

CURRICULUM VITAE

Dr. Erwin Buncel

Affiliation and official address: Queen's University, Department of Chemistry
Kingston, Ontario, CANADA K7L 3N6

EDUCATION (degrees, dates, universities)

- B.Sc., Chemistry, 1st class Honours, University of London, England, 1954
- Ph.D., Organic Chemistry, University of London, 1957
- D.Sc., Physical Organic Chemistry, University of London, 1970

ACADEMIC, RESEARCH AND INDUSTRIAL EXPERIENCE

<u>Positions Held</u>	<u>Dates</u>	<u>Department</u>	<u>Institution</u>
Professor Emeritus	1996	Chemistry	Queen ' s University
Visiting Professor	1996,1999	Chemistry	University of Versailles
Visiting Professor	1994 (Spring)	Chemistry	Korea University
Visiting Professor	1989 (Sept-Dec)	Chemistry	University of Paris
Visiting Scientist	1987 (June-July)	Chemistry	University of Warsaw
Visiting Professor	1987 (Spring)	Chemistry	Univ. of Surrey (U.K.)
Visiting Professor	1982 (June-July)	Chemistry	University of Paris
Professor	1970	Chemistry	Queen's University
Associate Professor	1966-1970	Chemistry	Queen's University
Assistant Professor	1962-1966	Chemistry	Queen's University
Research Chemist	1960-1962	Central Research	American Cyanamid
NRC Fellow	1958-1960	Chemistry	McMaster University
Postdoctoral Fellow	1957-1958	Chemistry	Univ. of N. Carolina

MEMBERSHIP OF PROFESSIONAL SOCIETIES

Canadian Chemical Society, Past Chairman of Organic Division, Chemical Institute of Canada, American Chemical Society, Royal Society of Chemistry, International Group for Correlation Analysis in Organic Chemistry, International Isotope Society (First President of Canadian Chapter).

HONOURS/AWARDS

Syntex Award in Physical Organic Chemistry (1985 - Chemical Institute of Canada, for distinguished research accomplishments in physical organic chemistry)

Fellow, Chemical Institute of Canada

Member of International Committee to evaluate research in physical organic chemistry in Swedish Universities for Swedish Natural Sciences Research Council, and of Berkeley National Tritium Lab.

Trustee, International Isotope Society

Canadian representative on IUPAC (International Union of Pure & Applied Chemistry) Committee for CHEMRAWN - Chemical Research Applied to World Needs (1993-)

1996 Ontario-Quebec Physical Organic Minisymposium dedicated to Buncel

Special Issue of Canadian Journal of Chemistry dedicated to Buncel (1998).

R.U. Lemieux Award in Organic Chemistry - Canadian Society for Chemistry (1999).

Fellow, World Innovation Foundation (2001).

GRADUATE STUDENTS AND POST-DOCTORAL FELLOWS

	<u>Successfully Completed</u>	<u>In Progress</u>
A. Doctoral theses	35	3
B. Master's theses	31	3
C. Post-doctoral fellows	52	2

PUBLICATIONS

Number of papers in refereed journals published or in press 302; Books 4; Chapters 10; Reviews 10; Edited monographs 15; Popular articles 5; Conference proceedings 20; presentations 210.

EDITORIAL ACTIVITIES:

Editor (Physical Organic Chemistry), Canadian Journal of Chemistry (1981-1993)

Editor, Journal of Labelled Compounds and Radiopharmaceuticals (1995-)

Advisory Board: Journal of Physical Organic Chemistry; U.K. Royal Society of Chemistry, Chemistry International.

Co-editor of monographs:

Comprehensive Carbanion Chemistry.

Isotopes in Organic Chemistry;

Isotopes in the Physical and Biomedical Sciences;

INVITED/PLENARY SPEAKER AT MAJOR CONFERENCES

Over the past 10 years Buncl has been invited/plenary speaker at 20 major conferences, including the 1st Latin-American Conference on Physical Organic Chemistry, Florianopolis, Brazil (Plenary Lecturer), 1991; the 5th Conference on Correlation Analysis in Chemistry, Paris (Invited Speaker), 1992; 4th International Symposium on Synthesis and Applications of Isotopes and Isotopically Labelled Compounds, Toronto (Invited Speaker), 1991; 77th Chemical Institute of Canada Conference, Winnipeg (Invited Speaker), 1994; 6th Conference on Correlation Analysis in Chemistry, Prague (Plenary Lecturer), 1994; International Conference on Electron Transfer Processes (Krakow, 1997, Declined); 8th International Conference on Correlation Analysis in Chemistry, India (Plenary Lecturer), 1999; 82nd Canadian Society for Chemistry, R.U. Lemieux Award Lecture (1999). Materials Chemistry Canada Colloquium, Victoria (2002).

INVITED LECTURES

70 research seminars presented at university and other research institutions in Canada, United States, England, Scotland, Ireland, France, Italy, Spain, Germany, Poland, Czech Republic, Israel, Brazil, Korea, Nigeria, and India.

ORGANIZATION OF SYMPOSIA/CONFERENCES

Buncl has organized 18 symposia, beginning in 1969 with the Symposium on Molecular Rearrangements (52nd CIC Conference, Montreal), through to 1994 with Experimental and theoretical approaches to transition states in organic chemistry (77th CIC Conference, Winnipeg), and 1996 with Symposium on isotopes in drug discovery, nuclear medicine,

nutrition, agriculture and protection (4th Meeting of Canadian Chapter of International Isotope Society, Toronto), including three Physical Organic Minisymposia at Queen 's. He was Co-Chair of the 4th International Symposium on Synthesis and Applications of Isotopes and Isotopically Labelled Compounds, Toronto, 1991. He served on the International Advisory Board of the 8th International Conference on Correlation Analysis in Chemistry (India, 1999).

INTERNATIONAL ACTIVITIES

International Union of Pure and Applied Chemistry (IUPAC) activities

Member of International Organizing Committee and Conference Editor for 5th International Conference on Physical Organic Chemistry, Santa Cruz, 1980.

Member of committees on symbolization and naming of organic reaction mechanisms.

Contributor to Glossary of Terms used in Physical Organic Chemistry.

Member of working party - Commission III.2 - Physical Organic Chemistry.

- CHEMRAWN - Canadian representative on CHEMRAWN (Chemical Research Applied to World Needs), (1993-) with the mission: (1) to identify human needs amenable to solution through chemistry with particular attention to those areas of global or multinational interest; (2) to serve as an international body and forum for the gathering, discussion, advancement and dissemination of chemical knowledge deemed useful for the improvement of humankind and the environment. As part of his CHEMRAWN activities, Buncl has attended meetings and conferences in Lisbon, Washington, Berlin, Paris and Seoul and has associated with like-minded scientists based world-wide. Special effort is directed toward developing countries - Erwin has forged a strong link with Nigerian scientists. He is Co-chair of the CHEMRAWN XII World Conference on Chemistry in the Service of Sustainable Agriculture and a Healthy Environment in Africa and the Developing World to be held in South Africa, 2002.
- Nato Collaborative Research Programs - A NATO grant awarded to Dr. J.R. Jones (U.K.) and Buncl enabled development of a joint program on the application of radio tracer techniques to the interaction of biomolecules with heavy metals such as mercury and cadmium. This led to a successful application to NSERC for a Strategic Grant in the area of Environmental Toxicology. Other NATO collaborative grants followed with Professors F. Terrier (France) and D. Spinnelli (Italy). In 1996 a joint NATO grant was approved with Professors J.F. Gal (France) and R.W. Taft (USA) for gas phase studies of the interaction of metal ions with organo phosphorus compounds. The information derived will be fundamental to understanding of the role of metal ions in biological systems, e.g. the phosphoryl moieties of DNA and ATP.

Involvement with developing countries - In 1987 a joint application between the University of Ibadan, Nigeria and Queen's University (with Buncel as Principal Investigator) was funded by CIDA for \$308,000 to establish a Centre for Environmental Studies. Following a visit by Buncel to Nigeria in 1991, a new proposal was funded by CIDA in 1992 at \$797,000 to establish a Centre for Agrochemical Technology at the University of Agriculture, Makurdi, Nigeria, with Buncel as the Project Director. The aims of the Centre can be summarized by the following key words: "sustainable agriculture, outreach, pesticide use and degradation, environmental preservation and education for clean environment". These activities are continuing.

REFEREEING ACTIVITIES

Referee for the Canadian Journal of Chemistry; Journal of Organic Chemistry; Journal of Physical Chemistry; Journal of the American Chemical Society; Advances in Chemistry; Accounts of Chemical Research; Chemical Reviews; Reviews of Chemical Intermediates; Journal of Molecular Structure (Theochem); Talanta; Bulletin of the Chemical Society France; Pakistani Journal of Chemistry; Journal of Carbohydrate Chemistry; Carbohydrate Research; Journal of Physical Organic Chemistry; Tetrahedron Letters; Organic Letters, Tetrahedron; Journal of Chemical Research; Royal Society of Chemistry; Synthesis, Journal of Organometallic Chemistry; Inorganica Chimica Acta; Bio-organic Chemistry;

Referee for Grant Applications: NSERCC, Canada Council (Killam), National Science Foundation; Research Corporation; American Chemical Society Petroleum Research Fund; Israel Basic Research Foundation; U.S. - Israel Binational Science Foundation; NATO; International Council for Canadian Studies; Alberta Cancer Board.

Referee for tenure, professional appointments and for Distinguished Research Professorships.

Member of Selection Committee for Syntex Award and Bader Award, Chemical Institute of Canada

Member of NIH Site Visiting Committee for National Tritium Facility at Lawrence Berkeley Laboratories, University of California

COLLABORATIONS IN RESEARCH

B.G. Cox (ICI, U.K.); R.A. Cox (Toronto); U. Edlund (Umea University, Sweden); J.F. Gal (University of Nice); S. Hoz (Bar-Ilan University, Israel); J.R. Jones (University of Surrey, U.K.); S.-R. Keum (Korea University, Korea); I. Onyido (Makurdi University, Nigeria); K.T. Park (Korea National Univ. of Education, Korea); P.M. Kazmaier (Xerox Research Centre of Canada); S.S. Shaik (Ben Gurion University, Israel); P.v.R. Schleyer (University Erlangen-Nurnberg, Germany); B.V. Smith (University of London, U.K.); F. Terrier (University of Versailles); J. Wojtyk (Royal Military College), W.J. Racz (Queen's Pharmacology), D.J. Walton (Queen's Biochemistry), M. Cunningham (Queen's Chemical Engineering) and following Queen's Chemistry faculty: S. Brown, R.P. Lemieux, G.W. vanLoon, H.F. Shurvell, and G.R.J. Thatcher.

HIGHLIGHTS OF CURRENT RESEARCH

Erwin Buncel's research in organic chemistry encompasses wide areas concerned with the understanding of chemical reactivity, and synthesis and investigation of novel

compounds. The work traverses areas of physical organic chemistry, bio-organic chemistry, and more recently bio-inorganic and environmental chemistry. Continuous exploration of fundamental structure-reactivity relationships as well as practical application, has characterized his research. The record is one of continuous involvement and growth. Erwin has made truly fundamental contributions to organic chemistry and the fruits of his research now permeate the fabric of current organic chemical research. Some of the highlights of the research are as follows, including references to pertinent publications (see Appendix):

1. Metal ion-biomolecule interactions

Work in this area has been directed towards understanding of the role of metal ions in biological systems, especially DNA bases where the first instance of covalent binding of methylmercury to carbon in nucleosides was observed, pointing to an alternative mercury toxicity mechanism^{101, 113, 121, 134}. This led to the discovery of a potentially useful protective agent in organomercurial intoxication¹²⁴, and the proposal of a model for putative mercury (II) interstrand cross-linking of DNA¹⁶³. Studies of platinum (II)-DNA base complexes (potential anti-tumour agents) are in progress^{227, 234, 236, 244}.

2. Organosulfur and organophosphorus reactivity: catalysis and inhibition

Erwin's work on nucleophilic reactivity revealed an unexpected behaviour of alkali-metal cations.^{183, 188} Catalysis by M^+ at phosphoryl centres contrasted with sulfonyl centres where both catalysis (Na^+ , K^+ , Cs^+) and inhibition (Li^+) was observed, pointing to the importance of such metal ion-substrate interactions in biological systems.^{184, 193, 212} A combination of experimental and theoretical approaches has been especially enlightening in this work. The results are of value in current work in pesticide stability, while also pertinent to understanding the fundamentals of catalytic/inhibitory mechanisms in general and transphosphorylation in particular (review 19, conference 16).

3. Carbanion studies - group 14 analogs (carbon, silicon, germanium, tin, lead)

Carbanions, fundamental intermediates in organic synthesis, have been investigated through structure-reactivity studies in several approaches: hydrogen isotope exchange^{18, 178}, including the fundamental acidity of molecular hydrogen; spectrophotometric¹³⁵ and multi-nuclear NMR studies, contrasting structure, bonding and electronic transmission for Group 14 elements in the Periodic Table, i.e., in carbon, silicon, germanium, etc. centred anions^{146, 170, 221, 229, 264}. Some of the research is included in the forthcoming text "Carbanion Chemistry. Structure and Mechanism" (Book 4) and in the edited monograph series "Comprehensive Carbanion Chemistry". Studies of electron transfer processes of carbanions could potentially lead into organic conductors and molecular electronics.

4. Electron-deficient aromatic-base (donor-acceptor) interactions

These studies concern charge-transfer, electron-transfer, proton-transfer and covalent adduct formation, and form the basis of the text "Electron-Deficient Aromatic- and Hetero-aromatic-Base Interactions" (Book 2) as well as ca. 50 original research papers. Of special interest is the discovery of super-electrophiles^{166, 175, 220, 241, 269} and of novel relationships concerning kinetic control and thermodynamic control in covalent (sigma) adduct formation, the role of stereoelectronic factors, and the discovery of ambident

reactivity of phenoxide and enolate nucleophiles^{200,213,237,245}. A relationship has been uncovered between super-electrophilicity and pericyclic reactivity.²⁷⁰ Classification of the different types of regioselectivity has been referred to as "*Buncel's nomenclature*" (R.A. Chamberlin and M.R. Crampton, *J.C.S. Perkin Trans. 2*, 1995, 1831). The covalent adducts serve as biochemical and biophysical probes¹²⁰. Study of the interaction of dopamine derivatives with electron deficient aromatics¹⁷³ could yield information on how deficiency of this neurotransmitter in the brain is implicated in the incidence of Parkinson's disease. Current investigations concern sigma complexes as cytotoxic agents and as potential radio-sensitizing and therapeutic agents in the treatment of cancer.

5. Fundamental studies of dye molecules - solvatochromism and photochromism

Buncel's studies of azo and azoxy dyes began with the goal of solving the long-standing riddle of the mechanism of the Wallach rearrangement of azoxyarenes (Chapter 20), and led to the discovery of solvatochromism in the resulting hydroxyazo merocyanine dyes, which form the basis of a new solvent polarity scale^{180, 187, 199}. Studies of the thermochromic and photochromic interconversion of merocyanines and spiropyrans are pertinent for energy storage.^{196, 205, 217, 232, 251, 254, 265} Collaboration followed with scientists at the Xerox Research Centre of Canada on photogenerator and photoreceptor organic dye and pigment molecules through fundamental studies and the requirements of process development^{208, 209, 228, 258}.

6. Cyclodextrin-based enzyme models

Studies with cyclodextrins (CDs) as enzyme models were initiated via attachment of catalytic groups (multifunctional catalysis and molecular recognition). The approach has been to derivatize the secondary face of CD because it is more open than the primary face and should be the preferential site for binding of large molecules including aromatic guests^{192, 223}. In a collaborative study with Dr. Walton (Biochemistry) modified CD catalysts are investigated as models for non-enzymic glycation of proteins; glycation often leads to deterioration of protein function and cross-linking which is partly responsible for age-related development of cataracts and stiffness of connective tissues.

7. Solvent effects on chemical reactions: transition-state structure and the alpha effect

The nature of the solvent as medium has a profound effect on chemical reactions (Book 3) -rates, equilibria, stereochemistry and yields. Buncel's group have approached this phenomenon from a fundamental viewpoint⁹⁸ and in a practical way¹⁰⁵, and have shown that the dependence of metal ion effects on the nature of the solvent medium are also subject to this approach¹⁹¹. A new solvent polarity scale has been proposed^{187, 230}. Currently a two-pronged approach to this problem is pursued: *ab initio* theoretical calculations and experimental gas phase determination of binding of metal ions to phosphorus- and sulfur-containing compounds^{243, 246}. These combined studies will also provide fundamental information on the origin of metal ion-biomolecule interactions.

Unexpectedly, it was found that the abnormal reactivity of alpha nucleophiles is solvent dependent (" α -effect":^{123, 132, 153} the abnormally high reactivity of nucleophiles containing an unshared electron pair adjacent to the nucleophilic centre, relative to normal nucleophiles of the same basicity or pK_a). The origin of the α -effect was ascribed to special

transition-state properties.^{225,259,268,272} Moreover, the use of solvent mixtures (DMSO-water) led to a novel method of constructing Bronsted plots,^{211,224,238} a recent paper by Francois Terrier and co-workers (*J. Org. Chem.* 1995, **60**, 1748) refers to this strategy as "the Buncel method".

8. Environmental Studies

Erwin's recent collaboration with environmental scientists on the fate of agrochemicals in the environment and soil remediation for organic contaminants, brings the perspective and methodology of physical organic chemistry to this science. While the vital role of organophosphorus and other classes of pesticides in increasing the world's food supplies over the last five decades is firmly established, the possible toxicity to humans and long-term environmental effects dictate that thorough and in-depth studies of their degradation mechanisms be undertaken. To that end the group has initiated studies on the mechanism of abiotic degradation and soil/water interactions of pesticides and other hydrophobic organic compounds,^{250,271,274} with the ultimate goal of providing rate data to aid in the assessment of the stability and persistence of these compounds in the environment. Erwin is ready to devote his energies to the challenges which the future holds, and to make his contribution.

IMPACT OF RESEARCH CONTRIBUTIONS

In summary of the above, Buncel is an acknowledged expert, worldwide, in physical organic chemistry. He is addressing current, important problems with both experiments and theory. Buncel's contributions have become landmarks for others in the field of nucleophilic substitution, ion pairing and catalysis, carbanion reactivities and structures, isotope effects and general methodology in physical organic chemistry. His work combines a thirst for understanding of the basics with a keen sense for potential applications. It is characterized by both high levels of originality and thoroughness, and is widely used and cited. Overall, Buncel has been ranked as one of the leading physical organic chemists.

It is difficult to evaluate the impact of scientific contributions and citations provide just one criterion. In that context it is noteworthy that the most recent edition of Jerry March's text, "Advanced Organic Chemistry. Reactions, Mechanisms and Structure", cites Erwin's work 29 times in 7 chapters according to the author index. Among the Canadian scientists cited, the former figure is in second place and the latter is tied for third place. In terms of overall ranking among the total authors cited in this text (ca. 20,000), the citations to Erwin's work fall in the top 1%. The recent text by F.A. Carroll, *Structure and Mechanisms in Organic Chemistry* gives similar prominence to Erwin's work. In the more specialized (graduate) text, *Nucleophilic Aromatic Displacement. The influence of the Nitro Group*, by François Terrier, Erwin's work figures prominently and is in the top 3% of research cited. Similarly, a scan of the IUPAC-sponsored Glossary of Terms in Physical Organic Chemistry reveals a generous helping of terms attributed to Erwin Buncel.

SPECIAL ISSUE ('FESTSCHRIFT')

Published by the *Canadian Journal of Chemistry* (1998) in honour of EB's contributions to chemistry in Canada and the world, contains 46 articles from scientists in 11 countries on 5 continents.