

**Quantum Chemical Studies of  
Thermochemistry, Kinetics and  
Molecular Structure.**

by

Naomi Louise Haworth

*A thesis submitted in fulfilment of the requirements for the  
degree of Doctor of Philosophy.*

School of Chemistry

University of Sydney

February, 2003

# Declaration

I hereby declare that this thesis is my own work and that, to the best of my knowledge, it contains no material previously published or written by another person nor material which has been accepted for the award of another degree or diploma at an institute of higher education, except where due acknowledgement is given.

Naomi Haworth

For the Glory of God

# Acknowledgements

I would like to express my extreme gratitude to my supervisor, Dr George Bacskay, for the wonderful way he has helped and guided me over the past four years. Thankyou particularly for your kindness, understanding and patience with me in the hard times. I would also like to thank my associate supervisor, Associate Professor John Mackie, for teaching and advising me in the kinetics work in this thesis and for proposing the projects on fluorocarbons, phosphorus compounds and  $\text{NNH} + \text{O}$ .

I am also grateful to the many other academics and students with whom I have shared collaborative projects, in particular Nathan Owens, Klaas Nauta and Scott Kable ( $\text{CFCIBr}_2$ ) and Charles Collyer and Matt Templeton (Phaseolotoxin). Thanks also to all my coworkers over the years (Jason, Jens, Kausala, Karina, Justin, Debbie, Adam, Keiran, Siobhan and many more) for their help and advice and for the fun we've shared.

I thank my family for their love and for supporting me and believing in me throughout all my academic career, and also my friends for their support and encouragement. Particular thanks go to Justine for all the ways, big and small, that you've helped me out over the past few months and for your patience; to Evan for trying to keep me sane; and to Geoff for helping with the proof reading.

I would like to thank the Australian Partnership for Advanced Computing (APAC) National Facility for access to the COMPAQ AlphaServer SC system and the Australian Centre for Advanced Computing and Communications (ac3) for access to their SGI Origin 2400 computer system. Finally, I express my sincere gratitude to the Australian Postgraduate Association for funding my PhD scholarship.

# Abstract

This thesis is concerned with a range of chemical problems which are amenable to theoretical investigation via the application of current methods of computational quantum chemistry. These problems include the calculation of accurate thermochemical data, the prediction of reaction kinetics, the study of molecular potential energy surfaces, and the investigation of molecular structures and binding.

The heats of formation (from both atomisation energies and isodesmic schemes) of a set of approximately 120 C<sub>1</sub> and C<sub>2</sub> fluorocarbons and oxidised fluorocarbons (along with C<sub>3</sub>F<sub>6</sub> and CF<sub>3</sub>CHF<sub>2</sub>) were calculated with the Gaussian-3 (G3) method (along with several approximations thereto). These molecules are of importance in the flame chemistry of 2-H-heptafluoropropane, which has been proposed as a potential fire retardant with which to replace chloro- and bromofluorocarbons (CFC's and BFC's). The calculation of the data reported here was carried out in parallel with the modelling studies of Hynes et al.<sup>1-3</sup> of shock tube experiments on CF<sub>3</sub>CHF<sub>2</sub> and on C<sub>3</sub>F<sub>6</sub> with either hydrogen or oxygen atoms.

G3 calculations were also employed in conjunction with the experimental work of Owens et al.<sup>4</sup> to describe the pyrolysis of CFCIBr<sub>2</sub> (giving CFCl) at a radiation wavelength of 265 nm. The theoretical prediction of the dissociation energy of the two C-Br bonds was found to be consistent with the energy at which carbene production was first observed, thus supporting the hypothesis that the pyrolysis releases two bromine radicals (rather than a Br<sub>2</sub> molecule). On the basis of this interpretation of the experiments, the heat of formation of CFCIBr<sub>2</sub> is predicted to be  $184 \pm 5 \text{ kJ mol}^{-1}$ , in good agreement with the G3 value of  $188 \pm 5 \text{ kJ mol}^{-1}$ .

Accurate thermochemical data was computed for 18 small phosphorus containing molecules (P<sub>2</sub>, P<sub>4</sub>, PH, PH<sub>2</sub>, PH<sub>3</sub>, P<sub>2</sub>H<sub>2</sub>, P<sub>2</sub>H<sub>4</sub>, PO, PO<sub>2</sub>, PO<sub>3</sub>, P<sub>2</sub>O, P<sub>2</sub>O<sub>2</sub>, HPO, HPOH, H<sub>2</sub>POH, H<sub>3</sub>PO, HOPO and HOPO<sub>2</sub>), most of which are important in the reaction model introduced by Twarowski<sup>5</sup> for the combustion of H<sub>2</sub> and O<sub>2</sub> in the presence of phosphine. Twarowski reported that the H + OH recombination reaction is catalysed by the combustion products of PH<sub>3</sub> and proposed two catalytic cycles, involving PO<sub>2</sub>, HOPO and HOPO<sub>2</sub>, to explain this observation. Using our thermochemical data we computed the rate coefficients of the most

## Abstract

important reactions in these cycles (using transition state and RRKM theories) and confirmed that at 2000K both cycles have comparable rates and are significantly faster than the uncatalysed H + OH recombination.

The heats of formation used in this work on phosphorus compounds were calculated using the G2, G3, G3X and G3X2 methods along with the far more extensive CCSD(T)/CBS type scheme. The latter is based on the evaluation of coupled cluster energies using the correlation consistent triple-, quadruple- and pentuple-zeta basis sets and extrapolation to the complete basis set (CBS) limit along with core-valence correlation corrections (with counterpoise corrections for phosphorus atoms), scalar relativistic corrections and spin-orbit coupling effects. The CCSD(T)/CBS results are consistent with the available experimental data and therefore constitute a convenient set of benchmark values with which to compare the more approximate Gaussian-*n* results. The G2 and G3 methods were found to be of comparable accuracy, however both schemes consistently underestimated the benchmark atomisation energies. The performance of G3X is significantly better, having a mean absolute deviation (MAD) from the CBS results of 1.8 kcal mol<sup>-1</sup>, although the predicted atomisation energies are still consistently too low. G3X2 (including counterpoise corrections to the core-valence correlation energy for phosphorus) was found to give a slight improvement over G3X, resulting in a MAD of 1.5 kcal mol<sup>-1</sup>. Several molecules were also identified for which the approximations underlying the Gaussian-*n* methodologies appear to be unreliable; these include molecules with multiple or strained P-P bonds.

The potential energy surface of the NNH + O system was investigated using density functional theory (B3LYP/6-31G(2df,p)) with the aim of determining the importance of this route in the production of NO in combustion reactions. In addition to the standard reaction channels, namely decomposition into NO + NH, N<sub>2</sub> + OH and H + N<sub>2</sub>O via the ONNH intermediate, several new reaction pathways were also investigated. These include the direct abstraction of H by O and three product channels via the intermediate ONHN, giving N<sub>2</sub> + OH, H + N<sub>2</sub>O and HNO + N. For each of the species corresponding to stationary points on the B3LYP surface, valence correlated CCSD(T) calculations were performed with the aug-cc-pVxZ (*x* = Q, 5) basis sets and the results extrapolated to the complete basis set limit. Core-valence correlation corrections, scalar relativistic corrections and spin orbit effects were also included in the resulting energetics and the subsequent calculation of thermochemical data. Heats of formation were also calculated using the G3X method. Variational transition

## Abstract

state theory was used to determine the critical points for the barrierless reactions and the resulting B3LYP energetics were scaled to be compatible with the G3X and CCSD(T)/CBS values. As the results of modelling studies are critically dependent on the heat of formation of NNH, more extensive CCSD(T)/CBS calculations were performed for this molecule, predicting the  $\Delta_f H_{298}^0$  to be  $60.6 \pm 0.5$  kcal mol<sup>-1</sup>. Rate coefficients for the overall reaction processes were obtained by the application of multi-well RRKM theory. The thermochemical and kinetic results thus obtained were subsequently used in conjunction with the GRIMech 3.0 reaction data set in modelling studies of combustion systems, including methane / air and CO / H<sub>2</sub> / air mixtures in completely stirred reactors. This study revealed that, contrary to common belief, the NNH + O channel is a relatively minor route for the production of NO.

The structure of the inhibitor *N*<sup>δ</sup>-(*N*'-Sulfodiaminophosphinyl)-L-ornithine, PSOrn, and the nature of its binding to the OTCase enzyme was investigated using density functional (B3LYP) theory. The B3LYP/6-31G(*d*) calculations on the model compound, PSO, revealed that, while this molecule could be expected to exist in an amino form in the gas phase, on complexation in the active site of the enzyme it would be expected to lose two protons to form a dinegative imino tautomer. This species is shown to bind strongly to two H<sub>3</sub>CNHC(NH<sub>2</sub>)<sub>2</sub><sup>+</sup> moieties (model compounds for arginine residues), indicating that the strong binding observed between inhibitor and enzyme is partially due to electrostatic interactions as well as extensive hydrogen bonding (both model Arg<sup>+</sup> residues form hydrogen bonds to two different sites on PSO). Population analysis and hydrogen bonding studies have revealed that the intramolecular bonding in this species consists of either single or semipolar bonds (that is, S and P are not hypervalent) and that terminal oxygens (which, being involved in semipolar bonds, carry negative charges) can be expected to form up to 4 hydrogen bonds with residues in the active site.

In the course of this work several new G3 type methods were proposed, including G3MP4(SDQ) and G3[MP2(Full)], which are less expensive approximations to G3, and G3X2, which is an extension of G3X designed to incorporate additional electron correlation. As noted earlier, G3X2 shows a small improvement on G3X; G3MP4(SDQ) and G3[MP2(Full)], in turn, show good agreement with G3 results, with MAD's of  $\sim 0.4$  and  $\sim 0.5$  kcal mol<sup>-1</sup> respectively.

*Abstract*

1. R. G. Hynes, J. C. Mackie and A. R. Masri, *J. Phys. Chem. A*, **1999**, *103*, 5967.
2. R. G. Hynes, J. C. Mackie and A. R. Masri, *J. Phys. Chem. A*, **1999**, *103*, 54.
3. R. G. Hynes, J. C. Mackie and A. R. Masri, *Proc. Combust. Inst.*, **2000**, *28*, 1557.
4. N. L. Owens, *Honours Thesis*, School of Chemistry, University of Sydney, **2001**.
5. A. Twarowski, *Combustion and Flame*, **1995**, *102*, 41.

# Publications

Parts of this work have been published or submitted for publication in the following journal articles:

N. L. Haworth, M. H. Smith, G. B. Bacskay, J. C. Mackie

Heats of Formation of Hydrofluorocarbons Obtained by Gaussian-3 and Related Quantum Chemical Computations.

*J. Phys. Chem. A* **2000**, *104*, 7600.

N. L. Haworth, G. B. Bacskay, J. C. Mackie

The Role of Phosphorus Dioxide in the H + OH Recombination Reaction: Ab Initio Quantum Chemical Computation of Thermochemical and Rate Parameters.

*J. Phys. Chem. A* **2002**, *106*, 1533.

N. L. Haworth, G. B. Bacskay

The Structure of  $N^{\delta}$ -( $N'$ -Sulfodiaminophosphinyl)-L-ornithine and its Binding to Ornithine Transcarbamoylase: A Quantum Chemical Study.

*Molecular Simulation* **2002**, *28*, 773.

N. L. Haworth, G. B. Bacskay

Determination of Accurate Quantum Chemical Energies and Heats of Formation for Phosphorus Compounds.

*J. Chem. Phys.* **2002**, *117*, 11175.

N. L. Owens, B. K. Nauta, S. H. Kable, N. L. Haworth, G. B. Bacskay

An Experimental and Theoretical Investigation of the Triple Fragmentation of CFCIBr<sub>2</sub> by Photolysis near 250nm.

*Chem. Phys. Lett.* **2003**, *370*, 469.

N. L. Haworth, G. B. Bacskay, J. C. Mackie

An Ab Initio Quantum Chemical and Kinetic Study of the NNH + O Reaction Potential Energy Surface: How Important is this Route to NO in Combustion?

*J. Phys. Chem. A*, in press.

The following publications are also closely related to the work presented in this thesis.

J. C. Mackie, G. B. Bacskay, N. L. Haworth

Reactions of Phosphorus-Containing Species of Importance in the Catalytic Recombination of H + OH: Quantum Chemical and Kinetic Studies.

*J. Phys. Chem. A* **2002**, *106*, 10825.

J. C. Mackie, N. L. Haworth, G. B. Bacskay

How Important is the NNH + O Route to NO in Combustion?

*2003 Australian Symposium on Combustion & The 8<sup>th</sup> Australian Flames Days, Melbourne, December 8-9, 2003*, submitted.

# Table of Contents

<b>1</b>	<b>Introduction .....</b>	<b>1</b>
1.1	References.....	6
<b>2</b>	<b>Theoretical Methods of Quantum Chemistry.....</b>	<b>8</b>
2.1	Introduction.....	9
2.1.1	The Born-Oppenheimer Approximation .....	10
2.2	Ab Initio Quantum Chemistry .....	12
2.2.1	Many-Electron Wavefunctions.....	12
2.2.1.1	The Independent Particle Model.....	13
2.2.1.2	Antisymmetry .....	14
2.2.1.3	Configuration Interaction Wavefunctions.....	15
2.2.1.4	The Variation Principle.....	16
2.2.2	Hartree-Fock Self Consistent Field Theory.....	18
2.2.2.1	The Self Consistent Field (SCF) Procedure.....	23
2.2.2.2	Spin Unrestricted Hartree-Fock Theory (UHF).....	24
2.2.2.3	Spin Restricted Closed Shell Hartree-Fock Theory (RHF) .....	26
2.2.2.4	Spin Restricted Open Shell Hartree-Fock Theory (ROHF).....	27
2.2.3	Electron Correlation .....	28
2.2.3.1	Multiconfigurational SCF Theory (MCSCF).....	29
2.2.3.2	Configuration Interaction (CI).....	30
2.2.3.3	Møller-Plesset Perturbation Theory (MPPT).....	33
2.2.3.4	Coupled Cluster Theory (CC).....	34
2.2.3.5	Quadratic Configuration Interaction (QCI) .....	38
2.3	Density Functional Theory .....	39
2.3.1	The Kohn-Sham Equations.....	39
2.3.2	The Local Density Approximation (LDA).....	41
2.3.3	Corrections to the LDA .....	43
2.3.4	Implementation of DFT.....	45
2.4	Basis sets.....	46

2.4.1	Gaussian Type Orbitals .....	47
2.4.2	Construction of Contracted Gaussian Basis Sets.....	48
2.4.3	Pople's Gaussian Basis Sets.....	49
2.4.4	Correlation Consistent Basis Sets.....	49
2.4.5	Basis Set Superposition Error.....	50
2.5	Derivatives of the Energy .....	52
2.5.1	Analytic Energy Derivatives .....	52
2.5.2	Geometric Derivatives.....	54
2.6	Molecular Properties.....	57
2.6.1	Geometry Optimisation .....	57
2.6.1.1	Partial Geometry Optimisation .....	60
2.6.2	Normal Mode Analysis.....	60
2.7	Computational Strategies for Chemical Accuracy.....	63
2.7.1	Isodesmic and Isogyric Reaction Schemes.....	63
2.7.2	Gaussian- <i>n</i> ( <i>Gn</i> ) Methods.....	65
2.7.2.1	Gaussian-1 (G1) Theory .....	65
2.7.2.2	Gaussian-2 (G2) Theory .....	67
2.7.2.2.1	G2-RAD Theory.....	68
2.7.2.3	Gaussian-3 (G3) Theory .....	68
2.7.2.3.1	G3-RAD Theory.....	70
2.7.2.4	Gaussian-3X (G3X) Theory.....	71
2.7.2.5	G3X2 Theory .....	71
2.7.3	Complete Basis Set Methods.....	72
2.8	Thermochemistry.....	75
2.8.1	Partition Functions .....	75
2.8.2	Thermodynamic Properties .....	78
2.9	Kinetics .....	79
2.9.1	Transition State Theory (TST) .....	79
2.9.2	Variational Transition State Theory (VTST) .....	81
2.9.3	RRKM Theory.....	81
2.10	Population Analysis.....	85
2.11	References.....	89

<b>3</b>	<b>Thermochemistry of Fluorocarbons.....</b>	<b>96</b>
3.1	Introduction.....	97
3.2	Theory and Computational Methods .....	100
3.3	Results and Discussion .....	105
3.3.1	Heats of Formation from G3 and Related Atomisation Energies.....	105
3.3.2	Heats of Formation from G3 and Related Isodesmic Reaction Enthalpies ...	114
3.3.3	Comparison of G2 and G3 Methods: Analysis of Atomisation Energies of Fluoromethanes.....	122
3.3.4	Heats of Formation by Complete Basis Set Coupled Cluster Calculations .....	126
3.4	Conclusion.....	130
3.5	References.....	131
<b>4</b>	<b>The Role of Phosphorus Compounds in the H + OH Recombination Reaction.....</b>	<b>136</b>
4.1	Introduction.....	137
4.2	Theory and Computational Methods .....	139
4.3	Results and Discussion .....	142
4.3.1	G2, G3, and G3X Thermochemistry .....	142
4.3.2	Reliability of G3, G3X and Related Methods .....	146
4.3.2.1	PO and G3(RAD) Procedures.....	147
4.3.2.2	Comparison with QCISD(T,Full) .....	150
4.4	Kinetic Parameters.....	152
4.5	Conclusion .....	161
4.6	References.....	162
<b>5</b>	<b>Accurate Thermochemistry of Phosphorus Compounds .....</b>	<b>165</b>
5.1	Introduction.....	166
5.2	Theory and Computational Methods .....	167
5.3	Results and Discussion .....	172
5.3.1	CCSD(T) Benchmark Calculations .....	172
5.3.1.1	Testing the B3LYP Geometry .....	172

5.3.1.2	Atomisation Energies and Extrapolation Schemes .....	175
5.3.1.3	Core-Valence Correlation, BSSE and Scalar Relativistic Effects .....	180
5.3.2	G3, G3X and G3X2 Calculations .....	182
5.3.2.1	Analysis of Molecules for which G3 <i>n</i> Methods Perform Poorly .....	188
5.3.2.1.1	P <sub>4</sub> .....	188
5.3.2.1.2	P <sub>2</sub> O, P <sub>2</sub> , P <sub>2</sub> H <sub>2</sub> .....	190
5.3.3	Enthalpies of Formation .....	193
5.4	Conclusion .....	196
5.5	References .....	197

## **6 The Role of the NNH + O Reaction in the Production of NO in Flames..... 201**

6.1	Introduction.....	202
6.2	Theory and Computational Methods .....	205
6.2.1	Quantum Chemical Calculations of Thermochemistry .....	205
6.2.2	Derivation of Rate Coefficients for Individual Reaction Channels.....	207
6.3	Results and Discussion .....	209
6.3.1	Quantum Chemistry.....	209
6.3.2	Potential Energy Surfaces and Reaction Paths.....	215
6.3.3	Kinetic Parameters.....	226
6.3.4	Comparison with Experiment.....	229
6.3.5	Kinetic Modelling.....	230
6.4	Conclusions.....	234
6.5	References.....	235

## **7 The Enthalpy and Mechanism of the Photolysis of CFCIBr<sub>2</sub>..... 239**

7.1	Introduction.....	240
7.2	Experimental Methods and Results .....	242
7.2.1	Methodology.....	242
7.2.2	Results .....	242
7.3	Theoretical Methods and Results.....	248
7.3.1	Methodology.....	248

7.3.2	Results .....	250
7.4	Discussion.....	251
7.5	Conclusion.....	254
7.6	References.....	255
<b>8</b>	<b>The Molecular Structure and Intra- and Inter-Molecular Bonding of PSOrn.....</b>	<b>257</b>
8.1	Introduction.....	258
8.2	Methods .....	260
8.3	Results and Discussion .....	261
8.3.1	Free (Model) Inhibitor.....	261
8.3.2	Bound (Model) Inhibitor .....	264
8.3.3	Charge Distribution and Bonding.....	271
8.3.3.1	Population Analysis .....	273
8.3.3.2	Hydrogen Bonding.....	276
8.4	Conclusion .....	280
8.5	References.....	281
<b>9</b>	<b>Conclusion.....</b>	<b>282</b>
	<b>Appendix 1 Fluorocarbons Supplementary Material.....</b>	<b>A1-1</b>
	<b>Appendix 2 Phosphorus Compounds Supplementary Material.....</b>	<b>A2-1</b>
	<b>Appendix 3 NNH + O Supplementary Material.....</b>	<b>A3-1</b>

# Chapter 1

## Introduction

Computational quantum chemistry is a cornerstone of modern theoretical chemistry. Research in this field is concerned with the description of atoms, molecules and solids at a fundamental electronic level. Such a description enables us to determine various properties of these systems through computation rather than via experiment; theoretical studies therefore provide excellent sources of information when experimental data is impossible or difficult to obtain and when additional data is required for the interpretation or confirmation of experimental results.

In this thesis the application of computational quantum chemistry to several important molecular problems is described; in particular, the calculation of accurate thermochemical data; the prediction of reaction kinetics and hence the modelling of complex chemical systems; the mapping and interpretation of molecular potential energy surfaces; and the interpretation of the nature of inter- and intra-molecular binding in various situations. Five distinct problems have been investigated in this work: the thermochemistry of fluorocarbons; the flame chemistry of small phosphorus containing molecules and also of diazenyl (NNH); the photodissociation of CFCIBr<sub>2</sub>; and finally the elucidation of the structure of the inhibitor *N*<sup>δ</sup>-(*N*'-Sulfodiaminophosphinyl)-L-ornithine (PSOrn) when bound to the enzyme ornithine transcarbamoylase (OTCase) and the source of its extremely high binding constant. In the course of this research we have also investigated the accuracy and reliability of a range of computational schemes for the calculation of thermochemical data and proposed several modifications which are intended to provide either improved accuracy or a reduction in computational expense.

With the introduction of the Montreal Protocol limiting the use of chloro- and bromo-fluorocarbon molecules (CFC's and BFC's), interest has turned to fluorocarbons themselves as potential replacements for use as fire retardants.<sup>1-6</sup> While fluorine atoms do not act catalytically to quench flames (unlike Cl and Br), their strong binding to hydrogen does result in rapid flame extinguishment. As this process is not catalytic, fluorine rich molecules, such as CF<sub>3</sub>CHF<sub>2</sub>CF<sub>3</sub> and C<sub>3</sub>F<sub>6</sub>, are favoured for this purpose.<sup>4-6</sup> Consequently, these species have been the subject of a number of recent shock tube experiments in order to elucidate their reaction and decomposition mechanisms.<sup>7-9</sup> Although experimental and/or theoretical thermochemical data have been reported for many of the species involved in these reactions, for some molecules, including CF<sub>3</sub>CHF<sub>2</sub>CF<sub>3</sub> itself, prior to this work there were no data

available while for others the precision was relatively low. We have used the G3 method (and two approximate versions thereof) to calculate the molecular energies and heats of formation for a set of  $\sim 120$  C<sub>1</sub> and C<sub>2</sub> fluorocarbons and oxidised fluorocarbons as well as CH<sub>3</sub>CHCH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>, CF<sub>3</sub>CFCF<sub>2</sub> and CF<sub>3</sub>CHF<sub>2</sub>. The use of isodesmic reaction schemes in order to improve the accuracy of these data was also investigated. The results are reported and discussed in **Chapter 3**, along with more accurate CCSD(T)/CBS calculations for several selected molecules for which the G3 results differed significantly from experimental values. These CBS calculations have confirmed the accuracy of the G3 heats of formation.

Phosphorus containing molecules have also been proposed as potential fire retardants;<sup>10</sup> this was largely inspired by the work of Twarowski<sup>11-14</sup> who showed that catalytic amounts of the decomposition products of phosphine could catalyse the recombination of H and OH radicals. Two reaction schemes were proposed to explain this catalysis; these involve the recombination of either H or OH with a PO<sub>2</sub> radical to give HOPO or HOPO<sub>2</sub> respectively, followed by abstraction by a hydrogen atom to regenerate the catalytic PO<sub>2</sub> and release water or H<sub>2</sub>. Unfortunately, at the time of Twarowski's investigation the available experimental and theoretical thermochemical data was not sufficiently accurate to allow the reliable prediction of relative reaction rates. The work presented in **Chapters 4** and **5** describes the use of G2, G3, G3X and CCSD(T)/CBS type schemes to calculate accurate thermochemical data for the molecules involved in these catalytic cycles and the subsequent prediction of reliable reaction rates for the catalysis. As phosphorus is a second row element, larger basis sets and more extensive calculations (higher levels of theory) are required than for first row elements in order to obtain a comparable level of accuracy. Given the paucity of reliable experimental data, the accuracy of computational schemes such as G2, G3 and G3X for phosphorus containing molecules could not be assessed without the generation of a theoretical benchmark, namely the CCSD(T)/CBS results. As this method represents the highest level of quantum chemical theory currently available for this class of molecules, the resulting thermochemistry is important not only as a benchmark against which the performance of G2<sup>15</sup>, G3<sup>16</sup>, G3X<sup>17</sup> and G3X2<sup>18</sup> (proposed as an improvement on G3X) may be assessed but also as a valuable resource for any future studies of phosphorus compounds.

The flame chemistry of nitrogen compounds is also of considerable recent interest, in particular with respect to the production of nitrous oxides, NO<sub>x</sub>. These species act as

pollutants in the atmosphere, and thus, as for CFC's and BFC's, they have attracted restrictions on the amounts which can be vented into the environment. The development of systems which minimise the generation and release of NO<sub>x</sub> requires accurate modelling of nitrogen flame chemistry. While NO production via the thermal, prompt-NO, N<sub>2</sub>O and fuel-NO routes has been recognised for some time<sup>19</sup>, more recently another source of NO, from the reaction of NNH with oxygen atoms, has been proposed<sup>20</sup>. Although several thermochemical calculations and modelling studies have been reported for relevant reactions of this system,<sup>20-23</sup> some potentially important reaction channels were not considered. This means that the results of the modelling studies reported to date may not be reliable, which could, at least in part, account for the apparent overprediction of NO production observed in several modelling studies.<sup>24,25</sup> **Chapter 6** describes a thorough investigation of the NNH + O potential energy surface, including: the identification of all stationary points and potential reaction paths; accurate calculations of thermochemical data at each stationary point; and mapping of the PES along each of the reaction coordinates. The rates for each of these reactions were then calculated using transition state theory and RRKM, followed by modelling studies to determine the importance of this route for NO production in combustion systems.

As noted earlier, the use of bromofluorocarbons has been limited by the Montreal Protocol due to the activity of the bromine atoms (produced by combustion or by UV photolysis in the atmosphere) in depleting stratospheric ozone. The photolysis mechanisms of these species are thus of considerable interest. It has been observed that some halomethane species, namely CF<sub>2</sub>Br<sub>2</sub>, CF<sub>2</sub>I<sub>2</sub> and CF<sub>2</sub>BrI, photolyse via a triple fragmentation pathway (loss of Br and/or I atoms) at relatively long wavelengths (> 200 nm)<sup>26-31</sup>; it was also noted that only the difluoromethanes appear to undergo this triple fragmentation. Recent experiments, however, have succeeded in producing CFCl from the CFCIBr<sub>2</sub> dibromomethane at a wavelength of 265 nm.<sup>32,33</sup> In order to help determine the heat of formation of CFCIBr<sub>2</sub> and to aid with the establishment of the mechanism of carbene production, G3 calculations were performed. Of particular importance was to resolve whether this photolysis can occur via a triple fragmentation pathway. The joint experimental and theoretical investigation of this problem is reported in **Chapter 7**.

PSOrn is the active component of a natural toxin, phasolotoxin.<sup>34,35</sup> This toxin is a powerful enzyme inhibitor<sup>36,37</sup>, binding to the enzyme ornithine transcarbamoylase (OTCase) with a

dissociation constant of  $1.6 \times 10^{-12}$  M at  $37^\circ\text{C}$  and  $\text{pH} = 8$ .<sup>38</sup> OTCase acts to catalyse the reaction between carbamoyl phosphate and L-ornithine to form L-citrulline and phosphate. As such it is essential for the biosynthesis of arginine in plants and microbes and acts as part of the urea cycle in mammals; such strong inhibition of the enzyme therefore results in cell death. Consequently, it is of great interest to determine the nature of this strong binding. In addition, PSOrn has a highly unusual molecular structure, containing a P-N-S linkage, thus the nature of the intramolecular bonding also warrants investigation. The X-ray crystal structure of PSOrn when bound to OTCase has recently been reported by Langley et al.<sup>38</sup> While this shows the positions of enzyme residues around the active site (and thus indicates possible hydrogen bonds between enzyme and inhibitor) hydrogen atoms themselves are, of course, not revealed. As a result there is some question over whether the nitrogen of the P-N-S linkage is protonated in a (chemically expected) amino form or deprotonated to give an imino structure. The relative stabilities of various amino and imino isomers were investigated both when bound to selected (model) enzyme residues and in the gas phase using density functional theory, specifically B3LYP/6-31G(d). Roby-Davidson population analyses were carried out in an effort to determine whether the bonds in PSOrn were single, double or semipolar and to estimate the charges carried by the atoms. The hydrogen bonding potential of some of these atoms was also investigated, so as to aid in the interpretation of the hydrogen bonding pattern observed in the crystal structure. The results of this work are presented in **Chapter 8**.

## 1.2 References

1. M. D. Nyden, G. T. Linteris, D. R. Burgess, Jr., P. R. Westmoreland, W. Tsang and M. R. Zachariah, *Flame Inhibition Chemistry and the Search for Additional Fire Fighting Chemicals in Evaluation of Alternative In-Flight Fire Suppressants for Full-Scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays*, W. Grosshandler, R. Gann, and W. Pitts, Eds.; NIST Special Publication 861; National Institute of Standards and Technology: Washington, D.C., **1994**. p. 467.
2. M. R. Zachariah, P. R. Westmoreland, D. R. Burgess, Jr., W. Tsang and C. F. Melius, *J. Phys. Chem.*, **1996**, *100*, 8737.
3. D. R. Burgess, Jr., M. R. Zachariah, W. Tsang and P. R. Westmoreland, *Prog. Ener. Comb. Sci.*, **1995**, *21*, 453.
4. O. Sanogo, J.-L. Delfau, R. Akrich and C. Vovelle, *Combust. Sci. Technol.*, **1997**, *122*, 33.
5. G. T. Linteris, D. R. Burgess, Jr., V. Babushok, M. Zachariah, W. Tsang and P. Westmoreland, *Combust. Flame*, **1998**, *113*, 164.
6. R. G. Hynes, J. C. Mackie and A. R. Masri, *Combust. Flame*, **1998**, *113*, 554.
7. R. G. Hynes, J. C. Mackie and A. R. Masri, *J. Phys. Chem. A*, **1999**, *103*, 5967.
8. R. G. Hynes, J. C. Mackie and A. R. Masri, *J. Phys. Chem. A*, **1999**, *103*, 54.
9. R. G. Hynes, J. C. Mackie and A. R. Masri, *Proc. Combust. Inst.*, **2000**, *28*, 1557.
10. J. Green, *Fire Sciences*, **1996**, *14*, 426.
11. A. Twarowski, *Combustion and Flame*, **1993**, *94*, 91.
12. A. Twarowski, *Combustion and Flame*, **1993**, *94*, 341.
13. A. Twarowski, *Combustion and Flame*, **1995**, *102*, 41.
14. A. Twarowski, *Combustion and Flame*, **1996**, *105*, 407.
15. L. A. Curtiss, K. Raghavachari, G. W. Trucks and J. A. Pople, *J. Chem. Phys.*, **1991**, *94*, 7221.
16. L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov and J. A. Pople, *J. Chem. Phys.*, **1998**, *109*, 7764.
17. L. A. Curtiss, P. C. Redfern, K. Raghavachari and J. A. Pople, *J. Chem. Phys.*, **2001**, *114*, 108.
18. N. L. Haworth, G. B. Bacskay and J. C. Mackie, *J. Phys. Chem. A*, **2002**, *106*, 1533.
19. J. A. Miller and C. T. Bowman, *Prog. Energy Combust. Sci.*, **1989**, *15*, 287.

Chapter 1. Introduction

20. J. W. Bozzelli and A. M. Dean, *Int. J. Chem. Kinet.*, **1995**, 27, 1097.
21. J. A. Harrison and R. G. A. R. MacIagan, *J. Chem. Soc. Faraday Trans.*, **1990**, 86, 3519.
22. J. L. Durant, Jr., *J. Phys. Chem.*, **1994**, 98, 518.
23. S. P. Walch, *J. Chem. Phys.*, **1993**, 98, 1170.
24. D. Charlston-Goch, B. L. Chadwick, R. J. S. Morrison, A. Campisi, D. D. Thomsen and N. M. Laurendeau, *Combust. Flame*, **2001**, 125, 729.
25. A. A. Konnov and J. De Ruyck, *Combust. Flame*, **2001**, 125, 1258.
26. P. Felder, X. Yang, G. Baum and J. R. Huber, *Israel J. Chem.*, **1993**, 34, 33.
27. T. R. Gosnell, A. J. Taylor and J. L. Lyman, *J. Chem. Phys.*, **1991**, 94, 5949.
28. J. van Hoeymissen, W. Uten and J. Peeters, *Chem. Phys. Lett.*, **1994**, 226, 159.
29. M. R. Cameron, S. A. Johns, G. F. Metha and S. H. Kable, *Phys. Chem. Chem. Phys.*, **2000**, 2, 2539.
30. M. S. Park, T. K. Kim, S.-H. Lee, K.-H. Jung, H.-R. Volpp and J. Wolfrum, *J. Phys. Chem. A*, **2001**, 105, 5606.
31. G. Baum, P. Felder and J. R. Huber, *J. Chem. Phys.*, **1993**, 98, 1999.
32. J. S. Guss, O. Votava and S. H. Kable, *J. Chem. Phys.*, **2001**, 115, 11118.
33. N. L. Owens, *Honours Thesis*, School of Chemistry, University of Sydney, **2001**.
34. A. R. Ferguson and J. S. Johnston, *Physiol. Plant Pathol.*, **1980**, 16, 269.
35. M. D. Templeton, R. E. Mitchell, P. A. Sullivan and M. G. Shepherd, *Biochem. J.*, **1985**, 228, 347.
36. R. E. Mitchell, J. S. Johnston and A. R. Ferguson, *Physiol. Plant Pathol.*, **1981**, 19, 227.
37. A. S. Bachmann, P. Matile and A. J. Slusarenko, *Physiol. Mol. Plant Pathol.*, **1998**, 53, 287.
38. D. B. Langley, M. D. Templeton, B. A. Fields, R. E. Mitchell and C. A. Collyer, *J. Biol. Chem.*, **2000**, 275, 20012.