Thesis titled:

Some Unusual, Astronomically Significant Organic Molecules

submitted for the Degree of Doctor of Philosophy (Ph.D.)

by

Salvatore Peppe
B.Sc. (Hons.)

of the

Department of Chemistry

THE UNIVERSITY
OF ADELAIDE
AUSTRALIA

June 2002
Contents

Contents ...................................................................................................................... 1
Abstract ...................................................................................................................... iv
Statement of Originality ............................................................................................ v
Acknowledgments ...................................................................................................... vi
List of Figures ........................................................................................................... ix

1.1 Molecules in The Interstellar Medium ............................................................ 1
   I. Introduction ........................................................................................................ 1
      A. Space: An Imperfect Vacuum ..................................................................... 1
      B. Stellar Evolution, Mass Outflow and Synthesis of Molecules .............. 5
      C. Astronomical Detection of Molecules ....................................................... 7
      D. Gas Phase Chemistry ................................................................................. 9
      E. Generation and Detection of Heterocumulenes in the Laboratory .... 13

1.2 Gas Phase Generation and Characterisation of Ions ...................................... 16
   I. Gas Phase Generation of Ions ..................................................................... 16
      A. Positive Ions ............................................................................................ 16
      B. Even Electron Negative Ions ................................................................ 17
      C. Radical Anions ....................................................................................... 21
   II. Mass Spectrometry ..................................................................................... 24
      A. The VG ZAB 2HF Mass Spectrometer .................................................... 24
      B. Mass-Analysed Ion Kinetic Energy Spectrometry ................................ 25
   III. Characterisation of Ions ............................................................................ 26
      A. Collisional Activation ............................................................................ 26
      B. Charge Reversal ..................................................................................... 28
      C. Neutralisation – Reionisation ................................................................ 29
      D. Neutral Reactivity .................................................................................. 33
   IV. Fragmentation Behaviour ............................................................................ 35
      A. Negative Ions ......................................................................................... 35
1.3 Theoretical Methods for the Determination of Molecular Geometries and Energetics

I. Molecular Orbital Theory
   A. The Schrödinger Equation
   B. Hartree-Fock Theory
   C. Electron Correlation
   D. Basis sets

II. Transition State Theory of Unimolecular Reactions

2. Covalently Bound Complexes of CO and CO₂

I. Introduction

II. Results and Discussion
   Part A: Covalently bound CO₂ dimers (O₂C-CO₂)²
      A. Generation of C₂O₃ Anions
      B. Neutral C₂O₄
   Part B: The Elusive Trioxycarboxylic Neutral (O₂C-CO)
      A. Experimental Approach Towards Neutral C₂O₃
      B. Theoretical Structures of the Isomers of C₂O₃
      C. Theoretical Investigation into the Formation of Neutral C₂O₃

III. Experimental Section
   A. Mass Spectrometric Methods
   B. Synthetic Procedures
   C. Theoretical Methods

3. Formation of Two Isomeric C₃HO Radicals From Charged Precursors in the Gas Phase
Abstract

To date, astronomical surveys have confirmed the existence of over 120 molecules from a variety of extraterrestrial sources. The diversity of the molecular content of circumstellar and interstellar space can only be surmised, and there is continuing debate over the processes by which molecules are formed within these extreme environments. In this thesis we describe experimental and theoretical studies on a number of unusual organic molecules that may have tangible existences in the rarefied environments of space, or in the upper atmosphere of Earth. Stable, neutral precursors of the molecular systems investigated in this work have been generated experimentally via unequivocal pathways by the application of conventional condensed phase synthetic techniques. The molecules, once prepared, were then probed by mass spectrometry. These investigations were supported by computer-based quantum chemical calculations, by which further understanding can be gained about the structures and energetics of the systems under investigation.

Accordingly, various covalently bound, anionic and neutral oxocarbon species, C_{2}O_{m} (n = 2, m = 3, 4) were formed and studied. These systems are particularly pertinent to atmospheric chemistry. Additionally, two analogous C_{3}HX (X = O, S) heterocumulenic systems were investigated. Some isomers of other system, when energised, were shown to undergo gas-phase rearrangement processes.