THE UNIVERSITY
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Studies in Gas Phase Ion Chemistry

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Copies of Publications:

Publications (A): Gas Phase Ion-Chemistry and Mass Spectrometry of Biomolecules

Publications (B): Inorganic and Organometallic Gas Phase Ion Chemistry

Publications (C): Organic Gas Phase Ion Chemistry

Publications (D): International Patent

Publications (E): Invited Reviews

Publications (F): Invited Book Chapters

Publications (G): Invited Encyclopedia Contributions

Publications (H): Other Invited Scientific Publications

Summary Supporting Claim for D.Sc.

The research described in this thesis represents a broad study of the gas phase ion chemistry of biomolecules, inorganic, organic and organometallic species. The unifying theme for many of these studies is the use of advanced mass spectrometry techniques coupled with theoretical calculations to gain detailed insights into structure, mechanisms and reactivity.

The first section reports on the gas phase ion-chemistry and mass spectrometry of biomolecules. This broad research area is further categorised into the sub areas of: Thermochemistry; Regioselectivity of alkylation reactions; Ion-molecule reactions as structural probes; Mechanisms of dissociation reactions of protonated and deprotonated peptides and oligonucleotides; Reactivity of radicals derived from peptides and oligonucleotides; Structure and reactivity of metallated peptides; Reactivity of non-covalent complexes; Analytical applications. Specific highlights include: the experimental determination of the gas phase acidities of the α amino acids; the development of a detailed understanding of the fundamental gas phase fragmentation mechanisms of α amino acids and peptides to the stage that a new proteomics approach has been patented; carrying out some of the first gas phase ion-molecule reactions of non-covalent complexes of biomolecules which demonstrate molecular recognition.

The second section describes inorganic and organometallic gas phase ion chemistry studies and is further categorised into the sub areas of: reactions of organosilicon, organophosphorus and organosulfur species; gas phase coordination chemistry of platinum; insights into catalysis by transition metal oxides and peroxides; synthesis and reactivity of organometallics. Specific highlights include: the discovery of a number of catalytic cycles; showing that collision-induced dissociation can be used to "synthesise" gas phase organometallic species for subsequent reactivity studies. Examples of catalysis include: oxidation of alcohols by the dimolybdate anion, $[Mo_2O_6(OH)]^-$; dehydration of acetic acid by group VI metal oxide anions, $[MO_3(OH)]^-$ and $[M_2O_6(OH)]^-$ (M = Mo and W); decarboxylation of acetic acid by the organomagnesate $CH_3MgCl_2^-$. The organometallic studies have revealed that: while the organocuprate $(CH_3)_2Cu^-$ reacts with methyl iodide via a C-C bond coupling reaction (occurring via a "T shaped" transition state), its silver congener is unreactive; the organomagnesates, $CH_3MgL_2^-$ (L = Cl and O_2CCH_3) show some of the reactivity of Grignard reagents, but fail to undergo the Grignard reaction. The subvalent silver hydride cluster, Ag_4H^+, has been assembled in an unique fashion from silver amino acid precursor, and has been shown to mediate the C-C bond coupling of allylbromide.

The final section reports on the gas phase ion-chemistry of organic species and is further categorised into: thermochemistry; mechanisms of ion-molecule reactions; formation of unusual species and reactive intermediates. An important finding on the mechanisms of substitution reactions at sp^2 hybridised C atoms shows that while acyl pyridnium ions can undergo substitution, aryl diazonium ions appear to be unreactive in the gas phase.