigation of the alkaloids of Halfordia scleroxyla has been extended to Halfordia kendock which was found to contain tertiary and quaternary bases of the pyridyl-oxazole and furoquinoline groups.

An extract of scale insects of the genus Eriococcus parasitic on Eucalyptus stems has yielded a series of crystalline pigments. Tentative structures have been assigned to some of these on the basis of their infra-red, nuclear magnetic resonance, and mass spectra. (Crow)

Synthetic work aimed at the production of a benzoxatropolone was commenced by the synthesis of 2,3-benzoxepin-4-one and a study of its bromination products. (Crow and Kendall)

The structure of a monomeric leuco-anthocyanidin that has been isolated from immature grapes by thin-layer chromatography is under investigation. Progress has been made in the study of the structure of the polymeric leuco-anthocyanidins which were isolated previously. (Crow and Kolar)

The identification of some extractives from leaves of Eucalyptus species which stimulate or inhibit germination of spores from fungi parasitic on the leaves, was undertaken in collaboration with W.A. Heather of the Botany Department. (Kolar)

The structures of the products obtained by platinum catalysed hydrogenation of 2-methyl-bicyclo-[2,2,1]-heptane-endo-2,3 dicarboxylic anhydride were determined by a study of chemical reactivity, deuterium labelling and nuclear magnetic resonance. The ring-opening reaction of the primary product, 2-methyl-5- β -hydroxy-3-keto-tricyclo[5,2,1,0^{2,6}]-4-oxadecane and the isomerisation of the resultant aldehyde were also studied. (Warrener, Sternhell*, Brown)

New syntheses of thiazines were achieved from readily available precursors and the thiazines were then converted to thiopyrimidines by treatment with aliphatic amines. Considerable progress has been made towards a general synthesis of 1-substituted orotic acids. (Warrener and Cain)

A reinvestigation, using nuclear magnetic resonance, of the dimer obtained by treatment of 4,6,6-trimethyl-2-thio-1,3-thiazine with acid, has lead to a correction of structure previously attributed to it. (Warrener and Sternhell*)

The study of the photochemical Diels-Alder reaction between dienophiles and benzene has been continued successfully. The results of the investigation will be presented at A.N.Z.A.A.S.

A method for the synthesis of 6-alkyl pyrimidines has been developed. (Warrener)

We acknowledge the help received from the Division of Coal Research, C.S.I.R.O., through the Chief of the Division and Dr. J.S. Shannon and Dr. S. Sternhell, in studies of mass spectra and nuclear magnetic resonance spectra. Dr. A. Robertson of the University of Sydney has also collaborated in the provision of nuclear magnetic resonance spectra. The Micro-Analytical Laboratory of C.S.I.R.O., under the direction of Dr. K. Zimmerman, has carried out the many organic analyses required.

(c) Physical Chemistry

Interfacial polycondensation produces a polymer by reaction at the interface between two immiscible solvents each of which normally contains one of the monomeric species. The rates of interaction and the degree of polymerisation obtained in such a polycondensation between sebacoyl chloride and piperazine are being studied. (Bradbury and Crawford)

The interfacial polymerisation of the hydrochloride of an amino-acylchloride has been applied to the preparation of poly-DL-leucine with a degree of polymerisation of about 25. The process is capable of development to produce polypeptides of known repeating sequence by starting with the similar derivative of a small peptide.

(Bradbury and Tilley)

Viscosity measurements with solutions of synthetic polypeptides in strongly acidic solvents, e.g. dichloroacetic acid, show evidence of a strong polyelectrolyte effect. This indicates a protonation of the amide group. (Bradbury and Fenn)

Methods have been perfected for the preparation of histologically pure specimens of the cuticle and cortical cells by the ultrasonic disruption of wool fibres in suspension in various liquids. A continuously recording amino-acid analyser has been brought into operation for the analysis of hydrolysates of these cells. (Bradbury, Chapman and King)

The study of hydrogen bonding in ortho-substituted primary aromatic amines was concluded by a re-examination of the infra-red spectra in the fundamental and overtone regions of 2-nitro-anilines and their N-deuterated derivatives. Interesting evidence of interaction between a primary amine group in the 2-position and heterocyclic nitrogen or sulphur was also recorded. (Hambly and O'Grady)

An examination of the infra-red spectra of hydrogen halides, phenol and phenyl acetylene in methylated and halogenated aromatic hydrocarbons showed, in agreement with previous reports, that there was complete hydrogen bonding of the solutes to the π electrons of the solvent molecules in solvents which did not have fluorine as substituent. The presence of two X-H absorption bands when fluorinated hydrocarbons were used as solvent was shown to be due to an equilibrium of bonded and non-bonded forms and not be bonding to fluorine atoms. (Hambly and Henry)

The apparatus described previously has been used to study the distribution of atoms of a large number of elements when solutions of their halides are sprayed into propane/air or acetylene/air flames at a conventional 10 cm. slit burner. This has shown that small area densities give much more sensitive measures of atomic concentration in some cases. Effective methods for concentrating selenium from organic and mineral samples into a solution for spraying have been developed and the assay of selenium by atomic absorption in flames has been improved. (Hambly and Rann)

The thirty-two percent difference in the solvolysis rates of methane sulphonyl chloride in light and heavy water has been shown to be due to an increased enthalpy of activation in deuterium oxide solution which more than compensates for the less negative entropy of activation. The maximum in reaction rate which occurs when either light or heavy water is mixed with small quantities of dioxan is also governed by changes in the enthalpy of activation. (Hambly and Tonnet)

An investigation of the polarographic reduction of nitro-amines and their cations has been commenced in an attempt to find an explanation for the anomalous values of the half wave potentials that have been recorded in the literature. (Hambly and Bryant)

An apparatus to be used for the study of the anodic dissolution and passivation of metals has been designed and constructed. Preliminary measurements of the rate of dissolution of palladium in hydrochloric acid and hydrochloric-perchloric acid mixtures have shown that the latter are more suitable for the study of the rate of dissolution of the metal as a function of the degree of coverage by a passivating layer. (Irwin)

OTHER ACTIVITIES

Professor Hambly continued as a member of the Editorial Advisory Board of the Australian Journal of Chemistry, and as a member of the Advisory Committee on candidates of the United States Education Foundation. He was also chairman of the local organising committees of the Fourth Australian Spectroscopy Conference and for Section B of A.N.Z.A.A.S. Drs. J.H. Bradbury and R.F.C. Brown have carried a major addition to their normal duties in acting as Joint Secretaries of Section B of A.N.Z.A.A.S. Dr. R.C. Irwin has been Sub Warden, Bruce Hall during 1963.

Associate Professor Crow, with Drs. R.F.C. Brown and R.H. Warrener, attended a conference on Nuclear Magnetic Resonance Spectroscopy at Melbourne in February. Dr. J.H. Bradbury presented a paper on "The Theory of Shrinkproofing of Wool" at the symposium at the Division of Protein Chemistry in October. Most members of the staff and research students attended the Fourth Australian Spectroscopy Conference and two papers were presented from the department. Professor Hambly gave lectures at Wollongong and Newcastle University Colleges and at the Summer School for Teachers conducted by the University of New South Wales.

Several discussions were held with the local branch of the Science Teachers Association on problems of mutual interest.

NEW DEVELOPMENTS

For 1964 and later years, the first-year class will be divided into two sections. Those students who have good school records in Chemistry and who intend to take the subject for two or more years will enter for Chemistry Part I. Those requiring a broad course not leading to Chemistry Part II will take General Chemistry.

An adult education class in general science will be conducted in the department during 1964.

A nuclear magnetic resonance spectrometer has been ordered under the A.U.C. grant for special apparatus. This will come into operation during 1964 and will help greatly for structural studies in both inorganic and organic chemistry. It will remove our dependence on C.S.I.R.O. and other universities for this essential technique.

A.N. Hambly,
Professor of Chemistry.

9th January, 1964.

DEPARTMENT OF CHEMISTRY

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HAWES, L.L.

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"Sulphur-selenium and sulphur-tellurium cyclic inter-chalcogen compounds." Nature, 198, 1267-1270, 1963.

* Not a member of this University.

Ø Based on work done prior to joining the University.

✗ A member of the Electron Microscopy Unit, J.C.S.M.R.