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THE AUSTRALIAN NATIONAL UNIVERSITY
SCHOOL OF GENERAL STUDIES
Department of Chemistry
Annual Report - 1964

51/1965

Staff

Professor and Head of Department	A.N. Hambly, M.Sc., Dip. Ed., F.R.A.C.I. (On study leave 1.8.64-4.11.64.)
Associate Professor (Organic Chemistry)	W.D. Crow, M.Sc., Ph.D. (On study leave for whole of 1964.)
Senior Lecturers	J.H. Bradbury, M.Sc., Ph.D., F.R.A.C.I. (On study leave for whole of 1965) R.F.C. Brown, M.Sc., Ph.D. N.S. Gill, M.Sc., Ph.D.
Lecturers	N.J. Daly, B.Sc., Ph.D. (from 11.12.64) L.L. Hawes, Jnr., B.Sc., Ph.D. R.C. Irwin, M.Sc., Ph.D., (resigned 31.12.64) R.N. Warrenner, M.Sc., Ph.D.
Temporary Lecturer	R. Hutchins, B.Sc., Ph.D. (from 10.2.64)
Rothmans' Research Fellow	J.M. Brown, M.Sc., Ph.D. (from 9.9.64)
Senior Demonstrators	G.F. Kolar, B.Sc. M. Sterns, M.Sc. M.L. Tonnet, M.Sc.
Demonstrator	M.P. Henry, B.Sc. (from 1.1.64)
Research Assistants	K.H.J. Bryant, B.Sc. G.V. Chapman, B.Sc. J.J. Foster, B.Sc. N.L.R. King, B.Sc. B.K. Solly, B.Sc. (from 16.3.64)
Head Technician	A.T. Miles, A.W.A.S.M.

DEVELOPMENTS DURING 1964

The first year class was divided into two sections. One group was given a broad course suitable for those who would not be making any further formal study, while the other was given a slightly more specialised and intense course. The two groups took almost identical practical courses. The success of this arrangement encourages us to continue it for the immediate future.

The post-graduate course is now well established. Three post-graduate degrees were conferred on former students of the department during 1964 and, in addition, I.D. Rae was admitted to the degree of Doctor of Philosophy for a thesis entitled "Synthetic approaches to thiolutin", while C.S. Rann was admitted

to the degree of Master of Science for a thesis on "Atomic Absorption Spectroscopy." Four students were granted scholarships to commence Ph.D. courses.

Many universities depend greatly on post-doctoral scholars for the strength of their research program. This university makes no provision for such applicants in the School of General Studies. The award of a Rothmans' Fellowship to Dr. J.M. Brown, who chose to work in this department was most welcome.

Associate Professor W.D. Crow was the first member of the department to receive study leave. He worked for a period of eleven months in the Noyes Laboratory of the University of Illinois with Professor N.J. Leonard on problems associated with a synthesis of penicillin. A novel synthesis of 3-iso-thiazolone was devised and studies were made of the stability of bonds between nitrogen and sulphur. Dr. Crow gave lectures on his recent research interests at the Universities of Arizona (Tucson), Arizona State (Phoenix), California (Los Angeles), Colorado and Washington, and to the American Chemical Society meeting at Chicago. Several universities in Great Britain and Ireland were visited during a five-week period after his visit to U.S.A.

Professor A.N. Hambly spent three months in the study of recent developments in the presentation of chemistry courses in Great Britain and U.S.A.

A short course in general science was presented in the department under the auspices of the Department of Adult Education. The lecture theatre has become a popular venue for the presentation of public lectures.

ENROLMENTS AND EXAMINATIONS

The total enrolment showed a smaller percentage increase than in 1963. Now that some of the laboratories, that were not furnished when the building was first occupied, have been fully equipped we do not anticipate any need to restrict enrolments before 1967.

The enrolments and examination results are shown in the following table:

Unit	Enrolment	Examined	Passed	Classified
General Chemistry	65	55	34	3,H.D.; 3,D.; 6,C.
Chemistry Part I	75	65	45	4,H.D.; 6,D.; 13,C.
Chemistry Part II	26	26	13	4,D.; 2,C.
Chemistry Part IIIA	4	4	4	1,C.
Chemistry Part IIIB	5	5	4	1,D.; 1,C.
Chemistry Part IV	1	1	(Honours only)	1, H2A,
M.Sc. (Qualifying)	6	6	5	(Pass only)
M.Sc. (Thesis)	3	1	1	
Ph.D.	10	1	1	

We were indebted to Dr. H.A. McKenzie and Dr. B. Preston, both of the Physical Biochemistry Department, I.A.S., and to Dr. S.R. Taylor (Department of Geophysics, I.A.S.) for lecture courses to senior students. We are also grateful to Professor M. Calvin (University of California, Berkeley) and Professor T.A. Geissman (University of California, Los Angeles) for lectures in our seminar program.

RESEARCH ACTIVITIES

(a) General

The research program was assisted by the installation of a high resolution, double beam, infra-red spectrophotometer which has been applied to problems in all sections of the department. A Perkin-Elmer, 60 Mc/s, nuclear magnetic resonance spectrometer, which is being installed at the present time, will make a major contribution to research in inorganic and organic chemistry. It will remove our past dependence on laboratories in Sydney. We are very grateful to Dr. S. Sternhell, of the University of Sydney, for his assistance in this field during 1964, and to Dr. J.S. Shannon of the Division of Coal Research, C.S.I.R.O., for studies of mass spectra.

(b) Inorganic Chemistry

Studies of the halogeno-complexes of divalent manganese have been continued. The crystallographic structures of $(\text{CH}_3)_4\text{N} \cdot \text{MnCl}_3$ and of $(\text{CH}_3 \cdot \text{NH}_3)_2 \cdot \text{MnCl}_4$ have been partially determined and a detailed interpretation of their electronic absorption spectra is being carried out. These and allied compounds show powerful fluorescence. (Gill and Foster)

Complexes of the picolines and halogen substituted pyridines with the divalent halides of metals of the first transition series have been prepared. The relationship between the nature of the metal-ligand bond and the infra-red spectra of these compounds has been examined for the region $1600\text{-}400\text{ cm}^{-1}$. (Gill and Kingdon)

The reaction, between primary aliphatic amines and the complexes formed by Schiff bases of amino acids with nickel (II) and copper (II), has been studied.

Octahedral complexes of cobalt (III) and nickel (II) with salicylidene-alanine and salicylidene-glycine have been prepared and a partial resolution of the cobalt salicylidene-alanine complex has been achieved. (Gill, Sargeson*, and Turnbull)

The investigation of the structures of the compounds $\text{P}_2\text{I}_4 \cdot 4\text{S}_8$ and of $\beta \text{SnI}_4 \cdot 2\text{S}_8$ has been continued. (Hawes)

The experimental work for a three dimensional, X-ray analysis of the structure of Pb_3UO_6 has been completed. Tentative positions of the metal atoms have been derived from a three-dimensional, Patterson summation and refinement of the structure is progressing. The calculations are being performed with the I.B.M. 7044 computer at the University of Melbourne. The local I.B.M. 1620 computer was suitable only for the initial calculations. (Sterns)

An analysis of the data obtained during studies at the University of Tasmania on the two-component system, chlorine-bromine, has been completed. (Scott)

(c) Organic Chemistry

After some alkaloids from Halfordia scleroxyla had been shown to contain a central oxazole ring an investigation of the mass spectra of diaryl-oxazoles was carried out. These spectra showed that there was a concerted elimination of the central aromatic nucleus (as HCN and CO) with a simultaneous trans-annular migration of one substituent. This is the first recorded case of such a reaction. (Crow, Hodgkin and Shannon*)

Studies of the leuco-anthocyanidins of immature grapes have concentrated on the structure of the monomeric constituent. The results to date indicate that this has an interesting structural difference from material isolated previously and solution of this structure will aid considerably the work on the polymeric substances that have been isolated. (Crow and Kolar)

In order to have suitable reference material in connection with the current investigation of the chemistry of aminodithioles, a survey of the nuclear magnetic resonance and mass spectra of dithioles has been made. (Brown, Rae, Sternhell*, Shannon*)

The ring expansion and contraction reactions of cyclic α -keto-nitrones and their derivatives have been investigated. (Brown and Subrahmanyam)

The pyrolysis of indantrione has been shown to form benzyne, which in the absence of other reactants dimerises to biphenylene. (Brown and Solly)

A cyclic bis-hydroxamic acid has been synthesised and condensation reactions, aimed at a synthesis of mycelianamide, are being studied. (Brown and Meehan)

The synthetic utility of 1,3-thiazines as pyrimidine precursors has been further investigated. A number of new routes to 1,3-thiazines have been developed and shown to be suitable for the specific introduction of alkyl groups into the N₁ or N₃ position of uracils.

An extension of this method to the synthesis of 6-hydroxymethyl uracils, which are then oxidised to the 6-carboxy derivatives, serves as a method of synthesis of orotic acid substituted on N₁.

Treatment of 1,3-thiazine with P₂S₅ in pyridine forms dithiolthiones, and is a good method for the preparation of the parent dithiolthione. (Warrener and Cain)

The synthesis of the photodimers of thymine has continued. During this investigation a new and interesting photochemical reaction of cyclic hexadienes has been discovered. (Warrener and Bremner)

Preliminary investigations on the photochemical decomposition products of nitrofurantoin and related compounds were unrewarding. The photochemistry of menadione, a synthetic compound with vitamin K activity, is currently under investigation. (Warrener and Anderson)

A new synthesis of 1,3-oxazines from acylurethanes has been developed. Preliminary investigations into the synthesis of 4-thiouracils, cytosines and 5-azauracils has shown considerable promise. (Warrener)

The preparation of nitrogen containing heterocycles useful as potential ligands in transition metal complexes has been undertaken in conjunction with some members of the Inorganic Chemistry Department of the University of New South Wales. S-triazine and 2,4,6-tris(2-pyridyl) triazine have been made and are found to be powerful ligands. (Warrener)

(d) Physical Chemistry

Improvements have been made in the methods for the separation of the histological components of the wool fibre. These have allowed the complete analysis of the cuticle and cortical proteins for their constituent amino acids. The methods have been applied to different wool types. Preliminary results have been obtained for the amino-acids in the epicuticle and in the cell membranes of the cortex. A study of the differences between the so-called "ortho" and "para" groups of cortical cells has been commenced. (Bradbury, Chapman and King)

The change in volume associated with the transition from helix to random coil for poly-(gamma-benzyl-L-glutamate) was determined by a dilatometric method. The study of the viscosity of solutions of this polymer in various solvents is being continued. (Bradbury and Fenn)

Apparatus, and techniques, for the systematic change of the physical variables, have been devised for the study of the kinetics of interaction between a diacyl chloride and a diamine. They are being applied to the interfacial polycondensation which yields poly-(terephthaloyl piperazine). (Bradbury and Crawford)

Studies of the half-wave potentials, for the reduction of aromatic nitro-amines at the dropping mercury electrode, have been continued. The effect of change of pH in the presence of various "maximum suppressors", and for pure solutions of the nitro amines at concentrations of 10^{-5} - 10^{-6} M, have been made. It has been established that the reported dependence of these potentials on the hydrogen bonding in ortho-nitro-anilines is incorrect. (Hambly and Bryant)

The investigation of the interaction between hydrogen bond donors and fluorine substituted aromatic compounds, has been completed. A study of the infra-red spectrum of phthalyl bromide

in C_2Cl_4 , over a wide temperature range, has failed to confirm the reported tautomeric equilibrium between the dibromophthalide and the normal acyl bromide structures. (Hambly and Henry)

Spectral sources for tellurium, selenium and arsenic have been developed and applied to the assay of these elements by atomic absorption spectroscopy. A method has been developed for the estimation of mercury in mineral samples which increases the usual sensitivity of the atomic absorption method at least one-thousand fold. (Hambly and Rann)

The study of the solvolysis of methane sulphonyl chloride in a full range of mixtures of light and heavy water has been completed. Apparatus has been constructed to measure the rate of these solvolyses at pressures up to 2000 atmospheres. The approximately two-fold increase in the rate of the reaction with both H_2O and D_2O which occurs when the pressure is increased to 2000 atmospheres is due almost entirely to a change in the entropy of activation. (Hambly and Tonnet)

OTHER ACTIVITIES

The meetings of Section B of A.N.Z.A.A.S. were held in the Chemistry building from January 20th to January 24th, 1964. Apart from some difficulties with the ventilation of the larger lecture theatre, the meetings were highly successful. The efficiency of the organising secretaries (Dr. J.H. Bradbury and Dr. R.F.C. Brown), and the willing co-operation of the technical staff under Mr. A. Miles, were largely responsible for this success. Members of the staff presented papers at this congress and also at a preliminary conference on heterocyclic chemistry that was arranged by the Royal Australian Chemical Institute.

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 Fulbright program candidates, for the United States Educational Foundation. He

also represented the University on the N.S.W. Chemical Education Committee.

Dr. R.C. Irwin was Sub-Warden for Women at Bruce Hall during 1964.

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