The Atmospheric Fate of Organic Nitrogen Compounds

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Department of Chemistry
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Abstract

Organic nitrogen compounds are present in our atmosphere from biogenic and anthropogenic sources and have impacts on air quality and climate. Due to recent advances in instrumentation, these compounds are being detected in the gas and particle phases, raising questions as to their source, processing and sinks in the environment. With their recently identified role as contributors to aerosol formation and growth, their novel large scale use as solvents in carbon capture and storage (CCS) technology and their emissions from cigarette smoke, it is now important to address the gaps in our understanding of the fate of organic nitrogen. Experimentally and theoretically, I studied the chemical atmospheric fate of specific organic nitrogen compounds in the amine, amide and isocyanate families, yielding information that can be used in chemical transport models to assess the fate of this emerging class of atmospheric molecules.

I performed kinetic laboratory studies in a smog chamber to measure the room temperature rate coefficient for reaction with the hydroxyl radical of monoethanolamine, nicotine, and five different amides. I employed online-mass spectrometry techniques to quantify the oxidation products. I found that amines react quickly with OH radicals with lifetimes of a few hours under sunlit conditions, producing amides as oxidation products. My studies on amides revealed that they have much longer lifetimes in the atmosphere, ranging from a few hours to a week. Photo-oxidation of amides produces isocyanates and I investigated these mechanisms in detail using ab initio
calculations. Furthermore, I experimentally measured isocyanic acid’s Henry’s Law constant as well as its hydrolysis rate constants to better understand its sinks in the atmosphere. Finally, I re-examined the structure-activity relationship (SAR) of organic nitrogen molecules for improved model parameterizations.
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This acknowledgment section is an important part of this thesis. The research done in the past four years has been collaborative with significant contributions from my supervisors, my PhD committee and my labmates and colleagues. I must also thank a number of frontline and behind-the-scenes supporters that have helped me in the past six years. I could not have survived graduate school without any of them.

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I would like to end this section by dedicating my PhD thesis to my grandfather Georges Borduas. Over the past months, his courage and strength through his illness has inspired me beyond imagination. When I couldn’t write or lost motivation, I talked to my grandfather and he gave me perspective. This is for you Pépé Georges! Merci pour ton amour et ton support. Je suis incroyablement fière de te dédier ma thèse de doctorat.
Preface

The research presented in this thesis was accomplished with valuable input from co-authors whose individual contributions are outlined here.

Chapter 1 is the introduction chapter and was written by myself with important feedback from Prof. Jon Abbatt and Prof. Jennifer Murphy.

Chapter 2 is a journal article published in Environmental Science and Technology in 2013 [DOI: 10.1021/es401282j]. I designed the experimental approach, performed the experiments and analyzed the data for this study. Prof. Jon Abbatt and Prof. Jennifer Murphy provided critical feedback throughout the process. I wrote the manuscript, again with valuable input from both supervisors. In this chapter, I also added unpublished data concerning the analysis of imines as a product of oxidation by GC-MS and an aerosol mass spectrometer spectrum of the MEA + OH experiment.

Chapter 3 is a journal article published in Journal of Physical Chemistry A in 2015 [DOI: 10.1021/jp503759f]. I designed the experimental approach, performed the laboratory experiments and subsequently analyzed the data. Prof. Gabe da Silva from the University of Melbourne performed the theoretical study and we both analysed the outputs. I wrote the majority of the manuscript and Prof. Gabe da Silva wrote the section on the ab initio calculations. Included in this chapter is the unpublished ab initio mechanism of formamide formation from N-methylacetamide computed by Prof. Gabe da Silva.

Chapter 4 is a journal article under review in the open access journal Atmospheric Chemistry and Physics Discussions in 2015 [DOI: 10.5194/acpd-15-24217-2015]. I designed the experimental approach with critical input from Prof. Jon Abbatt and Prof. Jennifer Murphy on the Henry’s Law experimental set up and from Prof. Jennifer Murphy and Gregory Wentworth on the ion chromatography method. I undertook the Henry’s Law experiments and Bryan Place conducted the HNCO hydrolysis experiments. I analysed the data from both sets of experiments and wrote the manuscript with feedback from all co-authors.

Chapter 5 is an ongoing project aimed at calculating the mechanisms of a range of organic nitrogen species to the goal to rewrite SAR group rate constants and substituent factors for this class of compounds. I performed the ab initio calculations on the Edward cluster at the University of
Melbourne. I analysed the data with feedback from Prof. Gabe da Silva, Prof. Jon Abbatt and Prof. Jennifer Murphy. I wrote this chapter with critical comments from Prof. Jon Abbatt and Prof. Jennifer Murphy.

Chapter 6 has yet to be drafted as a journal article. The design, kinetics and product study experiments and theoretical calculations were accomplished by me. The cigarette smoke study was conducted with the help of Dr. María Antiñolo, who also built the smoking machine set up and made Figure 6-1. I did the data analysis and wrote the chapter with important feedback from Prof. Jon Abbatt and Prof. Jennifer Murphy.

Chapter 7 is the conclusion chapter and was written by myself with critical comments from Prof. Jon Abbatt and Prof. Jennifer Murphy.
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1 Chapter 1

1.1 Introduction

Atmospheric chemistry research strives to characterise the properties of gas and particle phase molecules to better predict their impact on air quality and climate change. Once pollutants are emitted into the atmosphere, whether it be from natural or industrial sources, they may undergo a wide range of processes. Through laboratory experiments, we endeavor to study reactive processes in a controlled environment to elucidate mechanistic pathway and chemical outcomes. Understanding these reactions allows atmospheric chemists to condense this information into chemical transport models and predict the fate of pollutants. Another important component of atmospheric chemistry research is the direct measurement of pollutants in the atmosphere. Attempts are then made to match measurements with laboratory understanding of pollutant’s chemical fate to subsequently compare to model predictions. These three pillars of atmospheric science, laboratory, modeling and field studies, are essential in our comprehension of the atmosphere and have implications for air quality as well as climate science.¹

The research presented in this thesis addresses one of these pillars of atmospheric chemistry: laboratory investigations. We focus on a particular class of compounds, i.e. organic nitrogen. In the past decade, there has been an increase in field measurements of organic nitrogen from biogenic and anthropogenic sources and they are now starting to be represented in chemical transport models. However, there currently is a lack of understanding of how organic nitrogen molecules are processed in the environment and what their ultimate fate is. We contribute to the advancement knowledge on this class of compounds through experimental and theoretical work presented in this thesis.

1.2 Organic nitrogen compounds

The global biogeochemical cycle of nitrogen is vital to life on earth and governs important environmental processes.² The Earth’s atmosphere is the most abundant reservoir of nitrogen,
composed of 80% dinitrogen N\(_2\), which is mostly unavailable to organisms since dinitrogen has a strong triple bond and is thus unreactive. Nitrogen is present in amino acids, proteins and nucleic acids, molecules which sustain life. It is incorporated into biomolecules through microorganisms able to fix dinitrogen and to make it bioavailable. In the industrial world, it is the Haber-Bosch process which dominates the conversion of dinitrogen into ammonia for use as fertiliser worldwide.\(^3\) Ammonia, along with nitrogen oxides, are key atmospheric molecules in the context of air quality and climate change.\(^4,5\) However, organic nitrogen are expected to behave differently to ammonia and nitrogen oxides.

Organic nitrogen molecules by definition contain at least one carbon and one nitrogen atom. Hydrogen cyanide is therefore the smallest organic nitrogen compound present in the atmosphere. Molecules with functional groups such as amines, amides, aromatic nitrogen, carbamates, imines, isocyanates, nitramines, nitrosamines, nitriles and organic nitrates are prominent examples of organic nitrogen compounds (Figure 1-1). These molecules have been detected in the atmosphere and each have particular sources, processes and sinks which will be reviewed in this chapter.

We are interested in studying organic nitrogen compounds as they are an emerging class of pollutants in the atmosphere. Recent advances in measurement techniques have allowed for their quantification in ambient air, prompting atmospheric chemists to wonder why they are there and what happens to them in the atmosphere.\(^6\) In addition, the role of amines in new particle formation and particle growth has become an intensive area of research as particles have a large impact on climate through acting as cloud condensation nuclei and affecting the planet’s radiative balance.\(^5,7,8\) Indeed, amines may nucleate particles through acid-base reactions or contribute to the formation of secondary organic aerosol (SOA).\(^9,10\) Furthermore, organic nitrogen and specifically aminoalcohols are being used on an unprecedented scale in carbon capture and storage (CCS) technology. Certain organic nitrogen compounds are also toxic and carcinogenic and present a health concern, like isocyanates, nitramines and nitrosamines. Based on the aforementioned reasons, it is now recognized that a molecular-level understanding of how organic nitrogen compounds react in the environment is needed to allow scientists to develop models to predict their impact on air quality and climate. We present our own efforts towards this goal in chapters 2 to 6.
Organic nitrogen in ambient air

Organic nitrogen molecules have been identified and measured in ambient air, and a recent review by Ge et al. comprehensively tabulated these values (see Table 4 in Ge et al.). Mixing ratios vary from below pptv up to ppmv levels depending on the molecule, location, time of day and meteorology. The most frequently made measurements of organic nitrogen molecules are of amines. Mixing ratios of amines have been reported to be higher in rural areas (for example up to 40 pptv for trimethylamine) than in urban environments (up to 6 pptv for trimethylamine), since amines originate from agricultural activity and livestock operations. Zheng et al. recently reported average mixing ratios of 7.2 pptv for total amines quantified in a suburban site in Nanjing, China and saw concentration correlations with ammonia mixing ratios. Mixing ratios of alkylamines in coastal areas has also been observed up to 10 pptv at a German location and up to 2 pptv in Hawaii. Gas phase measurements at the CO$_2$ Technology Center Mongstad (TCM) in Norway over the stripper of a CCS plant included concentrations of monoethanolamine (MEA).
up to 10 ppbv, pyrazine up to 300 ppbv, and nitromethane up to 800 ppbv.\textsuperscript{17} Amides have very few reported ambient measurements but have been detected from cigarette smoke and gas phase nicotinamide has been measured in concentrations of 20 $\mu$g per smoked cigarette.\textsuperscript{18,19} N,N-Dimethylformamide has been measured up to 400 pptv near a waste water treatment plant.\textsuperscript{20} Isocyanic acid has recently been measured in the atmosphere and may have concentrations reaching 1 ppbv in rural areas impacted by biomass burning.\textsuperscript{21} Quantified ambient measurements of gas phase imines, nitramines and nitrosamines are lacking.

When organic nitrogen is quantified in both the gas and particle phases, the majority is typically found in the particle phase and often in the water soluble fraction of particles.\textsuperscript{6,7} For example, the concentration of aliphatic amines contributing to dissolved organic nitrogen in rainwater has been estimated to be $< 1$-$14$ nmol N m$^{-3}$.\textsuperscript{22} In Northern California, total organic nitrogen accounted for $\sim 13$% and $\sim 10$% by mass of the dissolved organic carbon in fog waters and in PM$_{2.5}$, respectively.\textsuperscript{23} In the MILAGRO field campaign in Mexico City, organic nitrogen was found to account for $\sim 9$% of organic aerosol mass as measured by aerosol mass spectrometry, and was thought to arise from local sources.\textsuperscript{24} Recently, Zhang et al. reported organic nitrogen mass contributions to PM$_{2.5}$ of 20 – 30% in Beijing, one of the most populated and polluted cities in the world.\textsuperscript{25} In Birmingham, England, Ozel et al. identified (but did not quantify) 114 organic nitrogen compounds ranging in functionality and structure in ambient aerosol, including nitriles, amides, amines, and nitro compounds.\textsuperscript{26} In downtown Toronto, VandenBoer et al. found alkylamine particulate concentrations up to 15 ng m$^{-3}$.\textsuperscript{27} Observations were made in Finland’s Hyttilälä Forest of aminium salts (23% of detected positive ions) present during new particle formation.\textsuperscript{28} Also, aminium salts have been measured over the North Atlantic Ocean in concentrations up to 56 ng m$^{-3}$.\textsuperscript{29} This subset of particle phase organic nitrogen identification and quantification field studies showcases the presence of organic nitrogen in our atmosphere in concentrations sufficient to impact particle phase chemistry. Reviews on particle phase organic nitrogen have been made by Cape et al., Qi et al., Ge et al. and Nielsen et al.\textsuperscript{6,7,11,30}

Ambient measurements of organic nitrogen molecules are complicated due to their basic (amines for example) or acidic (isocyanic acid and hydrogen cyanide for example) natures and thus to their ability to readily deposit and stick on surfaces. Sampling procedures specific to amines and organic nitrogen acids have been previously developed\textsuperscript{17,31-33} and our methods to avoid wall loss, sampling loss and heterogeneous chemistry are addressed individually in each chapter. Despite operational
difficulties in quantification, there is now a clear appreciation that organic nitrogen species are indeed present in ambient air, and have high enough concentrations to impact atmospheric processes, validating further study.

1.2.2 Health impacts

There is added interest in understanding the fate of organic nitrogen as some types of compounds are toxic to human health. The toxicology of organic nitrogen molecules has recently been reviewed and we present here a brief overview of some of the molecules relevant to this thesis. For example, the amine studied in Chapter 2 is monoethanolamine (MEA) which has a short term exposure limit of 6 ppmv and a time weighted average exposure limit of 3 ppmv in Canada. It also has a LD50 (lethal dose leading to 50 percent kill) of 1720 mg kg\(^{-1}\) in rats when taken orally. MEA can cause increases in intrauterine deaths, malformations, and slower intrauterine growth in rats depending on the dosage. This substance is destructive to the tissue of the mucous membranes and upper respiratory tract and inhalation should be avoided. Furthermore, MEA is soluble in water and may have significant negative impacts on aquatic ecosystems. In particular, this alcohoholamine is toxic to fish and the LD50 in Pimephales promelas (fathead minnow) was found to be 227 mg/l in 96 h. MEA may also be toxic to aquatic invertebrates and algae.

Nitrosamines and nitramines (see Figure 1-1 for structures) are known carcinogens and are formed via the photo-oxidation of alkylamines in the presence of NO\(_x\), particularly at night. Studies of the mutation frequencies of alkyl nitrosamines and alkyl nitramines relative to the parent amine on ribosomal DNA concluded that these compounds could be linked to cancer in testicular tissue. These compounds are short-lived in the presence of sunlight and are not expected to accumulate in the atmosphere but recent exposure concerns have been highlighted in the implementation of carbon capture and storage (CCS) technologies.

HNCO is also a known toxin and has been observed to cause protein carbamylation leading to cardiovascular disease, rheumatoid arthritis and cataracts. Exposure levels through biomass burning and diesel exhaust are currently of concern. Methyl isocyanate is a major health concern and was responsible for the death of thousands of residents in Bhopal, India during a methyl isocyanate leak from a nearby pesticide plant in 1984.
Organic nitrogen, particularly amines, are also known to contribute to the nucleation and formation of atmospheric particles which have known health hazards. Exposure to particulate matter through inhalation causes cardiovascular and cerebrovascular diseases and is ranked the 13th leading cause of mortality worldwide.\textsuperscript{55,56} The brief summary of organic nitrogen toxicology presented here validates the interest in studying the fate of these compounds in our environment.

### 1.3 Sources

Organic nitrogen compounds are emitted from both biogenic and anthropogenic sources.\textsuperscript{6,11} Natural sources of amines include oceans, biomass burning, vegetation and geological sources. Alkylamines are generally products of amino acid biodegradation and so plants, animals and vegetation all contribute to the emission of volatile alkylamines.

There are numerous anthropogenic sources of organic nitrogen. The recent review by Ge et al. highlights major sources which include livestock, tobacco smoke, polymer combustion industry, textile floor coverings, corrosion inhibitors, tire and car repair and sewage.\textsuperscript{11} In particular, Schade et al. estimated the annual alkyl-amine input from animal husbandry to the atmosphere to be 0.15 Tg N annum\textsuperscript{-1}.\textsuperscript{14} Cattle, sheep and swine excrete nitrogen-containing compounds mostly in the form of urea.\textsuperscript{57} Volatile amines are also produced via decarboxylation of amino acids.\textsuperscript{58} For example, the decarboxylation of serine yields MEA and carbon dioxide. This reaction occurs in the gastrointestinal tract of the animals and higher levels of alkylamines are detected during the storage of fresh manure.\textsuperscript{14} The water solubility (log$K_{ow}$ at 25 $^\circ$C = -1.31) property of MEA has applications in detergents and emulsifiers.\textsuperscript{59} Meat cooking has also been shown to contribute to atmospheric amide concentrations.\textsuperscript{60} Carbon capture and storage (CCS) is an emerging source of amines to the atmosphere and due to its relevance to Chapter 2 is described in more detail below. In addition, we further describe tobacco smoke as an atmospheric source of organic nitrogen as it pertains to Chapter 6.

#### 1.3.1 Carbon Capture and Storage (CCS)

The fastest growing industrial use of amines is in CO\textsubscript{2} capture and storage technology.\textsuperscript{30} With increasingly demanding environmental regulations, coal power plants are turning to CO\textsubscript{2} sequestration to reduce their greenhouse gas emissions.\textsuperscript{61-63} The overarching goal of the CCS technology is to capture the CO\textsubscript{2} emissions instead of releasing this greenhouse gas to the
atmosphere and returning it underground. A recent analysis by Cuellar-Franca et al. suggest that the global warming potential reduction from CCS implemented to a coal power plant could be as high as 82%. There exist many types of CCS approaches including the pre- and post-capture processes as well as the use of solvents, membranes and polymers. Underground storage of the sequestered CO$_2$ includes depleted gas reservoirs, salt caverns and the saline aquifer. The captured CO$_2$ can also be used to enhance oil and gas recovery by creating high pressures in the oil and gas reservoirs. In 2009, Atmospheric Degradation of Amines (ADA), an organization in Norway in collaboration with the Norwegian Institute for Air Research (NILU), was formed to assess and report on the atmospheric fate of amines from CCS facilities (http://ada.nilu.no). Pilot coal power plants integrating CCS technology were being built in Norway and environmental concerns were raised as to the unknown fate of the CO$_2$-capturing amines in the atmosphere.

Post-capture CCS technology requires aqueous solutions of amines, especially alcoholamines, to reversibly react with CO$_2$ and form a carbamate intermediate (Scheme 1-1). The carbamate salts precipitate and so only N$_2$ and water vapour are emitted into the atmosphere from the top of the absorption column. The carbamate salts are then transferred to the stripper where heat is applied to decarboxylate and to regenerate the CO$_2$ and the amine (reverse reaction in Scheme 1-1). The recovered amine in the stripper is transferred to the reboiler where it is heated and separated from any by-products and impurities to then be recycled back to the absorber column. Pure CO$_2$ formed in the stripper is compressed and transported to a storage site. In a typical CCS plant, between 300 to 1000 tons of amines are used to remove 1 million tons of CO$_2$ per year. Such large quantities of amines concentrated in one area of industrial usage creates large potential risks for the environment. Amine leakage (estimated at 40 to 160 tons per year) can occur at different stages of the CO$_2$ sequestration method and once in the atmosphere may react with oxidants and nitrogen oxides to form carcinogens such as nitramines and nitrosamines. This accidental release of amino compounds into the environment continues to be the subject of assessment studies to fully appreciate the impact of CCS technology on ecosystems.

Alkylamines are also employed as corrosion inhibitors, predominantly in steam boiler systems. The amines are present in the steam from the boiler and neutralize the acidity of the gas by reacting with carbon dioxide and sulfur dioxide (as in Scheme 1-1). This process minimizes corrosion of iron in heaters and in pipes from these gases. A study in a room humidified by steam from a boiler
system identified mixing ratios of 0.7-2.4 ppb of alkylamines in the indoor air and found that their fate was mostly deposition to surfaces.\textsuperscript{70}

\begin{equation*}
\text{HO-} \text{NH}_2 + \text{CO}_2 \text{ (g)} \xrightleftharpoons{\Delta} \text{HO-} \text{NH-} \text{COOH}
\end{equation*}

\textbf{Scheme 1-1: Reaction of MEA with CO\textsubscript{2} to form a carbamate}

\subsection*{1.3.2 Cigarette smoke}

Smoking cigarettes and inhaling cigarette smoke have well-documented serious negative health consequences for populations worldwide.\textsuperscript{71} There are three types of exposures to cigarette smoke: mainstream smoke, inhaled by the smoker, sidestream smoke (also referred to as second-hand smoke), emitted from the tip of a cigarette, and third-hand smoke, emitted from surfaces previously exposed to cigarette smoke.\textsuperscript{72} From an atmospheric chemistry perspective, we are interested in the fate of the sidestream smoke and how it is aged in an indoor environment. Sidestream emissions also exceed mainstream emissions, thus from an environmental point of view, it is important to accurately characterise the former.\textsuperscript{73} The combustion of tobacco is analogous to biomass burning, but differs since it is more relevant to indoor air chemistry.

Many organic nitrogen compounds are present in tobacco, as well as emitted during smoking, including C1-C8 alkylamines (up to 4.6 µg in smoke per cigarette), aromatic amines (up to 1.2 µg in smoke per cigarette), N-heterocyclic compounds (up to 218 µg in smoke per cigarette), amino acids, nitriles, nitroso-compounds including nitrophenols, nitrosamines and amides.\textsuperscript{18} Nicotine is the major organic nitrogen compound emitted in tobacco smoke with quantities up to 3000 µg in smoke per cigarette, accounting for \(\sim 1.5\%\) of a cigarette’s weight.\textsuperscript{18,73-75} Despite variability in tobacco harvests and cigarette brands, tar and nicotine levels in sidestream smoke are comparable regardless of whether they come from medium-, low-, or ultra-low tar cigarettes.\textsuperscript{76} Nicotine is a known health hazard and causes addiction, but is also used as a therapeutic for Parkinson’s and Alzheimer’s disease as well as a probe drug for phenotyping cytochrome P450 2A6 (CYP2A6), an oxidase enzyme in all domains of life.\textsuperscript{75}

Nicotine is expected to be rapidly removed by sorption to indoor surfaces, but may be re-emitted during ventilation, leading to concentrations of up to \(\sim 10\%\) of those observed during the smoking
phase. Nicotine emission factors from surfaces on which it was adsorbed are highly surface type dependant, but measured adsorption rate coefficients range from $1.5 \text{--} 6 \text{ h}^{-1}$. The sorbed nicotine and another cigarette smoke components can then contribute to third hand smoke exposure. Surprisingly, its rate coefficient with OH radicals has yet to be investigated and is thus addressed in Chapter 6. In an indoor environment, even with fewer OH radicals than outdoors, nicotine’s reactivity with OH radicals may still be competitive with deposition and air exchange rates. Furthermore, gas phase nicotine emissions from e-cigarettes and water pipes, where fewer particles are generated, may be more important than from tobacco cigarettes. Nicotine, as well as sorbed nicotine, can also contribute to the formation of secondary organic aerosol (SOA) through reaction with ozone. These recent studies raise concerns about exposures to second and third hand smoke.

1.4 Processing and sinks

Once emitted into the atmosphere, organic nitrogen compounds may undergo a variety of processes which ultimately lead to their removal. If the organic nitrogen is volatile, it may undergo oxidation via OH radicals, ozone, NO$_3$ radicals and/or Cl radicals as well as photolysis. Amines may also contribute to cluster formation and nucleate particles in the presence of other precursors or partition to existing particles and contribute to particle growth. The gas and particle phase processing of organic nitrogen is briefly reviewed in the following sections.

1.4.1 Fate through gas phase processing

1.4.1.1 By oxidation

Nitrogen-containing molecules react with atmospheric oxidants with rate coefficients that are functional group dependent: on the order of $10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for amines, $10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for amides and $10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for isocyanic acid. Reports of organic nitrogen’s gas phase fate have been relatively scarce in the literature until relatively recently. Among the first reported rate coefficients for organic nitrogen were for hydrazines and nitriles. The first published rates of reactions of amines with OH radicals were by Harris and Pitts in 1983. They studied the photo-oxidation 2-(dimethylamino)ethanol and 2-amino-2-methyl-1-propanol and found that their rate coefficient translated to lifetimes on the order of 2-4 hours. Their study was motivated by paint coating solubilizer applications and policy regarding solvent emissions in California at the time.
One of the most studied amine is MEA as it is currently the industrial solvent used to capture CO\textsubscript{2} in CCS. Its relative rate coefficient has been measured by Karl et al, Onel et al. and in this work (Chapter 2), employing different methods that consistently find a rapid rate coefficient equating to a lifetime of \(\sim 1\text{-}2\) hours in the atmosphere.\textsuperscript{88-90} Experimental and theoretical product studies support the conclusion that most of the reactivity of MEA occurs on the carbon backbone via C–H abstraction mechanisms.\textsuperscript{88,90-92} Carcinogenic nitramines have also been detected as a product of oxidation from MEA.\textsuperscript{91} Surface losses (chamber inlet, chamber wall, tubing) and particle losses of MEA have been addressed using the chamber aerosol model MAFOR (marine aerosol formation model) and found to be significant, \(\sim 20\%\).\textsuperscript{93} Karl et al. combine experimental and modeling studies to propose a series of reactions for the OH radical-initiated oxidation of MEA (Scheme 1-2). The major product of the photo-oxidation of MEA is the C2-peroxy radical of MEA. This compound can further react with NO to yield the C2-alkoxy radical. The fate of the C2-alkoxy radical depends on the presence/absence of oxygen, and can react with the latter, and form 2-hydroxyacetamide or fragment and generate formamide and formaldehyde. In addition, nitrosamines and nitramines may be formed from the N-centered MEA radical formed via N–H abstraction.

The gas phase reactions of some aminoalcohols with ozone have been investigated. Of particular interest, the absolute rate constant of 2-(dimethylamino)ethanol was determined to be \((6.76 \pm 0.83) \times 10^{-18}\) cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} by in situ FT-IR spectroscopy, a rate ten times slower than that of \(\alpha\)-pinene with ozone for comparison.\textsuperscript{94} Detected products of oxidation were amides and \(N\)-oxides and fragmentation products were formamide and formaldehyde. At a typical mixing ratio of ozone of 30 ppbv, the lifetime of amines is on the order of a week. The ozonation of amines would therefore only be expected to be of significance at high latitudes in the winter time when OH radicals are scarce. The reaction of ozone with amides is predicted to be \(< 10^{-20}\) cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} based on measurable loss above wall loss.\textsuperscript{95}

Nielsen et al. measured a rate coefficient for the reaction of NO\textsubscript{3} radicals with \(N,N\)-diethylamine to be \(5 \times 10^{-13}\) cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}.\textsuperscript{69} The reaction of amides with NO\textsubscript{3} radicals is an order of magnitude slower.\textsuperscript{96,97} Assuming a nighttime NO\textsubscript{3} radical concentration of \(10^8\) molec cm\textsuperscript{-3}, the characteristic time for the atmospheric removal of amines and amides will be 6 hours and 2 days respectively. NO\textsubscript{3} radical chemistry may therefore be a competitive nighttime sink for amines.
Very recently, the first rate coefficient of amines with the chlorine radical has been investigated. Nicovich et al. investigated the fate of methyl-, dimethyl- and trimethyl-azines against Cl and found very fast rate constants, $3-4 \times 10^{-10}$ cm$^3$ molec$^{-1}$ s$^{-1}$. There are also a few published rate coefficients for the reaction of amides with the Cl radical, and they proceed with rates from $4-25 \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$. However, as Cl radical concentrations are typically present in 1-10% of OH radical concentrations, Cl is unlikely to be a competitive sink for amines and amides.

\[
\text{H}_2\text{N}(-\text{CH}_2\text{OH}) + \cdot \text{OH} \quad \xrightarrow{\text{O}_2} \quad \begin{array}{c}
\cdot \text{O} - \text{O} - \text{OH} \\
\text{H}_2\text{N}(-\text{CH}_2\text{OH}) + \cdot \text{H}_2\text{N}(-\text{CH}_2\text{OH}) + \cdot \text{O}_2\text{H}
\end{array}
\]

80% 15% 5%

2-aminoacetaldehyde

\[
\text{H}_2\text{N}(-\text{CH}_2\text{OH}) + \text{NO} \quad \xrightarrow{} \quad \begin{array}{c}
\cdot \text{O} - \text{OH} \\
\text{H}_2\text{N}(-\text{CH}_2\text{OH}) + \text{NO}_2
\end{array}
\]

\[
\text{H}_2\text{N}(-\text{CH}_2\text{OH}) + \text{O}_2 \quad \xrightarrow{} \quad \begin{array}{c}
\cdot \text{O} - \text{O} - \text{OH} \\
2\text{-hydroxyacetamide}
\end{array}
\]

\[
\text{H}_2\text{N}(-\text{CH}_2\text{OH}) \quad \xrightarrow{} \quad \begin{array}{c}
\cdot \text{O} - \text{H} \\
\text{H}_2\text{N}(-\text{CH}_2\text{OH}) + \text{H}_2\text{O}
\end{array}
\]

formamide

\[
\text{H}_2\text{N}(-\text{CH}_2\text{OH}) + \text{NO} \quad \xrightarrow{} \quad \begin{array}{c}
\cdot \text{O} - \text{N} - \text{H} - \text{O} - \text{OH} \\
N-(2\text{-hydroxyethyl})\text{nitrous amide}
\end{array}
\]

\[
\text{H}_2\text{N}(-\text{CH}_2\text{OH}) + \text{NO}_2 \quad \xrightarrow{} \quad \begin{array}{c}
\cdot \text{O} + \cdot \text{N} - \text{H} - \text{O} - \text{OH} \\
N-(2\text{-hydroxyethyl})\text{nitramine}
\end{array}
\]

**Scheme 1-2: OH-initiated oxidation of MEA (adapted from Karl et al.)**

1.4.1.2 By photolysis

The photolysis of organic nitrogen compounds is relatively unknown in the actinic region, where amines, amides and isocyanates are not expected to photolyse. However, nitrosamines are readily photolysed in sunlight with an estimated lifetime under an hour. It is their N–N bond which make this class of organic nitrogen molecules so photolabile. Photolysis is hence only an appreciable sink for nitrosamines and nitramines.
1.4.2 Particle nucleation and phase partitioning

Nitrogenated bases play a role in particle nucleation and growth; this topic has recently been reviewed by Qiu et al. looking at the multiphase chemistry of organic nitrogen. There is particular interest in understanding the formation mechanism, the size distribution and the number distribution of particles worldwide as they are important climate forcers as well as health hazards. Atmospheric aerosols from biogenic and anthropogenic sources directly scatter the Sun’s incoming radiation or indirectly affect the Earth’s radiative balance by acting as cloud condensation nuclei. Recently, Zhang et al. reviewed the nucleation and growth of nanoparticles in the atmosphere, highlighting conflicting experimental, theoretical and field studies and suggesting the role of organic nitrogen in achieving some reconciliation. Indeed, amines have been shown to enhance particle formation rates with sulfuric acid more than a thousand times compared to ammonia at mixing ratios as low as 3 pptv and are thus important to take into consideration when modelling particle formation. Amines may contribute to particulate matter via three types of mechanisms, oxidation and condensation, acid-base reactions, and partitioning. Gaseous amines can be oxidized to form imines and/or amides, forming more polar substrates with lower vapour pressures. Due to the basicity of amines, they may participate in acid-base reactions with acidic aerosols and contribute to the particle’s nucleation and/or growth. Furthermore, amines may dissolve into the particles by diffusion playing a part in the formation of secondary organic aerosols (SOA).

Amines also contribute to particle transformation of submicron particles, altering the physiochemical properties of particles, including hygroscopicity, thermostability, density, phase, and optical properties. Ge et al. summarized the thermodynamic properties of amines and conclude that amines have a similar or greater tendency to partition to the particle phase than ammonia. Soluble organic nitrogen can participate in cloud-mediated reactions. Nielsen et al. have tabulated the experimental rate coefficients for OH radical reactions with amines in water at a variety of pH values and find that rate constants range from $10^8$ to $10^{10}$ M$^{-1}$ s$^{-1}$. OH radicals in cloud water are thus a very efficient sink for amines. In addition, recent studies have identified the presence of organic nitrogen compounds in brown carbon, atmospheric particles which absorb visible light and thus impact climate, recently reviewed by Laskin et al.
Understanding the involvement of organic nitrogen compounds, specifically amines, in particle nucleation and phase partitioning remains an important. Although particle formation and growth mechanisms are not addressed in this thesis, they serve as further motivation for better understand the gas phase chemistry of organic nitrogen presented in the subsequent chapters.

1.5 Methods

The methods employed throughout this thesis are now standard methods in atmospheric chemistry. Thus, only a brief overview is provided here for the instrumentation, the kinetic work, the theoretical methods and the predictive model. Further considerations specific to each project are detailed in the methods section of each chapter.

1.5.1 Instrumentation

1.5.1.1 Online mass spectrometry

Proton-transfer-reaction mass spectrometry (PTR-MS) allows for the online measurement of VOCs which have a proton affinity higher than that of water. Organic nitrogen compounds are polar and so are conveniently detected by PTR-MS with 3σ detection limits ranging from 1-15 ppbv. PTR-MS was first developed in the lab of Prof. Werner Lindinger from the University of Innsbruck and is now commercialised by Ionicon Analytik GmbH, Innsbruck Austria. Briefly, the instrument houses an ion source which consists of a flow of water vapour passing through a hollow cathode creating an intense source of hydronium ion, H₃O⁺. This flow of H₃O⁺ is transported to the drift tube where it reacts with the flow of analyte. For the detection of organic nitrogen we decreased the drift tube voltage from 600 V to 545 V to reduce the ion kinetic energy and thus limit fragmentation of the organic nitrogen, since we were observing loss of NH₃ in our experiments with amines. A fraction of the ions exiting the drift tube is then extracted into a quadrupole mass spectrometer. The majority of the experiments presented in this thesis were done using the selected ion mode with dwell times ranging from 250-500 ms. The scan mode was used in preliminary and control experiments. The interpretation of PTR-MS spectra involves normalizing the data to m/z 21, which is the O¹⁸ isotope of H₂O⁺.

Another important mass spectrometry technique employed throughout this thesis is chemical ionization mass spectrometry (CIMS). We had access to two types of CIMS: a high resolution time-of-flight CIMS operating in PTR and negative-ion proton transfer (NI-PT) modes (Aerodyne
Research Incorporated, Billerica, MA, USA), as well as a home-built quadrupole instrument operating solely in NI-PT mode (detection limit ~ 1 ppbv).\textsuperscript{32,111-114} A CIMS instrument typically consists of four separate chambers: the ion molecular region (IMR), the collisional dissociation chamber (CDC), the intermediate chamber (IC) and the multiplier chamber (MC).\textsuperscript{115} The analytes entering the CIMS through the inlet’s pinhole react with the reagent ion, generated by passing nitrogen through a polonium-210 source. The ions are subsequently transported through two subsequent octopoles in the CDC and IC chambers. They are then detected by either a time-of-flight or a quadrupole mass spectrometer. Data manipulation was conducted in the IGOR Pro software program for all mass spectrometry data.

The PTR-MS and CIMS are complementary methods. In the PTR-MS, the reagent ion is almost exclusively \(\text{H}_3\text{O}^+\) which allows for higher sensitivity. The CIMS has the advantage of being a switchable reagent ion instrument and we have exploited this capacity in using \(\text{H}_3\text{O}^+\), acetate ion and iodide ion to detect a range of different types of functional groups. Clustering occurs more readily in a CIMS instrument (since it does not have a drift tube) which complicates quantification of ions.

1.5.1.2 Ion chromatography

Ion chromatography (IC) can be used for the detection of basic and/or acidic organic nitrogen compounds. We developed an offline method to quantify the concentrations of amines\textsuperscript{27,116} and of isocyanic acid. The advantage of IC is its low detection limit compared to online mass spectrometry. However, the analysis must be made offline and thus requires sample preparation and manipulation before analysis which can be sources of error.

The detection of cations and anions was accomplished using a Dionex ICS-2000 system. The methanesulfonic acid (MSA) and the potassium hydroxide (KOH) eluents were generated from 18.2 MΩ deionised water and then passed through the sample loop or concentrator to enter the separation columns. In the case of amines, a trace cation concentrator column (TCC-ULP1, 5 mm ×23 mm i.d.) was used for pre-concentration and a Dionex CS17 (250 mm × 4 mm i.d.) fitted with a CG17 (50 mm × 4 mm i.d.) guard column was used for separation. In the case of isocyanic acid, a trace anion concentrator column (TAC-ULP1) or a 25 µL loop was used for pre-concentration and a Dionex AS19 hydroxide-selective anion exchange column fitted guard column were used for separation. Chromatography programs employed the step-wise gradient methods. Samples
were either loaded manually or by an autosampler (Dionex AS40, 5 mL aqueous sample, injection rate: 1 mL min\(^{-1}\)). Analyte peaks were visualized and integrated using the Chromeleon® v6.8 software package.

### 1.5.1.3 Smog Chamber

The kinetic measurements described in this thesis were made in a 1 m\(^3\) smog chamber which consisted of a Teflon FEP film (American Durafilm) bag (Ingeniven) mounted around a cubic Teflon-coated frame (Figure 1-3). The chamber has three UVB lamps (Microlites Scientific) centered at 310 nm, on four of its six sides. It does not contain a fan and has four ¼” ports as well as three 1” ports for the introduction and sampling of gas mixtures. A drawback with our smog chamber is that the temperature cannot be controlled, which limits experiments to room temperature. Illumination also tends to rise the temperature of the chamber by a few degrees (< 5 °C). As well, the impacts of wall reactions are hard to quantify. An advantage of using a smog chamber over a flowtube is the ability to operate in a batch mode and have a constant supply of OH radicals in photo-oxidation experiments, which is useful for longer-lived species. The smog chamber is also better suited to conduct product studies, especially for later generation products.

![Figure 1-2: Example of the experimental set up for kinetic measurements of organic nitrogen](image-url)
1.5.2Kinetics

To quantify how fast molecules react with one another, absolute or relative rate kinetic methods are used to measure rate coefficients. Greiner in 1967 was the first to measure kinetic data, specifically the rate coefficient of H₂, CO, CH₄, C₂H₆, C₃H₈ and C₄H₁₀ with OH radicals in the gas phase using flash-photolysis spectroscopy techniques. Flash-photolysis techniques continue to be extensively used for kinetic measurements. It employs absolute rate kinetic measurements where the analyte is in large excess (i.e. constant concentration) compared to the OH radical concentration, simplifying the analysis to pseudo-first order rate kinetics. Since this method uses OH radicals as the limiting reagent, the regeneration of OH radicals during oxidation may be an uncertainty. It also does not easily allow for product studies as the OH radical is the analyte monitored. Mainly for this latter reason, we opted to employ mass spectrometry techniques and a smog chamber. We use relative rate kinetics, which require the use of a reference compound with a well-established rate coefficient against OH radical (Equation 1). Examples used in chapters 2, 3 and 6 include 1,3,5-trimethylbenzene and n-butanol. The reference compound should appear at an unobstructed m/z ratio, not react with the analyte or its products and behave similarly to the analyte in the chamber (i.e. wall losses). We also conducted absolute rate kinetics in Chapter 2 where the ozone concentration remained in large excess to simplify the kinetics to pseudo-first order. This method cannot be used for OH radicals since their lifetime is too short and steady-state concentration too low to be in excess of a measurable amount of analyte (~ 10⁷ molec cm⁻³ in the chamber).

\[
\text{Equation 1:} \ln \left( \frac{[\text{organic nitrogen}]_{0}}{[\text{organic nitrogen}]_{t}} \right) = \frac{k_{\text{organic nitrogen}+\text{OH}}}{k_{\text{reference}+\text{OH}}} \ln \left( \frac{[\text{reference}]_{0}}{[\text{reference}]_{t}} \right)
\]

\[
\ln \left( \frac{[\text{organic nitrogen}]_{0}}{[\text{organic nitrogen}]_{t}} \right) / t = k_{\text{organic nitrogen}+\text{O}_3} [\text{O}_3]
\]

1.5.3Theoretical methods

The determination of photo-oxidation mechanisms for organic nitrogen presented in chapters 3, 5 and 6 have relied on computational chemistry methods. In quantum mechanics, particles are described by their wave function, Ψ, which contains information on the probability of finding a particle (i.e. an electron) in a particular location, at a specific time. The wave function is the solution of Schrödinger’s equation:
\[
\dot{\Psi}(r, t) = -\frac{\hbar^2}{2m}\nabla^2 \Psi(r, t) + V(r)\Psi(r, t)
\]

Where \(i\) is the imaginary unit, \(\hbar\) is \(\hbar/2\pi\) and \(\h\) is Planck’s constant, \(r\) is the particle’s position in space, \(t\) is time, \(m\) is the mass of the particle, \(\nabla^2\) is the del-squared operator and \(V\) is the potential field in which the particle is moving. Schrödinger’s equation can only be solved exactly for a one electron and one nucleus system, and so to solve for the wave function of more complex systems, a series of approximations are required which are discussed further along in this section. There are three classes of electronic structure methods: semi-empirical methods, which use experimentally-derived parameters to simplify the calculation, \textit{ab initio} methods, which use exclusively the laws of quantum mechanics and density functional methods (DFT), similar to \textit{ab initio} methods but which include parameters for electron correlations.

In this thesis, we employ Gaussian 09 for all our calculations using \textit{ab initio} and DFT methods. Gaussian 09 is a cluster model (opposed to a periodic boundary condition model) and thus requires two types of inputs to run a calculation: the method, dictating how the electron correlations are treated and the basis set, specifying the mathematical representation of the molecular orbitals.\textsuperscript{121} The approximations used to arrive at a solution to the Schrödinger equation distinguishes one method from another (and typically referred to as the level of theory). The \textit{ab initio} methods/approximations used include (1) Hartree-Fock (HF), where the HF energy is based on an average electron potential; (2) Moller-Plesset (MP), where MP energies add correlations between electrons; and (3) coupled cluster (CC), (and coupled cluster singles and doubles, CCSD) where CC energies adds further refinements to correlation energies.

Throughout our work, we use a DFT method, M06-2X, for structure optimization and then an \textit{ab initio} method, G3X-K, for single point energy calculations. The M06-2X method is one of the Minnesota Functionals used for kinetics which include exchange-correlation energy functionals.\textsuperscript{122} The optimization calculations begin with the specified geometry from the input file and varies the structure, more specifically the nuclear coordinates of the molecule, until a stationary point on the potential energy surface is found and the forces acting on the molecule are minimized. The G3X-K method is a composite method combining a series of calculations (HF, MP2, MP4 and CCSD) to minimise basis set truncation errors without performing the entire calculation at the highest level of theory (and with high computational cost).\textsuperscript{123} Energy calculations are single point energy
calculations which yield electronic energy as a function of the specified nuclear coordinates previously optimized. G3X-K theory is used in this thesis since it was specifically designed for thermochemical kinetics and reproduces barrier heights in the diverse barrier heights database DBH24/08 with an average accuracy of 0.6 kcal mol\(^{-1}\).\(^{123}\) However, nicotine (Chapter 6) contains too many atoms and G3X-K could not handle the size of the molecule. For nicotine’s theoretical method presented in Chapter 6, we used the DFT method M06-2X exclusively. The basis set consistently used throughout our calculations is the Pople basis set 6-31G(2df,p) as it allows for the accurate determination of energies at reasonable computational cost (at less than 120 hours per calculation).

In our theoretical energy diagrams presented in this thesis, we report the energies at 0 K and are calculated from the sum of the electronic energy and the zero point energy. The sum of the reactants’ ground state energy is set to 0 kcal mol\(^{-1}\) as the reference point. A positive transition state energy value is interpreted as needing more energy than the entrance level energy of the reactants, and vice versa. We use the transition state energy to provide semi-quantitative information on favourable reaction pathways and compare them to measured rate coefficients.

1.5.4 Models

1.5.4.1 Structure-Activity Relationship (SAR) models

There is significant utility in atmospheric chemistry to develop structure-activity relationships (SAR) models in order to predict the fate of pollutants.\(^{124,125}\) SAR models were developed in the 1980s and 1990s to calculate the rate coefficient of VOCs at ambient temperature and thus predict their atmospheric lifetime against the OH radical.\(^{124,125}\) It was also later extended for other atmospheric oxidants like ozone.\(^{126}\) The general approach of the SAR model consists of predicting an overall rate coefficient by summing the individual rates constants of every reactive site on a molecule of interest. Mechanisms currently incorporated into SAR models are H-abstraction, addition to unsaturated carbon-carbon bonds and addition to heteroatoms.\(^{124}\) First, there is the SAR group rate constants for H-abstractions from any atom (C, N, O, etc.), denoted by a \(k\) value with a subscript denoting the site (or functional group) of the H-abstraction. Three main SAR group rate constants relevant to C–H abstractions exist for each type of carbon centre: a primary (\(k_{\text{prim}}\)), secondary (\(k_{\text{sec}}\)) or tertiary (\(k_{\text{tert}}\)) carbon center. The value of these group rate constants are determined using a large set of experimental data. Second, specifically for C–H abstractions, the
SAR group rate constant \((k_{\text{prim}}, k_{\text{sec}}, \text{or } k_{\text{tert}})\) is then multiplied by a substituent factor denoted as \(F(X)\) to obtain an overall rate constant specific for the functional group’s reactivity. Sample equations for C–H abstractions are given below and values are tabulated in Table 1-1.

\[
k_{\text{overall}}(CH_3 - X) = k_{\text{prim}}F(X)
\]

\[
k_{\text{overall}}(Y - CH_2 - X) = k_{\text{sec}}F(X)F(Y)
\]

\[
k_{\text{overall}}(Z>CH - X) = k_{\text{tert}}F(X)F(Y)F(Z)
\]

There are published SAR group rate constants for N–H abstractions for amines, carbamates and thiocarbamates as well as SAR substituent factors for C–H abstractions occurring adjacent to an amine, a carbamate or a thiocarbamate functionality derived from experimental rate coefficients.\(^{124,125,127,128}\) There are currently no SAR group rate constants for amides or isocyanates. To circumvent this problem, the U.S. Environmental Protection Agency’s (EPA) Estimation Program Interface (EPI) Suite model uses estimated values based on carbamate or thiocarbamate factors to predict the atmospheric fate of amides.\(^{129}\)

### Table 1-1: SAR parameters for OH radical reactions with amines\(^{125,129}\)

<table>
<thead>
<tr>
<th>Group constant</th>
<th>rate (k_{298K})</th>
<th>Substituent factor</th>
<th>(F(X))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_{\text{prim}}) (−CH₃)</td>
<td>0.136 (10^{-12}) cm (^{3}) molec (^{-1}) s (^{-1})</td>
<td>−NH₂, −NH−, &gt;N−</td>
<td>9.3</td>
</tr>
<tr>
<td>(k_{\text{sec}}) (−CH₂−)</td>
<td>0.934</td>
<td>−CH₃</td>
<td>1.0</td>
</tr>
<tr>
<td>(k_{\text{tert}}) (&gt;CH−)</td>
<td>1.94</td>
<td>−CH₂−, &gt;CH−, &gt;C&lt;</td>
<td>1.23</td>
</tr>
<tr>
<td>(k_{\text{OH}})</td>
<td>0.14</td>
<td>−OH</td>
<td>3.5</td>
</tr>
<tr>
<td>(k_{\text{NH2}})</td>
<td>21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_{\text{NRH}})</td>
<td>63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_{\text{NR2}})</td>
<td>66</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1.5.4.2 Example of an SAR analysis

To help understand the SAR analysis, which is treated in detail in Chapter 5, we provide here a sample calculation for MEA. MEA possesses four different reactive sites as outlined in Figure 1-4. The sum of the two SAR group rate constants for H-abstraction from a heteroatom \( (k_{-OH} \text{ and } k_{-NH2}) \) and the \( (1^{st}) \) SAR group rate constant \( k_{sec} \) multiplied by its substituent factors \( (F(-OH) \text{ and } F(-CH2-)) \) and the \( (2^{nd}) \) SAR group rate constant \( k_{sec} \) multiplied by its substituent factors \( (F(-NH2) \text{ and } F(-CH2-)) \) yield the overall rate coefficient for MEA. We then pool the values for each factor from published values by Kwok et al. and obtain a value of \( 3.6 \times 10^{-11} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1} \) (see Table 1-1). In this particular instance, the SAR underpredicts the experimental rate coefficient of MEA by a factor of 2.88-90

\[
k_{overall}(MEA) = k_{-OH} + k_{sec}F(-OH)F(-CH2-) + k_{sec}F(-NH2)F(-CH2-) + k_{-NH2}
\]

Figure 1-3: The four H-abstraction mechanisms possible for MEA with their respective SAR group rate constants and substituent factor.

1.6 Summary and Outline

In summary, organic nitrogen compounds, such as amines, amides, aromatic nitrogen, carbamates, imines, isocyanates, nitramines, nitrosamines and nitriles, are present in ambient air in both the gas and particle phases. Some of these compounds are toxic and/or carcinogenic as well as contribute to particulate matter which is a health hazard. These compounds are emitted from biogenic sources like oceans, vegetation and biomass burning as well as from anthropogenic sources like animal husbandry, agriculture, carbon capture and storage (CCS) technology and tobacco smoke. Nitrogenated compounds once emitted into the atmosphere may undergo gas phase processes like oxidation and photolysis or may contribute to the nucleation and growth of particles thereby impacting climate directly and indirectly. In this thesis, we contribute to the laboratory pillar of atmospheric chemistry by characterizing the fate of organic nitrogen experimentally and theoretically (Figure 1-5).
In Chapter 2, we study the fate of monoethanolamine (MEA) as the benchmark solvent in CCS technologies. To better predict the impact of fugitive emissions of MEA on surrounding population centres, models must know how quickly MEA is oxidized and what are its oxidation products. We contribute to this knowledge by measuring the third published rate coefficient of MEA + OH radicals using relative rate kinetics and online mass spectrometry as well as the first rate coefficient for MEA + ozone using absolute rate kinetics. We identify and quantify its oxidation products which include formamide and isocyanic acid. We are the first to report the production of isocyanic acid from the oxidation of amines, an important observation in the context of population exposures to this toxic molecule. Highlighted in red in Figure 1-5 are the processes evaluated in Chapter 2.

In Chapter 3, we present the first rate coefficient of formamide with OH radicals as well as for four additional alkylamides. We find that their atmospheric lifetimes span a long range, from 0.5 days to a week. To better understand this difference in reactivity within the same functional group, we employ ab initio calculations to support our mechanistic understanding of the oxidation of amides in the atmosphere. Finally, we show experimentally and theoretically that the oxidation of amides yields isocyanates. Our findings from Chapter 3 are highlighted in green in Figure 1-5.

In Chapter 4, we study the fate of isocyanic acid as it partitions to the aqueous phase and is subsequently hydrolysed. We measure the second Henry’s Law coefficient of solubility for isocyanic acid and its first enthalpy of dissolution for implementation into chemical transport model. We also quantify the rate coefficients of hydrolysis of isocyanic acid from its three pH and temperature dependant mechanisms. We predict from these experimental data the lifetime of isocyanic acid in the aqueous phase to be on the order of days to weeks in atmospheric aerosols, years in oceans and months in human blood in the context of exposure. The fate of isocyanic acid is highlighted in yellow in Figure 1-5.

In Chapter 5, we look at the three protagonist molecules from the preceding chapters, i.e. amines, amides and isocyanates, in addition to carbamates and study all possible mechanisms involved in their oxidation by OH radicals using ab initio calculations. We show that an important C−H abstraction mechanism (formyl C−H) for amides has been omitted from structure activity relationship (SAR) models. We also highlight the differences in N−H abstraction transition state energies from each type of functional group and show that this mechanism is only competitive for amines. OH additions to carbonyls are expected to be slow but are exothermic, whereas OH
additions to the nitrogen atom in any of the organic nitrogen compounds investigated is consistently prohibitively high in energy and endothermic. These mechanisms in the context of the development of new SAR factors of organic nitrogen compounds is also further discussed. In Figure 1-5, Chapter 5 is represented as the Gaussian 09 transition state output of isocyanic acid + OH radical.

In Chapter 6, we take what we learned from all previous chapters about the fate of amines, amides and isocyanates as well as their oxidation mechanisms and look at a more complex amine, nicotine. We report the first rate coefficient of nicotine with OH radicals and characterize its oxidation products which include formamide and isocyanic acid as second or third generation products. We calculate using computational chemistry all possible C−H abstraction mechanisms for nicotine and show that many are competitive, pointing towards a complex oxidation mechanism. Finally, we study the fate of tobacco-derived nicotine in a smog chamber and show that the formation of formamide, nitrous acid and isocyanic acid are caused by photo-oxidation of the sidestream smoke of a cigarette. Our results from Chapter 6 are highlighted in purple in Figure 1-5.

Finally, in Chapter 7, we summarize our findings on the fate of organic nitrogen molecules in the atmosphere and provide our insights into future directions relevant to the field, including questions which we raised through our work and which remain outstanding.

The key research questions that guided our experimental and theoretical studies and that we sought to address throughout each chapter are listed below:

1. What is the lifetime of organic nitrogen molecules in the atmosphere?

2. What products do organic nitrogen compounds form upon processing in the atmosphere?

3. How do organic nitrogen compounds (isocyanic acid) partition to the aqueous phase?

4. What are the mechanisms involved in the atmospheric oxidation of organic nitrogen molecules?

5. Can we better predict the fate of organic nitrogen molecules in the atmosphere using structure-activity relationship (SAR) models?
Figure 1-4: The atmospheric fate of organic nitrogen discussed in this thesis. Emission sources of organic nitrogen are presented as CCS (and other industries), animal husbandry, biomass burning and cigarette smoke. Chapter 2 is represented in red, Chapter 3 in green, Chapter 4 in yellow and Chapter 6 in purple. Chapter 5 pertains to ab initio work accomplished using Gaussian 09.

1.7 References


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Chapter 2
Gas Phase Oxidation of Monoethanolamine (MEA) with OH Radical and Ozone

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2 Chapter 2

2.1 Abstract

Monoethanolamine (MEA) is currently the benchmark solvent in carbon capture and storage (CCS), a technology aimed at reducing CO₂ emissions in large combustion industries. To accurately assess the environmental impact of CCS, a sound understanding of the fate of MEA in the atmosphere is necessary. Relative and absolute rate kinetic experiments were conducted in a smog chamber using online proton transfer reaction mass spectrometry (PTR-MS) to follow the decay of MEA. The room temperature (295 ± 3K) kinetics of oxidation with hydroxyl radicals from light and dark sources yield an average value of \((7.02 \pm 0.46) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\), in good agreement with previously published data. For the first time, the rate coefficient for MEA with ozone was measured: \((1.09 \pm 0.05) \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\). An investigation into the oxidation products was also conducted using online chemical ionization mass spectrometry (CI-TOFMS) where formamide, isocyanic acid as well as higher order products including cyclic amines were observed. Significant particle numbers and mass loadings were observed during the MEA oxidation experiments and accounted for over 15% of the fate of MEA-derived nitrogen.
2.2 Introduction

The most rapidly increasing use for monoethanolamine (MEA) is in carbon capture and storage (CCS) technology, where MEA has become the benchmark solvent due to its optimal properties towards CO₂ capture.¹⁻³ Compared to many other amines, MEA is cheap, has a high absorption capacity and reacts quickly with gaseous CO₂.⁴⁻⁵ In a CCS plant with a capacity of 1 million tons of captured CO₂ per year, it is estimated that approximately 40-160 tons of amines could be emitted to the atmosphere.⁶ Such quantities of aminoalcohols, a class of amines which also contain an alcohol group like MEA, concentrated in one area of industrial usage create potential risks for the environment. Indeed, a worst-case scenario evaluated by Karl et al. predicts toxicity limits of MEA for aquatic organisms to be exceeded by factors of 3 to 7.⁷ Anthropogenic emissions of aminoalcohols other than from CCS also include animal husbandry, corrosion inhibitors, detergents and emulsifiers.⁸ Natural sources of amines include oceans, biomass burning, vegetation and geological sources.⁸ The aminoalcohols are generally products of amino acid biodegradation and so plants, animals and vegetation all contribute to emissions of volatile amines.

In the atmosphere, the likely fate of MEA is gas phase oxidation, competitive with particle uptake. There are currently two published rate coefficients for the oxidation of MEA by OH radicals. The first rate coefficient was determined using relative rate kinetics at the European Photoreactor (EUPHORE) chamber where Karl et al. obtained a value of (9.2 ± 1.1) × 10⁻¹¹ cm³ molec⁻¹ s⁻¹ at 298K using a proton transfer reaction time-of-flight mass spectrometer (PTR-TOFMS) and a fast Fourier transform infrared spectrometer (FT-IR).⁹ The work also used a chamber aerosol model to estimate the contribution of particle loss of MEA and concluded that wall loss of MEA to the chamber represented a significant source of uncertainty. At EUPHORE, Nielsen et al. identified photo-oxidation products of MEA and found that formamide and formaldehyde were major products.¹⁰⁻¹¹ They also qualitatively detected higher order products potentially formed via condensation reactions. The second published rate coefficient for MEA with OH radicals used absolute rate kinetics and obtained a rate coefficient of (7.61 ± 0.76) × 10⁻¹¹ cm³ molec⁻¹ s⁻¹.¹² Onel et al. relied on laser-induced fluorescence to follow the decay of OH radicals. They also noted a slight negative temperature dependence of the rate coefficient from 296 to 510 K due to the formation of pre-complexes.
Gaining insight into the atmospheric fate of MEA, the current benchmark solvent in CCS, is of prime importance as this compound starts to be used on a large industrial scale. This study confirms previous experimentally measured rate coefficients of MEA with OH radicals by employing two different sources of OH radicals to minimize error. We also describe the first rate coefficient of MEA with ozone thereby supplying a more complete understanding of MEA's removal processes in the atmosphere for modeling purposes. Furthermore, this work outlines the fate of N in MEA oxidation and highlights some potentially toxic products. Of particular interest, formamide and isocyanic acid (HNCO) were detected in the gas phase along with potential condensation products of amines with carbonyls. N was also detected in the particle phase.

2.3 Experimental methods

The oxidation kinetics of MEA were studied in a 1 m\(^3\) Teflon FEP film (American Durafilm) bag (Ingeniven) mounted around a cubic Teflon-coated frame. The chamber has three UVB lamps (Microlites Scientific), centered at 310 nm, on four of its six sides and does not contain a fan. Connected to the chamber were a quadrupole proton transfer reaction mass spectrometer (PTR-MS) (Ionicon Analytik GmbH, Innsbruck Austria)\(^{13}\) and a high resolution chemical ionization time-of-flight mass spectrometer (CI-TOFMS) (Aerodyne Research Incorporated, Billerica, MA, USA)\(^{14}\) (Figure S1). See Appendix A for operating details of the PTR-MS and the CI-TOFMS.

The organic compounds used in this study were purchased from Aldrich and used without further purification. Liquids were dispensed into the chamber by passing clean air over a known injected amount of analyte into a 0.635 cm o.d. glass tube while gently heating the glass tube with a heat gun (Figure S1). All experiments were carried out at room temperature, 295 ± 3K. The chamber was regularly flushed and refilled with clean air from a pure air generator (AADCO 737-series; <1 ppbv ozone, methane, hydrocarbons, NO/NOx, H\(_2\)S, SO\(_2\) and all particles). The absence of NO\(_x\) chemistry was further confirmed with a ThermoScience model 42i trace level NO-NO\(_2\)-NO\(_x\) analyzer instrument with NO\(_x\) (= NO\(_2\) + NO) mixing ratios not exceeding its detection limit of 0.5 ppbv.

OH radicals were generated using two complementary methods. The first method used the reaction of \(6.1 \times 10^{13}\) molec cm\(^{-3}\) (2.4 ppmv) of tetramethylethylene (TME) with a constant flow of ozone as a dark, dry OH source.\(^{15-17}\) Ozone generation was accomplished by passing a flow of 0.2 L min\(^{-1}\) of oxygen or purified air past a 185 nm Pen-Ray Hg lamp and the ozone concentration inside the
chamber was monitored by a ThermoScience model 49i ozone analyzer and remained below 3.7 \times 10^{13} \text{molec cm}^{-3} (1.5 \text{ppmv}). Only experiments with 70 data points or more for the decay corresponding to more than six minutes were considered for the rate coefficient calculation to minimize error. The second method involved the photolysis of hydrogen peroxide by UVB lights centered at 310 nm. Hydrogen peroxide was added using a flow of clean air (~0.45 L min\(^{-1}\)) through a bubbler containing a 30\% by weight aqueous solution of hydrogen peroxide for an hour. For both sets of experiments, the initial MEA concentrations ranged from 0.9-1.7 \times 10^{13} \text{molec cm}^{-3} (400-700 ppbv).

Rate coefficients for the OH radical reactions were determined using relative rate experiments.\(^{18}\) 1,3,5-Trimethylbenzene (TMB) with concentrations ranging from 0.9 to 1.7 \times 10^{13} \text{molec cm}^{-3} (400-700 ppbv) was used as the reference compound since its rate coefficient with OH radicals and its related uncertainty is well characterized in the literature, \(k_{\text{TMB}} = (5.73 \pm 0.53) \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}.\)^{19} Based on this rate constant, the steady state OH radical concentrations were determined to be 2.0 \times 10^{7} \text{molec cm}^{-3} and 7.5 \times 10^{6} \text{molec cm}^{-3} for the dark and light sources respectively using \([\text{OH}] = \ln([\text{TMB}]_0/[\text{TMB}])/(k_{\text{TMB}}+\text{OH}t)\). Furthermore, its rate coefficient with OH radicals is on the same order of magnitude as that of MEA and it is non-reactive with MEA, water or light. If the reference compound and MEA are assumed to be removed solely by oxidation reactions with OH radicals, then the TMB integrated rate law can be substituted into the MEA integrated rate law expression yielding a relationship between the two compounds, independent of the concentration of OH radicals. The slope of a plot of the natural logarithm of the change in concentration of MEA versus the same for TMB represents the ratio of both rate coefficients \(k_{\text{MEA}}/k_{\text{TMB}}\) (Equation 1). Due to the nature of relative kinetic experiments, the mass spectrometer signals did not require absolute calibrations.

The rate coefficient for the reaction of MEA with ozone was determined using absolute rate kinetics.\(^{18}\) In this experiment, the concentration of ozone inside the chamber was in a large excess (> 14 ppmv) and changed by less than 15\% over the course of the experiment. By integrating the rate law of the decay of MEA as a function of time and assuming reaction with ozone is the only sink for MEA, Equation 2 is obtained. The slope of the graph generated by plotting the natural logarithm of the change in concentration of MEA as a function of time yields the rate coefficient multiplied by the average concentration of ozone. If the concentration of ozone is assumed to be
constant over the period of the decay of the compound of interest, then the rate coefficient can be reliably obtained.

Equation 1: $\ln \left( \frac{[MEA]_0}{[MEA]_t} \right) = \frac{k_{MEA+OH}}{k_{TMB+OH}} \ln \left( \frac{[TMB]_0}{[TMB]_t} \right)$

Equation 2: $\ln \left( \frac{[MEA]_0}{[MEA]_t} \right) / t = k_{MEA+O_3}[O_3]$

MEA possesses a polar primary amine functional group and is therefore expected to stick readily to the walls. Indeed, this phenomenon was observed and thus the chamber, the Teflon tubing as well as the instruments needed to be conditioned with MEA before reproducible and reliable signals could be obtained. Once the experimental set up was conditioned appropriately, the gas-phase MEA was collected in a water bubbler and quantified using ion chromatography (IC). The IC results indicated that >90% of the aminoalcohol injected remained in the gas phase. Furthermore, the MEA mass spectrometry signal was stable over several hours, indicating minimal wall participation after conditioning. Flushing experiments gave expected removal rates implying that MEA partitioning off the walls was negligible.

2.4 Results and discussion

2.4.1 MEA oxidation with hydroxyl radical

2.4.1.1 TME and ozone experiment

The reaction of tetramethylethylene (TME) with ozone rapidly generates OH radicals and is described as a dark and dry OH source. During the kinetic experiments, TME, MEA and TMB were injected into the chamber and the oxidation reaction started upon addition of a flow of ozone. There was a short delay between the start of the addition of ozone and the observed decay of MEA and TMB, due to ozone diffusing through the chamber to react with TME (see Figure 2-1A). Therefore, the decay time points used to create Figure 2-2B were from 0.2 to 0.6 hours. The slope of Figure 2-1B yields the rate coefficient ratio between $k_{MEA+OH}$ and $k_{TMB+OH}$ according to Equation 1. Of note, an important background signal was observed at m/z 121, the mass to charge ratio monitored by the PTR-MS for the reference compound TMB. A correction was applied by taking the background signal on the PTR-MS obtained at long reaction times and subtracting this value from the entire TMB decay (see Figure 2-1A), under the assumption that this background signal
was constant. With the help of high-resolution mass spectrometry, part of the background signal was attributed to a TMB oxidation product $\text{C}_8\text{H}_9\text{O}^+$ (m/z 121.065) and consequently the background correction using a constant subtracted value may not be accurate. Note that TMB is not detected in the positive mode of the CI-TOFMS and so the high resolution mass spectrometry technique could not be used for the kinetic calculations. Since a second set of oxidation experiments using hydrogen peroxide as the OH radical source (described in the following section) did not produce a background at m/z 121, the $\text{C}_8\text{H}_9\text{O}^+$ product is likely generated by ozonolysis of an olefin produced by the reaction of TMB with OH radicals. The small MEA background signal at long reaction times was also taken to be constant and subtracted from the time trace. This background may be attributed to instrument conditioning issues. The ozone mixing ratio was monitored *in situ* during the course of the experiment, and didn't exceed 1.3 ppmv to minimize the contribution of ozone to the oxidative decay of MEA (see Figure 2-1A). The average of four experiments gave a value of $(7.24 \pm 0.40) \times 10^{-11}$ molec cm$^{-3}$ where the standard deviation represents the variability between experiments.
Figure 2-1: For TME and ozone as the OH radical precursor; A) MEA and TMB time traces where each point represents a 500 ms dwell time on the m/z every approximately 5 s and where the black lines represent 5 point averages and circles are ozone mixing ratios; B) Plot of Equation 1 for MEA and TMB from 0.2 to 0.6 h time points, where each point represents was taken approximately every 5 s. The linear regression is forced through the origin and the standard deviation in the slope is 0.02.

2.4.1.2 Hydrogen peroxide experiment

To support the validity of the rate coefficient obtained using TME and ozone as an OH source, a different source of OH radicals was employed. In the second set of relative rate experiments, MEA and TMB were injected into the chamber prior to the addition of gas-phase hydrogen peroxide. However, during the addition of hydrogen peroxide to the chamber in the dark, the MEA signal substantially decreased whereas the TMB signal remained stable. This drop in signal suggests that MEA reacts with hydrogen peroxide. Although no particles were observed during the addition of hydrogen peroxide, N-containing products were detected in the gas phase by CI-TOFMS. Spirina
et al. reported solution-phase chemistry between ethanolamine and hydrogen peroxide, identifying 2-aminoacetaldehyde and N-hydroxyethanolamine by IR as the two products.\textsuperscript{22} Interestingly, using the CI-TOFMS, the m/z ratio corresponding to both of these products (m/z 60.044 for aminoacetaldehyde and m/z 78.055 for N-hydroxyethanolamine) grew over time during the dark addition of gas phase hydrogen peroxide. Nonetheless, after stopping the addition of hydrogen peroxide, the MEA signal stabilized and reproducible decay traces for MEA and TMB were obtained upon UVB light irradiation to form OH radicals (Figure 2-2A).

At the end of the decay, the TMB signal reached zero, indicating the absence of background issues and complete consumption of TMB by the OH radical. The rate coefficient ratio \( k_{\text{MEA}+\text{OH}} / k_{\text{TMB}+\text{OH}} \) was calculated from time points between 0 to 1.6 hours (Figure 2-2A). However, complete decay to zero normalized counts was not observed for MEA in the hydrogen peroxide experiments and its background signal was attributed to \(^{13}\text{C}\)-acetic acid and a small constant background similar to the TME and ozone experiment. To correct the MEA decay, first the MEA trace was subtracted by 0.02% of the acetic acid signal, \( \text{CH}_3\text{CO}_2\text{H}_{2}^+ \) trace at m/z 61, a percentage that represents the natural abundance of \(^{13}\text{C}\) in acetic acid, creating an isobaric interference with MEA. Second, a constant background obtained at long reaction times was subtracted from the remaining MEA trace, similarly to the MEA background subtraction in the TME and ozone experiments. The result of these corrections are depicted in Figure 2-2A.

Although there is background reactivity between MEA and hydrogen peroxide in the dark, the rate coefficients extracted from this second set of experiments were reproducible and two experiments yielded an average of \( 6.59 \pm 0.08 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \), closely related to the values obtained with TME and ozone as the OH radical precursor. Control experiments confirmed that photolysis at 310 nm of MEA is negligible and that gas-phase MEA and water vapour do not react with one another. Of note, the OH concentrations were lower using hydrogen peroxide photolysis as the OH source and thus the oxidation was carried out over longer periods of time (~120 mins) to achieve full MEA decay.
Figure 2-2: For H₂O₂ as the OH radical precursor; A) Decay of MEA and TMB over time where each point represents a 500 ms dwell time on the m/z approximately every 5 s and where the black lines represent 5 point averages; B) Plot of Equation 1 for MEA and TMB where each point was taken approximately every 5 s. The linear regression is forced through the origin and the standard deviation in the slope is 0.01.

Averaging six experiments using the two different sources of the OH radical leads to a rate coefficient of $(7.02 \pm 0.46) \times 10^{-11}$ cm$^3$ molec$^{-1}$ s$^{-1}$, where the error is the standard deviation of the individual rate coefficients experimentally determined. We also add a 9% systematic error to our determined rate coefficient based on the uncertainty in the rate coefficient of TMB.$^{19}$

To further validate the rate coefficient of MEA with OH and eliminate potential error introduced by the TMB rate coefficient uncertainty, other reference compounds were screened for relative
rate kinetics. Of note, averaging four experiments (data not shown) with β-pinene as the reference and TME and ozone as the source of OH radicals gave a rate coefficient of \((7.3 \pm 1.4) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\), a value closely related to the one obtained with TMB. The rate coefficient for β-pinene and OH radicals was taken to be \((7.05 \pm 1.60) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\), but since this value has a 23% uncertainty, we chose not to include these experiments in our overall analysis.

Our rate coefficient for MEA and OH radicals compares well with previously published data: the absolute rate coefficient from Onel et al., \((7.61 \pm 0.76) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\), and the relative rate coefficient from Karl et al., \((9.2 \pm 1.1) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\).\(^9,12\) Given that Karl et al. used the same reference compound as this study, we would expect the rate coefficients to agree within the experimental error, yet the Karl et al. value is higher. Differences between the two studies include the volume of the chamber and the composition of the air inside the chamber. There are inherent differences in wall loss chemistry between the two chambers, as well as alternative removal processes. Nonetheless, the three studies on the oxidation kinetics of MEA and OH radicals are in reasonable agreement, highlighting the robust nature of the measured rates for modeling purposes and leading to a short lifetime of MEA against OH radicals in the atmosphere, i.e. on the order of 2 h for an OH concentration of \(2 \times 10^6 \text{ molec cm}^{-3}\).

As previously published by Karl et al.\(^9\) and summarized by Nielsen et al.\(^24\), the structure and reactivity (SAR) method\(^25\) underestimates the rate coefficient of MEA by a factor of 2-3, thereby concluding that MEA is an outlier in the ability for SAR to predict its rate coefficient with OH radicals. In comparison to alkylamines, aminoalcohols have a hydroxyl moiety added to the chain length. This difference in polarity, linked to MEA's ability to H-bond intra- and inter-molecularly, imparts enhancements in reactivity towards OH radicals from alkylamines to aminoalcohols.\(^26\)

### 2.4.2 MEA oxidation with ozone

To better evaluate the atmospheric lifetime of MEA, its rate coefficient with ozone was studied with the same experimental setup as for the OH radical experiments. The experiment was run by first introducing ozone into a MEA-conditioned chamber, followed by injection of a known amount of MEA. With PTR-MS, CI-TOFMS and AMS, no additional signals were observed during the 2 h-long addition of ozone (Figure 2-3A) implying stable conditions inside the chamber, i.e. no product formation and no particle generation. The oxidation kinetics of MEA followed the expected pseudo-first order decay (Figure 2-3A). The rate coefficient was calculated using
Equation 2 and found to be \((1.09 \pm 0.04) \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) where the error represents the standard deviation of three experiments. To ensure the loss of MEA was solely due to reactivity with ozone and not secondary OH radical chemistry, cyclohexane (8 ppmv) was added to scavenge any OH radical formed and did not affect the rate coefficient of MEA with ozone. Nonetheless, the obtained rate coefficient should be considered an upper limit since alternative removal processes like deposition to the surfaces could have affected the measured rate. Also, the rate coefficient confirms that the reaction of MEA and ozone in the dark and dry OH experiment described above accounts for less than 2% of the MEA decay.

This study is the first to report a rate coefficient for MEA and ozone. Even so, the evaluated value can be compared with previously published rate coefficients for other amines. Compared to other primary amines, MEA reacts faster with ozone by over two orders of magnitude.\(^{27}\) However, \(N, N\)-dimethylethanolamine, a tertiary amine, has a faster rate of reaction with ozone, \((6.76 \pm 0.83) \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) than MEA, a primary amine.\(^{27}\) The fastest known amine to react with ozone appears to be triethylamine, a tertiary amine.\(^{28}\) These results are consistent with the amine moiety acting as a nucleophile towards ozone; the more electron rich the amine, the faster it will react with the ozone electrophile. In all, the calculated lifetime of MEA against ozone in a typical urbanized area (30 ppbv) is on the order of 12 days, limiting its atmospheric relevance to high latitudes in winter time.
Figure 2-3: A) Injection and subsequent decay of MEA in the presence of ozone over time where each point represents a 500 ms dwell time on the m/z every approximately 5 s and where the black lines represent 5 point averages; B) Decay of MEA/MEA$_0$ over time where each point represents one time point every approximately 5 s. Time points used from Figure 2-4A are from 2.4 to 3.8 hours.

2.5 Product and particle study

Studies with the PTR-MS, the CI-TOFMS and aerosol characterization instruments were conducted to obtain a better understanding of the fate of the N during the oxidation of MEA with OH radicals and with ozone. To deconvolve the complex mixture of products generated during the oxidation experiments, the reference compound was omitted from these experiments. We observed gas phase products from fragmentation reactions (amides, organic acids) and from condensation reactions (cyclic amines) and particle formation.

In the gas phase photo-oxidation of MEA, the OH abstracts H from C preferably over N or O, a conclusion supported by branching ratios obtained from modeling the experimental product
distribution. To further support an H-abstraction mechanism from the C backbone, we can compare the rate coefficients of MEA with morpholine, a cyclic version of MEA in which the O is an ether and the N is a secondary amine. Indeed, morpholine reacts with OH radicals with a rate coefficient of \((8.0 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\),\(^{29}\) in good agreement with the value for MEA, consistent with reactivity at C for both molecules. According to da Silva's calculation, the C-centered radical generated after H abstraction goes on to react with molecular oxygen and rearranges to form 2-iminoethanol (Scheme 2-2 in Appendix A).\(^{30}\) The signal at m/z 60.044 which corresponds to 2-iminoethanol was indeed detected as a short-lived species by the CI-TOFMS operating in positive mode (Figure 2-4). However, 2-iminoethanol and 2-aminoacetaldehyde (see Scheme 2-2 in Appendix A for mechanism) both have the same mass to charge ratio, and attempts to differentiate them using an offline analysis by gas chromatography mass spectrometry (GC-MS) were unsuccessful. However, evidence for the presence of 2-iminoacetaldehyde was observed and is further discussed in Appendix A. Imines have higher proton affinities than ammonia and are expected to be detectable by proton transfer reaction,\(^{31}\) yet their unambiguous identification in the atmosphere remains elusive, perhaps due their instability within the instruments as well as the difficulty in synthesizing imine standards.

Formamide was unambiguously identified as a first generation gas phase product by the CI-TOFMS in positive mode (i.e. with H\(_3\)O\(^+\) and water clusters as reagent ions). Quantification of the signal was accomplished with a calibration curve obtained by injecting known amounts of formamide in triplicate inside the chamber and subsequently detecting the corresponding signal by CI-TOFMS. Formamide appeared to have minimal wall losses, required no conditioning and remained stable over long periods of time. Formamide was produced in 4 ± 2% yield in the OH and ozone oxidation experiments assuming >90% of the MEA injected went to the gas phase, suggesting this value is a lower limit (Figure 2-4).
Figure 2-4: Time profiles of gas phase products of MEA detected during a TME and ozone experiment. The positive mode normalization involves dividing the CI-TOFMS signal by the sum of H$_3$O$^+$, H$_3$O(H$_2$O)$^+$ and H$_3$O(H$_2$O)$_2$$^+$. The negative mode normalization involves dividing the CI-TOFMS signal by the acetate signal. Because the CI-TOFMS can only operate in one mode at a time, the positive mode and negative mode traces are from two separate experiments with identical operating conditions.

Importantly, isocyanic acid (HNCO) was detected as a long-lived gas phase product using CI-TOFMS in the negative mode, (i.e. with H$_3$CCOO$^-$ as the reagent ion) as m/z 41.998 (Figure 2-4). We assign the entire signal to CNO$^-$ based on discussions in Roberts et al. and on studies by Mladenovic et al. which conclude that the most thermodynamically stable isomer with a chemical formula of CHNO is HNCO.$^{32,33}$ This study is the first to detect HNCO as a product of amine oxidation. HNCO has been detected in tobacco smoke and more recently in biomass burning plumes, raising concerns of harmful human exposure.$^{34}$ HNCO is a weak acid with a pK$_a$ of 3.7 and as such is soluble at physiological pH. HNCO is known to undergo protein carbamylation leading to cardiovascular disease, rheumatoid arthritis and cataracts.$^{34}$ and references therein In this study, HNCO was reproducibly generated in both sets of experiments with different OH sources as well as with ozone as the oxidant. Barnes et al. have experimentally detected HNCO using Fourier
transform infrared spectroscopy (FT-IR) as a product from the OH oxidation of formamide (Scheme 2-2 in Appendix A). It is likely that the HNCO detected in these MEA experiments is in part a product of formamide oxidation but the origin of HNCO from the ozone experiments is currently unclear. Further work is currently underway in our laboratory to quantify HNCO, to understand its production mechanism and to better evaluate its health impact on CCS technology.

Many higher order products, i.e. compounds with more carbon atoms than MEA, containing nitrogen were detected both in positive and negative modes with the CI-TOFMS. Examples in the positive mode include C$_3$H$_8$NO$^+$, C$_3$H$_6$NO$^+$, C$_4$H$_{10}$NO$_2^+$, C$_4$H$_8$NO$_2^+$, C$_5$H$_{10}$NO$_2^+$, C$_8$H$_{15}$NO$_2^+$ (see Table 2-1 (Appendix A) for a larger list and proposed structures) and in the negative mode include NO$_3^-$, C$_6$H$_8$N$_3$O$_6^-$ (Figure 2-4). They are likely originating from condensation reactions with carbonyls to form imines, but the phase in which this reaction takes place is unknown. Attempts to place a filter between the chamber and the CI-TOFMS were unsuccessful at discriminating between gas phase and particle phase products, since all nitrogen-containing compounds stuck to the filter.

The detection of oxazolidine (C$_3$H$_8$NO$^+$) by the PTR-MS (m/z 74) and the CI-TOFMS (m/z 74.060) is evidence of high order products originating from condensation reactions, where oxazolidine is proposed to be produced by the condensation reaction of MEA with formaldehyde, itself an oxidation product, to form an imine simultaneous with the loss of water (Figure 2-4, and in Appendix A, Scheme 2-1, Table 2-1). The imine then undergoes intramolecular attack from the hydroxyl group to form oxazolidine. The products from the further oxidation of oxazolidine were also detected and further support its structure assignment (Figure 2-4). Interestingly, the production of these cyclic amines is fastest in the TME and ozone experiments where the OH concentration peaks rapidly but is then consumed rapidly. Assuming a similar sensitivity between formamide and oxazolidine on the CI-TOFMS, we estimate its yield to be on the order of 5 times that of formamide and may account for a significant portion of the N mass balance. In theory, if more carbonyl compounds are present in the TME and ozone experiment, condensation reactions may be a considerable sink of MEA and lead to an overestimation of the rate coefficient with OH radicals. However, the data points used for the rate coefficient from the TME and ozone experiment were early in the experiment, minimizing the influence of carbonyls. Further evidence that this chemistry did not substantially influence our calculated rate coefficients is the agreement
with the absolute kinetics study by Onel et al.\textsuperscript{12} where imine formation would not have been a problem in the absolute rate experiment.

There are fewer references for a proposed mechanism involving MEA and ozone, nonetheless, the reactivity trends observed suggest a nucleophilic attack of the amine onto ozone to form hydroxyamines in the case of primary and secondary amines.\textsuperscript{27} According to our product study, gas phase products including formamide (with identical yields as in the MEA and OH oxidation experiments, \(4 \pm 2\%\)), 2-aminoacetaldehyde and/or 2-iminoethanol and isocyanic acid were observed along with higher order products like oxazolidinone and its products.

To try and account for the N mass balance, an Aerodyne high-resolution aerosol mass spectrometer (AMS)\textsuperscript{37} and a scanning particle mobility sizer (SMPS) were connected to the chamber. Indeed, significant particle numbers (\(10^6\) particles/cm\(^3\)) and mass loadings (25 \(\mu g/m^3\)) of N-containing aerosol were detected during every oxidation experiment. In the presence of a reference compound (i.e. TMB), the mass loading rose to 1000s of \(\mu g/m^3\). Considerable amounts of organic N for a small molecule like MEA was found in the particle (Figure 2-5) with ratios of N/C averaging 0.2 during a TME and ozone experiment. For the mass balance, at least 15\% of the MEA-derived nitrogen went to the particle phase, 5\% went to formamide and an unknown amount went to higher order products and to HNCO.

\begin{figure}[h]
\centering
\includegraphics[width=\linewidth]{figure2-5.png}
\caption{Average aerosol mass spectrum of MEA + OH (from a TME + O\textsubscript{3} experiment) coloured by fragment family.}
\end{figure}

Amines are effective at nucleating particles due to their ability to undergo acid-base reactions.\textsuperscript{38} Particle formation from amines has been examined in the presence of nitric acid\textsuperscript{9,39} and methanesulfonic acid and water.\textsuperscript{40} However, there is little nitric acid in our system (see Figure 2-
4). The high particle loading observed can be attributed to a combination of mechanisms, including the formation of aminium salts with organic acids and the condensation of low-volatility products forming secondary organic aerosol (SOA)-like particles. Further work is warranted to understand the role of amines, including MEA, in particle chemistry.

2.6 Acknowledgements

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2.7 References


2.8 Appendix A

The PTR-MS data were used for the relative and absolute rate kinetics experiments. The PTR-MS pulled air from the chamber at 0.1 L min\(^{-1}\) and used protonated water vapor as its reagent ion. The measurements made with the PTR-MS were in selected ion mode where the m/z ratios monitored were chosen from preliminary kinetic experiments in scan mode. The inlet of the PTR-MS was maintained at 50 °C throughout the measurements. The drift tube voltages and the water flow to the source of the PTR-MS were optimized to minimize dehydration of protonated MEA (MEA + H: m/z 62 versus MEA + H – H\(_2\)O: m/z 44). The signals of the compounds of interest were normalized to m/z 21 corresponding to the H\(_3\)\(^{18}\)O\(^+\) ion.

The data obtained with the CI-TOFMS were used for product studies only. The CI-TOFMS sampled air from the chamber at 0.05 L min\(^{-1}\), which was diluted into a N\(_2\) make-up flow of 1.95 L min\(^{-1}\). The \(^{210}\)Po source on the CI-TOFMS ionizes the flow of water vapor or gaseous acetic anhydride to form H\(_3\)O\(^+\) (and water clusters) or H\(_3\)CCOO\(^-\) (and acetic acid clusters) reagent ions, respectively. The measurements made with the CI-TOFMS were analyzed with Tofwerk software in the IGOR Pro data analysis package. The analyte responses were normalized to their respective reagent ion signal, H\(_3\)O\(^+\), H\(_3\)O(H\(_2\)O)\(^+\) and H\(_3\)O(H\(_2\)O)\(_2\)\(^+\) or H\(_3\)CCOO\(^-\).

Table 2-1: List of higher order products detected by the CI-TOFMS with proposed structures

<table>
<thead>
<tr>
<th>m/z</th>
<th>Molecular formula of ion and relative signal strength</th>
<th>Proposed structure of analyte</th>
<th>m/z</th>
<th>Molecular formula of ion and relative signal strength</th>
<th>Proposed structure of analyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>74.060</td>
<td>C(_3)H(_8)NO(^+)  high</td>
<td>oxazolidine</td>
<td>115.086</td>
<td>C(<em>3)H(</em>{11})N(_2)O(^+)  low</td>
<td></td>
</tr>
<tr>
<td>72.044</td>
<td>C(_3)H(_8)NO(^+)  high</td>
<td>formamide</td>
<td>46.029</td>
<td>CH(_4)ON(^+)  high</td>
<td></td>
</tr>
<tr>
<td>116.071</td>
<td>C(<em>5)H(</em>{10})NO(_2)(^+)  high</td>
<td></td>
<td>100.076</td>
<td>C(<em>3)H(</em>{10})NO(^+)  low</td>
<td></td>
</tr>
<tr>
<td>Mass</td>
<td>Formula</td>
<td>Structure</td>
<td>Mass</td>
<td>Formula</td>
<td>Structure</td>
</tr>
<tr>
<td>-------</td>
<td>---------------</td>
<td>-----------</td>
<td>-------</td>
<td>---------------</td>
<td>-----------</td>
</tr>
<tr>
<td>104.071</td>
<td>C₄H₁₀NO₂⁺</td>
<td><img src="image1" alt="Structure" /></td>
<td>88.039</td>
<td>C₃H₆NO₂⁺</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>102.055</td>
<td>C₄H₈NO₂⁺</td>
<td><img src="image3" alt="Structure" /></td>
<td>88.076</td>
<td>C₃H₁₀NO⁺</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>90.055</td>
<td>C₃H₈NO₂⁺</td>
<td><img src="image5" alt="Structure" /></td>
<td>81.054</td>
<td>C₄H₅N₂⁺</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>60.044</td>
<td>C₂H₆ON⁺</td>
<td><img src="image7" alt="Structure" /></td>
<td>56.049</td>
<td>C₃H₆N⁺</td>
<td><img src="image8" alt="Structure" /></td>
</tr>
<tr>
<td>171.113</td>
<td>C₈H₁₅N₂O₂⁺</td>
<td><img src="image9" alt="Structure" /></td>
<td>74.096</td>
<td>C₄H₁₂N⁺</td>
<td><img src="image10" alt="Structure" /></td>
</tr>
<tr>
<td>86.060</td>
<td>C₄H₈NO⁺</td>
<td><img src="image11" alt="Structure" /></td>
<td>18.034</td>
<td>NH₄⁺</td>
<td><img src="image12" alt="Structure" /></td>
</tr>
</tbody>
</table>

In Table 2-1, product m/z 116.07 had a small signal strength for the MEA and ozone oxidation and products m/z 171.113, m/z 115.086, m/z 100.076, m/z 74.096 and m/z 18.034 were not observed in the MEA and ozone oxidation experiment.

Scheme 2-1: Proposed mechanism for the production of oxazolidine via a condensation reaction and its subsequent oxidation reaction products.
imine formation:

\[
\begin{align*}
\text{H}_2\text{N} & - \text{OH} \quad \cdot \text{O}^+ \quad \text{H}_2\text{O} \\
\text{MEA} & \quad \xrightarrow{O_2} \quad \text{H}_2\text{N} & \cdot \text{OH} \\
& \quad \xrightarrow{O_2} \quad \text{HN} & \cdot \text{OH} \\
& \quad \xrightarrow{- \text{HO}_2^+} \quad \text{HN} & \cdot \text{OH} \\
& \text{2-iminoethanol} \\
\end{align*}
\]

aldehyde formation:

\[
\begin{align*}
\text{H}_2\text{N} & - \text{OH} \quad \cdot \text{O}^+ \quad \text{H}_2\text{O} \\
\text{MEA} & \quad \xrightarrow{O_2} \quad \text{H}_2\text{N} & \cdot \text{OH} \\
& \quad \xrightarrow{O_2} \quad \text{H}_2\text{N} & \cdot \text{O}^+ \cdot \text{O}^- \\
& \quad \xrightarrow{- \text{HO}_2^+} \quad \text{H}_2\text{N} & \text{=} \\
& \text{2-aminoacetaldehyde} \\
\end{align*}
\]

isocyanic acid formation:

\[
\begin{align*}
\text{H} & \cdot \text{NH}_2 \\
& \quad \xrightarrow{\cdot \text{O}^+ \cdot \text{H}_2\text{O}} \\
\text{Formamide} & \quad \xrightarrow{O_2} \quad \text{H} & \cdot \text{NH}_2 \\
& \quad \xrightarrow{\text{HO}_2^+} \quad \text{HN} &= \text{C} = \text{O} \\
\end{align*}
\]

Scheme 2-2: Mechanism for the production of 2-iminoethanol and 2-aminoacetaldehyde from MEA by da Silva and for the production of HNCO from formamide oxidation adapted from Barnes et al.

2-Iminoethanol (see Scheme 2-3 for structure) was detected as a short lived species by the CI-TOFMS operating in positive mode. However, 2-iminoethanol and 2-aminoacetaldehyde (see Figure 2-6 for structure) both have the same mass by CI-TOFMS and an offline analysis by gas chromatography mass spectrometry (GC-MS) was used to attempt to differentiate the two products. Using a derivatization method with o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA)\textsuperscript{41,42}, 2-iminoacetaldehyde (HNCHCHO) was identified as a double derivatized PFBHA compound (Figure 2-7) and must have originated from two H-abstractions, one on each carbon of MEA. However, the derivative could have come from glyoxal, but since glyoxal was not detected by the CI-TOFMS, we conclude that the result supports the formation of both 2-iminoethanol and/or 2-aminoacetaldehyde. The gas phase oxidation of MEA is expected to predominantly proceed via the imine pathway (Scheme 2-3).
The offline analysis of the gas phase products was done by passing a flow of ~150 sccm of chamber air through a bubbler containing a solution of 5 mg/mL of o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) in water. The solutions were then extracted with ethyl acetate and analyzed by an Agilent 7890A gas chromatography and an Agilent 5975-inert mass spectrometer (GC-MS). The GC had an Agilent DB-1701 column (30 m × 0.25 mm) and the MS was operated by chemical ionization with methane gas in both positive and negative modes.

![Chemical structures](image)

**Figure 2-6: Previously detected products in MEA oxidation**

![Chemical structures](image)

**Figure 2-7: Molecules used and detected in the product offline analysis by GC-MS**
Scheme 2-3: Mechanism for the production of 2-iminoethanol and formamide from MEA
Chapter 3
Experimental and Theoretical Understanding of the Gas Phase Oxidation of Atmospheric Amides with OH Radicals


3 Chapter 3

3.1 Abstract

Atmospheric amides have primary and secondary sources and are present in ambient air at low pptv levels. To better assess the fate of amides in the atmosphere, the room temperature (298 ± 3 K) rate coefficients of five different amides with OH radicals were determined in a 1 m³ smog chamber using online proton-transfer-reaction mass spectrometry (PTR-MS). Formamide, the simplest amide, has a rate coefficient of \((4.44 \pm 0.46) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) against OH, translating to an atmospheric lifetime of ~ 1 day. N-methylformamide, N-methylacetamide and propanamide, i.e. alkyl versions of formamide, have rate coefficients of \((10.1 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\), \((5.42 \pm 0.19) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) and \((1.78 \pm 0.43) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) respectively. Acetamide was also investigated but due to its slow oxidation kinetics, we report a range of \((0.4–1.1) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) for its rate coefficient with OH radicals. Oxidation products were monitored and quantified and their time traces were fitted using a simple kinetic box model. To further probe the mechanism, ab initio calculations are used to identify the initial radical products of the amide reactions with OH. Our results indicate that N–H abstractions are negligible in all cases, in contrast to what is predicted by structure-activity relationships. Instead, the reactions proceed via C–H abstraction from alkyl groups and from formyl C(O)–H bonds when available. The latter process leads to radicals that can readily react with \(\text{O}_2\) to form isocyanates, explaining the detection of toxic compounds such as isocyanic acid (HNCO) and methyl isocyanate (CH₃NCO). These contaminants of significant interest are primary oxidation products in the photochemical oxidation of formamide and N-methylformamide, respectively.
3.2 Introduction

Amides are emitted directly to the atmosphere from biological sources as well as from industrial processes and are present at pptv levels in the atmosphere.\(^1\) In particular, tobacco smoke is a source of formamide, acetamide and propanamide, presumably formed during the combustion process.\(^2\) Mixing ratios of over 400 pptv of \(N,N\)-dimethylformamide have been observed near waste and sewage operations and an emission rate of 10 mg/kg of \(N,N\)-dibutylformamide has been measured from charbroiling hamburgers.\(^3,4\) \(N,N\)-dimethylformamide has also been detected from textile floor coverings from a polyamide composite.\(^5\) Amides have also been detected in ambient particles, biomass burning aerosols and fogwater.\(^6-8\)

Amides have secondary as well as primary sources to the atmosphere. For example, they can be formed via amine oxidation by OH radical. Since amines also have biogenic and anthropogenic sources to the atmosphere, including their use in large quantities in carbon capture and storage (CCS) technology, they may represent a significant source of amides to ambient air.\(^9\) This secondary source is of particular concern since amides are typically longer-lived species than amines.\(^9\) Indeed, a recent report by Zhu et al. detected formamide, potentially from amine oxidation, from an industrial scale carbon capture facility in Norway.\(^10\) The mechanism of gas-phase oxidation of amines to amides has also been investigated through ab initio calculations.\(^11,12\)

Only a few studies have looked at the atmospheric fate of amides. Chakir and co-workers measured the cross-section of \(N,N\)-dialkylated amides and determined that its value was smaller than or equal to \(3 \times 10^{-20}\) cm\(^2\) molec\(^{-1}\) beyond 270 nm, indicating that photolysis is a negligible sink for amides.\(^13\) Koch et al. were the first to report rate coefficients for the reaction of OH radical with amides, and they specifically looked at \(N\)-alkylated acetamides and propanamides, determining values between \(5-14 \times 10^{-12}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\).\(^14\) 1-Methyl-2-pyrrolidinone, 2-chloro-\(N\)-isopropylacetanilide and \(N\)-ethylperfluorobutyramide have been the subject of atmospheric fate studies where rate coefficients with OH and NO\(_3\) radicals and with ozone were reported; OH reactivity was found to dominate the fate of these amides.\(^15-17\) Solignac at al. studied the kinetics of OH and Cl radicals with \(N\)-alkylated formamides and acetamides and later determined the rate coefficients of OH radicals with cyclic amides.\(^18,19\) In addition, Barnes et al. reviewed these results and completed a product study of the smaller amides, identifying isocyanates as potential oxidation products.\(^20\) NO\(_3\) radicals react with \(N,N\)-dimethylated amides with rate coefficients on the order of \(10^{14}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\).
making the sink of amides towards NO$_3$ radicals competitive with OH radicals only at night.$^{21}$ These kinetics studies have been recently reviewed by Nielsen et al. in the context of the impact of amines on CCS.$^9$ Furthermore, amides may partition to aerosols but whether this sink is competitive with gas phase oxidation is unknown.

Despite the work summarized above, the atmospheric behaviour and reactivity of formamide, the smallest and most volatile of amides, has yet to be investigated. To address this gap, five different amides – (i) formamide, (ii) $N$-methylformamide, (iii) acetamide, (iv) $N$-methylacetamide and (v) propanamide – were investigated to elucidate their reactivity trends towards the OH radical, their atmospheric lifetimes and ultimately their atmospheric fate. Relative rate coefficients were measured in a smog chamber using online mass spectrometry and the oxidation products’ traces were fitted using simple box model kinetics. The mechanism was further evaluated using ab initio calculations to determine the location of the H-abstraction and fate of the resultant radicals.

### 3.3 Experimental and theoretical methods

#### 3.3.1 Laboratory study

The relative rate kinetics of five amides were measured using a previously described experimental setup.$^{22}$ Briefly, a proton-transfer-reaction mass spectrometer (PTR-MS) (Ionicon Analytik GmbH, Innsbruck Austria)$^{23}$ was connected to a 1 m$^3$ Teflon FEP film (American Durafilm) bag (Ingeniven) mounted on a Teflon-coated frame, surrounded by a total of twelve UVB lamps (Microlites Scientific). The chamber did not contain a fan. The PTR-MS was connected to the chamber by a ~1 m long 1/16” ID silco-coated steel inlet (Ionicon’s standard transfer line) heated to 50 °C linked to an FEP tubing that sampled from the middle of the chamber. The flow through the inlet of the PTR-MS was 100 sccm. These inlet conditions are similar to conditions optimized by Gylestam et al. for the detection of isocyanates by PTR-MS.$^{24}$ The signals of the compounds of interest were normalized to m/z 21 corresponding to the H$_3^{18}$O$^+$ ion.

The amides were purchased from Sigma-Aldrich and used as is with > 96% purities. The amide calibrations on the PTR-MS were accomplished by injecting known amounts of an aqueous solution of the analyte into a glass tube connected to the chamber. A flow of pure air passed through the glass tube adding the amide to the chamber and resulting in mixing ratios ranging from 40-300 ppbv. Amides were all monitored at their respective protonated molecular ion m/z, and all
had linear calibrations with sensitivities ranging from 14 to 18 ncps/ppbv (see Table 3-1 and Equation S1 in Appendix B).

A typical oxidation experiment consisted of injecting a known amount of an aqueous solution of amide into the dark 1 m$^3$ chamber. $n$-Butanol was added as the reference compound and detected by the PTR-MS at m/z 57, corresponding to the loss of water from the protonated molecular ion. Compared to amines$^{22}$, amides were better behaved in the smog chamber; little to no conditioning of the walls was required and the amides were detected by the PTR-MS with quick response times. Stable amide signals could also be monitored for hours, further demonstrating their stability within the experimental setup and on the time scale of the oxidation experiment. Most amides, with the exception of acetamide, experienced no decay under lit conditions, in the absence of hydrogen peroxide and on the time scale of the oxidation experiments. Following the establishment of a stable amide signal from the chamber, pure air from an AADCO 737-series generator was bubbled through an aqueous solution of 30 % hydrogen peroxide at a rate of 500 sccm. Approximately 15 minutes later, the UVB lights surrounding the chamber were turned on to generate OH radicals in concentrations of approximately $2 \times 10^7$ molec cm$^{-3}$, inferred from the loss rate of $n$-butanol. Hydrogen peroxide was continuously added to the chamber to keep the supply of OH radical precursor approximately constant during the experiment. Experiments were conducted under dry (< 1 % RH) and NO$_x$-free conditions.

HNCO was detected as an oxidation product and was quantified using PTR-MS (detected at m/z 44), ion chromatography (IC) and a homemade HNCO source. A flow of HNCO was generated by heating cyanuric acid inside a stainless steel tube to 250 °C, controlled by a thermocouple, while passing a flow of 200 sccm of nitrogen over the headspace of the tube. A dilution flow was added to the headspace flow to avoid high gas-phase concentrations of HNCO and thus polymerization of HNCO in the tubing. The source showed variability in its HNCO permeation rate from week to week, so the PTR-MS was independently calibrated by bubbling HNCO through bubblers filled with deionized water at a known rate and for a known amount of time and quantified by IC (see Graph 3-2 in Appendix B). Further experimental details are available in Appendix B. We ruled out any interference from CO$_2^+$ (also detected at m/z 44), since ambient CO$_2$ concentrations of ~380 ppmv do not produce any significant signal at m/z 44 in the PTR-MS. Control experiments involving H$_2$O$_2$ and UVB light, but in the absence of a gas-phase amide showed production of HNCO, implying a background signal for this weak acid in the chamber. We suspect HNCO to
come from wall reactions where amines and amides may be present. This background was accounted for in the yield calculation by averaging the final HNCO signal of more than ten control experiments and subtracting this value (ranging from 8-40 % of the total signal) from the final HNCO signal in the amide oxidation experiments. The yield reported is the quotient of moles of product produced (corrected by its respective background signal) divided by the moles of amide that decayed away at the end of the reaction, i.e. when the lights surrounding the chamber were turned off. This method of calculating yields was verified by plotting the appearance of product versus the loss of starting material and taking the slope of that plot as the yield as well as verified by the kinetic model fits. The yields reported represent the range measured during different experiments.

Methyl isocyanate was also detected as an oxidation product at m/z 58. To correct for its decay, the methyl isocyanate time trace was subtracted by 4 % of the n-butanol signal at m/z 57, a percentage that represents the natural abundance of $^{13}$C in n-butanol, which has an isobaric interference with methyl isocyanate. Formamide (m/z 46) was corrected by subtracting 2 % of the acetaldehyde signal at m/z 45 to account for its $^{13}$C contribution to m/z 46.

Following each oxidation experiment, the chamber was purged at least overnight with pure air. The chamber was also cleaned on a weekly basis by bubbling 30 % hydrogen peroxide into an amide-free chamber with the UVB lights turned on for several hours. A small background signal of formamide and HNCO was observed during these control experiments, suggesting a contribution of wall chemistry within this experimental set up. The product yields reported have been corrected using these background signals.

3.3.2 Ab initio study

The mechanism of OH radicals reacting with the five studied amides, as well as the reaction of select product radicals with O$_2$, was investigated using computational ab initio methods. Structures were optimized using the M06-2X density functional with the 6-31G(2df,p) basis set.$^{25}$ Subsequent higher-level energies were obtained using the G3X-K composite theoretical method.$^{26}$ This method has been designed specifically for accurate thermochemical kinetics, and utilizes the M06-2X/6-31G(2df,p) structures in a series of single point energy calculations with basis sets of incrementally decreasing size, from Hartree-Fock theory to perturbation theory (MP2, MP3, MP4), and ultimately to coupled cluster theory (CCSD(T)). Energies calculated at these levels are
combined with empirical scaling terms to arrive at the final G3X-K energy. Energies quoted here are 0 K enthalpies (i.e., electronic energy + zero point energy), and are expected to be accurate to within 1 kcal mol\(^{-1}\), on average.\(^{26}\) All calculations were performed using the Gaussian 09 code.\(^{27}\)

### 3.4 Results and discussion

#### 3.4.1 Kinetic results

Upon exposure to OH radicals inside the 1 m\(^3\) smog chamber, the amides under study exhibited pseudo-first order decay kinetics at room temperature (298 ± 3 K) and atmospheric pressure. The relative rate method\(^{28}\) allowed for the determination of their respective bimolecular rate coefficients using \(n\)-butanol as the reference compound. Accurate knowledge of the rate coefficient of \(n\)-butanol with OH radicals, \((8.86 ± 0.85) \times 10^{-12}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\), is necessary to employ Equation 1.\(^{29}\) A plot of the natural logarithm of the normalized amide decay signal as a function of the natural logarithm of the normalized \(n\)-butanol decay signal yields the ratio of both rate coefficients, \(k_{amide+OH}/k_{butanol+OH}\) (Figure 3-1, A-D). Note that \(n\)-butanol served as a good reference compound as it does not react with amides, has no observable wall loss, and is detected at m/z 57 by the PTR-MS, which does not interfere with other signals of interest.

Rate coefficients were determined based on a minimum of three reproducible experiments for: formamide \((4.44 ± 0.46) \times 10^{-12}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\), \(N\)-methylformamide \((10.1 ± 0.6) \times 10^{-12}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\), \(N\)-methylacetamide \((5.42 ± 0.19) \times 10^{-12}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\) and propanamide \((1.78 ± 0.43) \times 10^{-12}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\). See Figure 3-1, A-D, for typical relative rate plots for the four amides studied. Furthermore, forcing the linear regression through the origin does not change the slope by more than 5 \%, a value consistently less than the reported standard deviation of the experiments.

Barnes et al. used an FTIR technique to study the kinetics of other amides but reported interference in the method when looking at formamide.\(^{20}\) Consequently, this study represents the first reported experimental rate coefficient for formamide and compares well with Barnes’ predicted value of \(4 \times 10^{-12}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\). In addition, our value for \(N\)-methylformamide lies within the uncertainty of Barnes et al.’s value of \((8.6 ± 2.4) \times 10^{-12}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\).\(^{20}\) \(N\)-methylacetamide’s reaction with OH radicals has been previously investigated, once by Koch et al., \((5.2 ± 0.19) \times 10^{-12}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\), and again by Barnes et al., \((11 ± 3) \times 10^{-12}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\).\(^{14,20}\) The value obtained in this relative rate study closely matches Koch et al.’s value, measured by absolute rate kinetics using
flash photolysis coupled to resonance fluorescence. This study is also the first to report the rate coefficient of propanamide with OH radicals. Since its rate coefficient is significantly slower than the reference compound, a slightly more scattered rate plot was observed (Figure 3-1D).

The uncertainty reported with the rate coefficients represents the standard deviation of multiple experiments and is less than a 10 % error for formamide, N-methylformamide and N-methylacetamide. An additional uncertainty arises from the rate coefficient of the reference compound i.e. n-butanol with OH radicals, and consequently a total uncertainty closer to 20 % should be considered when using these rate coefficients in model evaluations. Propanamide’s rate coefficient is approximately five times slower than the reference compound n-butanol which leads to an uncertainty of 24 %.

Acetamide was also investigated under identical conditions but since its oxidative decay was difficult to reproduce, in part due to a slow reaction and an unsteady signal inside the chamber, a large uncertainty on the rate coefficient was obtained. Based on three experiments, an average rate coefficient of \((0.77 \pm 0.35) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) was measured for acetamide (see Graph 3-4 in Appendix B for a typical plot). The previously published value by Barnes et al. of \((3.5 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) is quite high compared to our experimental results.\(^\text{20}\) We choose to report a range of \((0.4−1.1) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) for acetamide to take into consideration the large uncertainty associated with this measurement.

\[
\text{Equation 1: } \ln \left( \frac{[\text{amide}]_0}{[\text{amide}]_t} \right) = \frac{k_{\text{amide}+\text{OH}}}{k_{\text{butanol}+\text{OH}}} \ln \left( \frac{[\text{butanol}]_0}{[\text{butanol}]_t} \right)
\]
Figure 3-1: Plot of Equation 1 for formamide (A), N-methylformamide (B), N-methylacetamide (C) and propanamide (D) where the linear regression is forced through the origin.

3.4.2 Reaction products and mechanisms

The experimental decays of formamide, N-methylformamide, N-methylacetamide and propanamide and the production of their respective oxidation products were fitted using simple kinetic box model equations (see Appendix B for full description of equations). The yields of the oxidation products were also quantified (see Scheme 1). Because the reaction of acetamide was slower, we were unable to reproducibly quantify the yields of its oxidation products. HNCO was detected under all experimental conditions as a primary product from formamide and possibly as a primary or secondary product from the other amides investigated. HNCO is toxic through protein
carbamylation and so exposure levels through biomass burning and diesel exhaust are currently of concern.\textsuperscript{30,31} A recent report evaluating HNCO concentrations at three different urban and regional sites in the US found mixing ratios ranging from < 0.003 to 1.2 ppbv and suggest the presence of both primary and secondary sources to explain observed diurnal profiles.\textsuperscript{32}

Methyl isocyanate was detected solely in the oxidation of \textit{N}-methylformamide by OH radicals. This product is of major health concern and was responsible for the death of thousands of residents in Bhopal, India during a methyl isocyanate leak from a nearby pesticide plant in 1984.\textsuperscript{33} Methyl isocyanate was previously detected by FTIR from the oxidation of \textit{N}-methylformamide but the product yield was not quantified.\textsuperscript{20} In this study, we quantify methyl isocyanate by assuming it has the same sensitivity in the PTR-MS as the average of the amides quantified (17.1 npcs/ppbv) (see Table 3-1 in Appendix B).

We employ ab initio calculations to assist in understanding the kinetics of the OH radical reactions with the amides investigated here, as well as the mechanism of isocyanic acid and methyl isocyanate formation. Results are presented for the five amide + OH radical systems, so as to first understand the radical products arising from these reactions and to gain insight into the differences measured in their kinetics. Following this first step, the secondary reactions of key radical products with O2 are examined, shedding light on the first generation products arising from the photochemical oxidation of these amides.

### 3.4.2.1 Formamide

Figure 3-2A shows the oxidative decay of formamide and the production of HNCO. The formamide decay is well captured by the pseudo-first order fit (red line in Figure 3-2A). The yield of HNCO was measured to be 17-19 % in a set of six reproducible experiments. When fitting the HNCO trace with Equation S8 in a kinetic box model, we find that a yield (\(\gamma_2\)) of 25 % best fits the data, similar to the experimental value. Note that HNCO has no appreciable gas-phase loss rate to oxidants within the time frame of these oxidation experiments. Indeed, its ambient temperature lifetime with OH radicals, extrapolated from high-temperature data, is on the order of decades.\textsuperscript{34} We consequently do not consider a sink for HNCO when fitting its time trace. To further explore the site of H-abstraction on formamide and the mechanism of HNCO formation from formamide, we turn to ab initio calculations.
In Figure 3-3, an energy diagram is provided for the formamide + OH radical reaction, where abstraction can take place from either the formyl C–H site (right hand side, Figure 3-3) or from the amide N–H site (left hand side). In both cases, reaction initially proceeds via the formation of a pre-reaction complex, followed by an H-abstraction transition state that exothermically leads to water and the corresponding CNOH₂ radical product. For N–H abstraction the overall reaction is only mildly exothermic (ca. 3 kcal mol⁻¹), reflecting the very high dissociation energy for this bond (116 kcal mol⁻¹). Accordingly, the transition state for N–H abstraction is high in energy – over 6 kcal mol⁻¹ above the reactants – and abstraction from this site will proceed very slowly and is unlikely to contribute in any substantial way to the formamide + OH reaction. The C–H bond in formamide is considerably weaker than the N–H bond (bond dissociation energy of about 93 kcal mol⁻¹), and abstraction at this site is therefore much more facile. Here, the abstraction transition state lies just above the energy of the reactants (0.16 kcal mol⁻¹), and we suggest that this reaction almost exclusively accounts for the formamide + OH products, which would be the NH₂CO radical (+ H₂O).

When considering the first generation products for formamide, the NH₂CO radical appears to be the exclusive reaction product, and in the atmosphere it will readily associate with O₂ to yield a peroxy radical, NH₂C(O)O₂. An energy diagram for this reaction is provided in Figure 3-4. We see that O₂ addition to NH₂CO is exothermic by over 35 kcal mol⁻¹, providing considerable excess vibrational excitation to the peroxy radical intermediate. Bath gas collisions would be expected to remove this excess energy, providing a thermalized peroxy radical that could then be lost by bimolecular reactions with NO and other species. Instead, however, the α-amino group provides a low-energy avenue to unimolecular reaction before collisional deactivation can proceed, as recently discovered for α-aminoalkylperoxyl radicals.³⁵,³⁶ Here, the HO₂ radical is expelled in a concerted process via the transition state shown as an inset in Figure 3-4. This transition state energy is 19 kcal mol⁻¹ above the peroxy radical and a substantial 18 kcal mol⁻¹ below the reactants; the vibrationally excited peroxy radical adduct will initially have more than enough energy to surmount this barrier. Following HO₂ loss, a weak H-bonded adduct is formed, which can dissociate along a barrierless potential to yield isocyanic acid (+ HO₂). This process therefore explains the experimental observation of isocyanic acid as the major primary oxidation product of formamide. Based upon the reaction energetics and the known chemically activated reaction kinetics of similar peroxy radicals,¹¹,³⁷,³⁸ we expect almost quantitative production of HNCO +
HO₂ upon reaction of formamide with OH at tropospheric conditions, and therefore suggest a theoretical yield of 100 % (see Scheme 1).

The experimentally measured HNCO yield of 17-19 % only accounts for a fraction of the mass balance (Figure 3-2A). It is therefore possible that surface interactions of HNCO may be affecting its concentration in the gas phase. Perhaps HNCO uptake onto particles or surfaces is also taking place in the chamber. Alternatively, quenching of the NH₂C(O)O₂ radical could be an appreciable process, in which case bimolecular chemistry is expected to lead to the carbonyloxy radical NH₂C(O)O, which would likely dissociate rapidly to CO₂ and the aminyl radical NH₂. Further investigation of HNCO’s heterogeneous chemistry is currently ongoing in our laboratory to address this discrepancy.

Figure 3-2: (A) Oxidative decay of formamide and formation of its major primary product, HNCO. The dots represent the 10-second PTR-MS data and the solid red lines represent the
exponential fits (Equations S4 and S8 (where \( \gamma_2 = 25 \%) \) for formamide and HNCO respectively). (B) Oxidative decay of \( N \)-methylformamide and its products, methyl isocyanate, formamide and HNCO. The dots represent 10-second PTR-MS data and the solid red lines represent the exponential fits (Equations S4, S8 (where \( \gamma_2 = 50 \%) \), S6 (where \( \gamma_1 = 15 \%) \), S9 (where \( \gamma_1 \gamma_2 = 15 \%) \), for \( N \)-methylformamide, methyl isocyanate, formamide and HNCO respectively).

Figure 3-3: Theoretical energy diagram for formamide + OH. Energies are 0 K enthalpies in kcal mol\(^{-1}\), at the G3X-K level of theory.
Figure 3-4: Theoretical energy diagram for formamide’s formyl radical + O₂. Energies are 0 K enthalpies in kcal mol⁻¹, at the G3X-K level of theory.

3.4.2.2 N-Methylformamide

The progress of the reaction of N-methylformamide with OH radicals is illustrated in Figure 3-2B. Methyl isocyanate appears to be the major product and was measured in 36-40 % yield. The fit using Equation S8 with a γ₂ = 50 % seems to reproduce the data well. The fit for methyl isocyanate in Figure 3-2B does not consider any sink terms, as its reactivity towards OH radicals is estimated to be ~10⁻¹³ cm³ molec⁻¹ s⁻¹ by the EPI Suite model and would account for < 1 % difference in the fit. Formamide (fit of 15 %) and HNCO were also detected as oxidation products (Figure 3-2B). Note that in Figure 3-2B, HNCO is treated as a secondary product arising solely from the oxidation of formamide (Equation S9).

Figure 3-5 depicts a theoretical energy diagram for the N-methylformamide reaction with OH, proceeding via abstraction at either of the two unique C–H sites. Abstraction of an N–H hydrogen is again energetically uncompetitive (with transition state 4 kcal mol⁻¹ above the reactants) and is shown in Appendix B (Figure 3-10). We observe in Figure 3-5 that the OH radical can abstract an H atom from either carbon, leading to the CH₂NHCHO (left hand side) or CH₃NHCO (right hand side) radicals. In both cases, the transition states lie below the reactants in energy, at -1.30 kcal mol⁻¹ and -0.67 kcal mol⁻¹, for the respective alkyl and formyl abstractions. This result is consistent
with the rate coefficient of N-methylformamide being more than twice that of formamide. Considering the uncertainty of the calculations reported here, we cannot definitively discriminate between the CH$_2$NHCHO and the CH$_3$NHCO radical products. As such we assign theoretical yields of 50% to both products, as a rough initial estimate (see Scheme 1).

Energy diagrams for the reaction of O$_2$ with the respective CH$_2$NHCHO and CH$_3$NHCO radicals are shown in Figure 3-6. For the CH$_2$NHCHO radical (top of Figure 3-6), the resultant peroxyl radical can eliminate HO$_2$ to yield an imine, but the required barrier heights are at around the energy of the entrance channel, and the initially excited peroxyl radical will be rapidly deactivated to below the required thresholds. Interestingly, the high barrier for this process arises from the reaction thermodynamics, with the conjugated imine product CH$_2$NCHO being comparatively unfavorable. Note also from Figure 3-6 that an intramolecular abstraction from the formyl group can take place, at 4.44 kcal mol$^{-1}$ below the reactants, forming a radical intermediate that can ultimately dissociate to HNCO and CH$_2$OOH (although again at above the reactant energy). Indeed, HNCO was detected experimentally in < 5% yield, and may have two gas phase sources within these experiments: a primary product from the reaction of CH$_2$NHCHO + OH (as discussed above) and/or a secondary product from the oxidation of formamide which was also detected in the oxidation of N-methylformamide.

According to our theoretical results, the O$_2$:CH$_2$NHCHO peroxyl radical can be collisionally deactivated under tropospheric conditions, allowing it to be removed through bimolecular chemistry (Scheme 3-2 in Appendix B). If this peroxyl radical is converted to the corresponding alkoxyl radical, OCH$_2$NHCHO, through reaction with NO (and other radicals), β-scission at the C–N bond could then lead to formaldehyde and the NHCHO radical, whereas C–H scission (or H abstraction by O$_2$) would yield NH(CHO)$_2$, diformamide (Scheme 3-2 in Appendix B). The NHCHO aminyl radical formation is of interest as they are generally thought to be removed from the atmosphere through reaction with radical species such as NO and NO$_2$, potentially leading to toxic compounds that include nitrosamines and nitramines. If the NHCHO aminyl radical is formed in the N-methylformamide chamber experiments, it could be long lived enough to abstract an H from another compound in the chamber and produce formamide, which was detected as an oxidation product, albeit with low yields (< 30%). However, the production of formamide in these oxidation experiments does not show purely first order kinetics, underlining the possibility that heterogeneous chemistry may also be occurring on the chamber walls (Figure 3-2B). On the other
hand, Barnes et al. detected diformamide as an oxidation of $N$-methylformamide in an estimated 50 % yield.\textsuperscript{20} In our oxidation experiments, the diformamide protonated molecular ion (m/z 74) was detected by the PTR-MS but as a trace product with signal intensities consistently less than the signal of HNCO (see Figure 3-2B) and so we did not quantify its yield.

Upon reaction of the CH$_3$NHCO radical with O$_2$, a facile unimolecular reaction pathway is available, as illustrated in the bottom half of Figure 3-6. Similar to the formamide NH$_2$CO radical, O$_2$ addition produces a peroxyl radical that can eliminate HO$_2$ via a barrier 18 kcal mol$^{-1}$ below the reactants. This reaction leads to the experimentally observed reaction product methyl isocyanate. A second mechanism that also proceeds with a transition state energy below the reactants is available with a relative barrier height of around -7 kcal mol$^{-1}$. In this case, the peroxyl group abstracts an H atom from the $N$-methyl moiety, ultimately yielding CH$_2$NH and CO$_2$ and regenerating the OH radical in the process. This mechanism has been identified in secondary and tertiary amines, and is known to be uncompetitive with the facile HO$_2$ elimination reaction, when available.\textsuperscript{41} The experimental methyl isocyanate yield of 36-40 % is commensurate with similar yields of both CH$_2$NHCHO and CH$_3$NHCO evolving from the reaction of OH radicals with $N$-methylformamide, followed by almost quantitative conversion of CH$_3$NHCO to CH$_3$NCO + HO$_2$. These results are also consistent with methyl isocyanate detected by Barnes et al. from the oxidation of $N$-methylformamide.\textsuperscript{20}
Figure 3-5: Theoretical energy diagram for N-methylformamide + OH. Energies are 0 K enthalpies in kcal mol\(^{-1}\), at the G3X-K level of theory. The N–H abstraction requires a significant barrier (4.03 kcal mol\(^{-1}\)) and is shown in Figure 3-10 in Appendix B.
Figure 3-6: Theoretical energy diagrams for N-methylformamide’s methyl radical + O₂ (top) and formyl radical + O₂ (bottom) reactions. Energies are 0 K enthalpies in kcal mol⁻¹, at the G3X-K level of theory.
### Scheme 3-1: Product identification and quantification of amide oxidation by OH radicals in a 1 m³ Teflon FEP film bag and in the absence of NOx based on experimental and theoretical evidence. The yields represent the range measured during different experiments.

#### 3.4.2.3 Acetamide

Acetamide reacted away too slowly within our experimental setup to analyze its products. We show through ab initio calculations that acetamide is indeed expected to react more slowly than the other amides considered in this study. A theoretical energy diagram for the acetamide + OH reaction is provided in Figure 3-11 in Appendix B. Here, an H-abstraction can again transpire at the nitrogen, but with a barrier significantly above the reactant energies (> 5 kcal mol⁻¹), and this process is expected to be negligible. Instead, abstraction from the methyl group is thought to dominate, proceeding via a transition state at 2 kcal mol⁻¹ above the reactants, leading to the CH₂C(O)NH₂ radical as the major product. The relatively large barrier for this reaction can explain the slow kinetics reported here, where the rate coefficient is measured to be a fraction that of the formamide + OH reaction. The slow rate of reaction also likely contributes to the difficulties associated with obtaining reproducible measurements of the acetamide + OH rate coefficient in the chamber experiments. According to these calculations, the N-H abstraction is uncompetitive, in contrast to the proposed mechanism by Barnes et al., and we therefore suggest that the abstraction occurs solely on the methyl group. The products have yet to be quantified although we did detect formamide and HNCO but we believe that the proposed 100 % yield for HNCO by Barnes et al. is unlikely.
3.4.2.4  \textit{N}-Methyl acetamide

Time traces of the evolution of the products of \textit{N}-methylacetamide are presented in Figure 3-8 in Appendix B. Formamide was detected as the major product with measured yields between 62-87 \% and a fit of 80 \% yield best reproduced its experimental trace. A product at m/z 60 was also observed and could be either \textit{N}-methylformamide or acetamide. Its trace was fitted with a yield of 10 \% using Equation S6 under the assumption that m/z 60 is a primary product but has a sink with a rate coefficient similar to acetamide’s with OH. HNCO was also detected as a product and was fitted with Equation S9.

A theoretical energy diagram for \textit{N}-methylacetamide’s reaction with OH is provided as Figure 3-12 in Appendix B. The \textit{ab initio} calculations once again indicate that abstraction from the N–H site requires a large barrier (3.35 kcal mol\(^{-1}\)) and it is not discussed further. There are two unique C–H bonds in \textit{N}-methylacetamide, analogous to the respective methyl group abstractions in acetamide and \textit{N}-methylformamide. The lowest barrier to reaction corresponds to H atom abstraction from the N-methyl group, producing the CH\(_2\)NHC(O)CH\(_3\) radical. This radical should be the dominant reaction product, accompanied by lesser quantities of CH\(_3\)NHC(O)CH\(_2\). The calculated overall barrier height for \textit{N}-methyl H-abstraction (-2.0 kcal mol\(^{-1}\)) is similar to, but somewhat less than, the equivalent H-abstraction in \textit{N}-methylformamide (-1.3 kcal mol\(^{-1}\)) due to the introduction of the acetyl functional group. The substantially higher experimental rate coefficient for the \textit{N}-methylformamide vs. \textit{N}-methylacetamide reaction with OH therefore provides further support for our finding that formyl C–H abstractions are primary processes in the photochemical oxidation of amides, when available. The barrier for H-abstraction from the acetyl group in \textit{N}-methylacetamide (1.3 kcal mol\(^{-1}\)) is also reduced somewhat from that for the analogous process in acetamide (2.0 kcal mol\(^{-1}\)) by introduction of the \textit{N}-methyl substituent, although it remains above the reactant energies.

Formamide may arise as a secondary oxidation product of the CH\(_2\)NHC(O)CH\(_3\) radical (by analogy to \textit{N}-methylformamide); being the major reaction product this is consistent with the observation of formamide yields in the range of 62-87 \%. Formamide may also be produced as an oxidation product of \textit{N}-methyl acetamide originating from the CH\(_2\)NHC(O)CH\(_3\) radical and we present the energy diagram for this process in Figure 3-13 in Appendix B. We also cannot rule out the possibility that formamide is being produced via heterogeneous chemistry occurring on the
walls of the chamber and the exact mechanism of formamide production remains unclear. Comparatively, Barnes et al. state that they were unable to detect formamide in their experimental setup due to interferences with the OH radical precursor, CH$_3$ONO, and potential oxidation products.$^{20} $

### 3.4.2.5 Propanamide

Time traces of the evolution of the products of propanamide are presented in Figure 3-9 in Appendix B. The major oxidation product detected is formamide but its experimentally measured yield fell within the uncertainty associated with the formamide production during amide-free control experiments so we only report a $< 30 \%$ yield. On the other hand, using Equation S6 in a kinetic box model to fit the formamide trace, we obtain a yield of 60 %. The discrepancy between the measured and fitted yields is likely due to the presence of a sink for formamide at long reaction times (see Figure 3-9 in Appendix B). HNCO was detected during the experimental oxidation and again may be a primary or secondary product.

When the methyl group in acetamide is extended to an ethyl group, as in the case of propanamide, we find that N–H abstraction still requires a significant barrier, but that abstraction from the now secondary C–H carbon has a slightly lower (but still positive) transition state barrier of +0.34 kcal mol$^{-1}$ (Figure 3-14 in Appendix B). On the other hand, abstraction from the primary C–H site proceeds with a barrier just below the reactants (-0.30 kcal mol$^{-1}$). Within the accuracy of the reported calculations, we therefore suggest that both the CH$_2$CH$_2$C(O)NH$_2$ and CH$_3$CHC(O)NH$_2$ radicals will arise as products of the propanamide + OH reaction. These results also support a rate coefficient for the reaction of propanamide with OH that is towards the lower end of the amides measured in this study.

Even though we are not quantitative about the yield of formamide from the oxidation of propanamide, its production could originate from the minor NH$_2$C(O)CHCH$_3$ radical product, relative to the NH$_2$C(O)CH$_2$CH$_2$ radical (which we then hypothesize cannot lead to formamide production). Irrespective of these speculations, the specific pathways that result in relatively high yields of formamide from oxidation of all of the substituted amides studied here remain to be resolved and the role of heterogeneous chemistry should also be considered.
3.4.3 Reactivity trends

Figure 3-7 provides the structures of nine simple amides and includes a summary of the rate coefficients measured in this work and in previous work. The compounds are arranged in rows with increasing degree of N-alkylation from left to right, and in columns with increasing length of alkyl chain from top to bottom. The rate coefficients increase as a function of increasing number of methyl groups on the nitrogen. This observation may be explained by the addition of a methyl group which adds a competitive reactive pathway for H-abstraction from the methyl C–H. Yet, the ability of the methyl group to donate electron density to the amide bond facilitates the H-abstraction of the acetyl C–H by the electrophilic OH radical. There is a decreasing reactivity trend from formamide to propanamide to acetamide towards OH radicals which also seems to hold true for their methylated analogues. This trend is not straightforward since the H-abstraction occurs at different locations on the H/alkyl functional group attached to the carbonyl, dictating the preferred mechanistic pathway and hence influencing the experimental rate coefficient.

The rate coefficients of amides with OH radicals are slower than with their homologous amine. For example, the rate coefficient of methylamine, the homologue of formamide has a rate coefficient of \((17.3 \pm 1.1) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\), almost four times the rate of formamide.\(^{42}\) The carbonyl moiety draws electron density from the functional groups on either side of its carbon atom, rendering them less reactive towards an OH radical. This chemical property explains why amides are longer lived in the atmosphere than amines. The incomplete homologous summary for amines is depicted in Figure 3-15 in Appendix B.

The US Environmental Protection Agency’s (EPA) Estimation Program Interface (EPI) Suite model was used to compare the experimentally determined amide rate coefficients shown in Figure 3-7 with their empirical estimates.\(^{40}\) The AOPWIN module (v1.92) within the EPI suite model employs structure-activity relationships (SARs) for estimating OH reaction rate coefficients based upon those developed by Atkinson and co-workers.\(^{28,43,44}\) Graph 3-1 shows the correlation between the predicted rate coefficients using EPI Suite and the measured rate coefficients; the numbers (1°, 2°, 3°) represent the degree of N-methylation on the amide, and the colors match the amide groups in Figure 3-7. The model appears to correctly predict the influence of changing degree of N-methylation, but struggles to represent the primary amides (formamide, acetamide and
propanamide). These primary amides are the slowest to react with OH, and consequently have the longest atmospheric lifetimes.

Upon consultation of the AOPWIN user guide, we can better assess the origin of the predicted rate coefficients. Interestingly, the AOPWIN model does not consider formyl C–H abstractions in amides, but does include N–H abstractions, along with reaction at saturated carbon atoms (see Appendix B for relevant AOPWIN notes). However, our ab initio and product detection results demonstrate that the formyl C–H and the alpha C–H abstractions are likely to be major reaction channels for the amides. Furthermore, we show that N–H abstractions, when available, should in all cases be negligible. Attempts to determine a value for the substituent factor $F(-\text{C(O)N}<)$ for amides in the context of the SAR model of Kwok and Atkinson\textsuperscript{44} proved to be difficult with the limited dataset of rate coefficients presently available, and further kinetic studies are needed. However, our experiments on formamide suggest that the rate coefficient term $k(\text{HC(O)N}<)$ should be around $4 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$ and this number is also compatible with the available data for N-methyl and $N,N$-dimethyl formamide. In comparison, the analogous aldehyde C–H abstraction rate coefficient term would be \textit{ca.} $17 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$.\textsuperscript{44} It is therefore apparent that the $-\text{NH}_2$ group is deactivating the formyl C–H abstraction, although not to the extent where it can be neglected altogether (as is presently the case). The rate coefficient component attributable to N-methyl abstractions would be \textit{ca.} $5 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$, consistent with most of the reactivity occurring on the methyl group for $N$-methylacetamide for example. Furthermore, a total rate coefficient on the order of $10 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$ for $N$-methylformamide agrees well with the reaction proceeding at almost equivalent rates at the alkyl and formyl substituents. It does appear that $N$-methylation of amides has a minor impact upon the reactivity of the acetyl functionality, and \textit{vice versa}.

This analysis prompted us to consider the analogous series of amines shown in Figure 3-15 in Appendix B and their predicted rate coefficients are plotted against the experimentally measured rate coefficients of amines with OH radicals in Graph 3-5 in Appendix B. The AOPWIN output predicts a major contribution from the N–H abstraction mechanism. Nonetheless, the N–H abstraction channel appears to be of more significance for amines than for amides.\textsuperscript{11,45} This study’s mechanistic work suggests a reevaluation of the way that H-abstraction is treated for organo-nitrogen compounds within the AOPWIN model and ongoing work in our laboratory aims to address this issue.
Figure 3-7: Summary of room temperature rate coefficients with OH radical of nine amides based on their alkyl chain length (grouped by colors) and degree of N-methylation (grouped by column).
Graph 3-1: Estimated rate coefficients using EPA’s EPI Suite as a function of experimentally measured rate coefficients for nine amides. The numbers represent the level of N-methylation on the amide, so that 1° represents primary amides, 2° represents secondary amides and 3° represents the tertiary amides. The color coding matches Figure 3-7, so that the blue series represents formamide and its alkylated analogues, the red series represents acetamide and its alkylated analogues and the green series represents propanamide and its alkylated analogues. The solid line is the 1:1 relationship, and the dotted lines have slopes differing by a factor of two from the 1:1 relationship.

3.5 Conclusion

The rate coefficients of the oxidation of five different amides with OH radicals were measured for formamide \((4.44 \pm 0.46) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\), N-methylformamide \((10.1 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\), acetamide \(((0.4–1.1) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})\), N-methylacetamide \((5.42 \pm 0.19) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) and propanamide \((1.78 \pm 0.43) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) using relative rate experiments in a 1 m³ smog chamber. These rate coefficients correspond to lifetimes against OH radicals on the order of 0.5 – 7 days using an OH radical concentration of \(2 \times 10^6 \text{ molec cm}^3\). It is therefore likely that reactions with OH radicals are the dominant daytime sink for amides.
The evolution of the amides was monitored by PTR-MS and so was the production of \( N \)-containing products which included toxic gas-phase molecules like HNCO and methyl isocyanate. The time trace of the oxidation products were also modelled using kinetic equations. The ab initio calculations presented can explain the observation of HNCO and \( \text{CH}_3\text{NCO} \) upon the reaction of formamide and \( \text{N}-\text{methylformamide} \) respectively with OH radicals. The peroxyl radical mechanisms developed here are also consistent with no direct isocyanate formation from any of the other amides investigated in this study (although other isocyanates could be reasonably expected to form in the OH radical reactions of other \( \text{N} \)-substituted derivatives of formamide). The mechanism for formamide production from \( \text{N}-\text{methyl formamide} \) and the other substituted amides, however, remains unclear. Furthermore, we expect that reactions with \( \text{NO}_3 \) radicals or Cl radicals would lead to similar mechanistic pathway assuming a H-abstraction mechanism.

### 3.6 Acknowledgement

The authors acknowledge the Canada Foundation for Innovation and the Ontario Research Fund for infrastructure support and NSERC and Environment Canada for operational support. NB would like to thank Vanier Canada Graduate Scholarships for funding. GdS is grateful for support through the Australian Research Council (DP110103889, DP130100862, FT130101304). The authors would also like to thank John Liggio for donating the HNCO source as well as Gregory Wentworth for help with the ion chromatograph.

### 3.7 References


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3.8 Appendix B

3.8.1 Instrument details

The PTR-MS data were used for the relative rate kinetics experiments. The PTR-MS pulled air from the chamber at 0.1 L min\(^{-1}\) and used protonated water vapor as its reagent ion. The measurements made with the PTR-MS were in selected ion mode where the m/z ratios monitored were chosen from preliminary kinetic experiments in scan mode. The inlet of the PTR-MS (Ionicon’s standard transfer line) was maintained at 50 °C throughout the measurements. The drift tube voltages and the water flow to the source of the PTR-MS were optimized to US = 30 V, USO = 90 V, drift = 545 V, UQL = 49 V, UNC = 6.2 V, source = 6.5 mA. The signals of the compounds of interest were normalized to m/z 21 corresponding to the H\(^3\)\(^{18}\)O\(^+\) ion.

The calibration of the HNCO source involved bubbling the nitrogen/HNCO flow into approximately 20 mL of deionized water inside a bubbler for a known amount of time (between 1 - 2 hours) at a known rate (between 0.45 - 0.50 L min\(^{-1}\)). This procedure was repeated four times for different flows to calibrate the PTR-MS signal at m/z 44, i.e. HNCO. Breakthrough experiments indicated that all the HNCO was efficiently scavenged in the first bubbler. The volume from the bubbler was then transferred to a 50 mL volumetric flask and topped up with deionized water. Then, 5 mL of this solution was injected into an IC (Dionex). Following the injection, the analyte accumulated on a concentrator which was then flushed with the potassium hydroxide eluent through an IonPak AS17 column (4 × 250 mm). The IC was calibrated using standard solutions of potassium isocyanate (See Graph 3-3 in Appendix B). The error on the PTR-MS calibration from this procedure is estimated to be 14%, based on the standard deviation of the slope of the linear regression.

Table 3-1: Table of sensitivities of amides and isocyanic acid on the PTR-MS in normalized counts per second per part per billion. The methyl isocyanate sensitivity is based on the average sensitivity of the six other amides, i.e. no direct calibration with methyl isocyanate was performed.

<table>
<thead>
<tr>
<th>Amide</th>
<th>sensitivity (ncps/ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formamide</td>
<td>17.1</td>
</tr>
<tr>
<td>N-methylformamide</td>
<td>18.1</td>
</tr>
<tr>
<td>N-methylacetamide</td>
<td>15.1</td>
</tr>
<tr>
<td>Propanamide</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-------</td>
</tr>
<tr>
<td>Acetamide</td>
<td>14.7</td>
</tr>
<tr>
<td>Isocyanic acid</td>
<td>22.6</td>
</tr>
<tr>
<td>Methyl isocyanate</td>
<td>17.1</td>
</tr>
</tbody>
</table>

Equation S1: Sensitivity equation for formamide (m/z 46):\(^{23}\)

\[
\text{sensitivity} = \left( \frac{m/z \ 46}{m/z \ 21} \right) \left( \frac{1 \times 10^6}{ppbv \ of \ formamide} \right)
\]

3.8.2 Box model equations

Equations used in the box modelling of the amide kinetics are detailed below. \([x]\) represents the mixing ratio of the molecule \(x\) inside the square brackets; \([\text{OH}]\) is determined experimentally using the \(n\)-butanol rate coefficient and Equation S2; \(k\) is the rate coefficient of the amide and OH experimentally determined in this work, \(k_1 = (4.44 \pm 0.46) \times 10^{-12} \ \text{cm}^3 \ \text{molec}^{-1} \ \text{s}^{-1}\); \(\gamma_1\) is the yield of formamide production from an alkylated amide; \(\gamma_2\) is the yield of HNCO production specifically from formamide; \(\gamma_3\) is the yield of HNCO production from an alkylated amide; \(t\) is time in seconds from start of reaction.

Equation S2:

\[
\ln \left( \frac{[\text{butanol}]_0}{[\text{butanol}]_t} \right) \left( \frac{1}{k_{\text{butanol}+\text{OH}t}} \right) = [\text{OH}]
\]

Equation S3: Evolution of the parent amide as a function of time (also true for the oxidative kinetics of formamide

\[
\frac{d[\text{amide}]}{dt} = k[\text{amide}][\text{OH}]
\]

Equation S4: Analytical solution for the parent amide decay

\[
[\text{amide}]_t = [\text{amide}]_0 e^{-k[\text{OH}]t}
\]
Equation S5: Evolution of formamide as a function of time, when formamide is an intermediate product between the parent amide and HNCO. This equation also describes the production of the oxidation product at m/z 60.

\[
\frac{d[formamide]}{dt} = \gamma_1 k[amide] - k_1[formamide][OH]
\]

Equation S6: Analytical solution for the evolution of formamide

\[
[formamide]_t = \frac{\gamma_1 k[amide]_0}{k_1 - k} \left( e^{-k[OH]t} - e^{-k_1[OH]t} \right)
\]

Equation S7: Evolution of HNCO as a function of time, when HNCO is a product solely from formamide with yield ($\gamma_2$). This equation also describes the production of methyl isocyanate from N-methylformamide and all other primary products without an appreciable sink within the time frame of the experiments.

\[
\frac{d[HNCO]}{dt} = \gamma_2 k_1[formamide][OH]
\]

Equation S8: Analytical solution for the evolution of HNCO with yield ($\gamma_2$) when formamide is the starting amide

\[
[HNCO]_t = \gamma_2 [formamide]_0 \left( 1 - e^{-k_1[OH]t} \right)
\]

Equation S9: Analytical solution for the evolution of HNCO as a secondary product from the starting amide, with formamide as the intermediate, itself produced with a yield ($\gamma_1$)

\[
[HNCO]_t = \gamma_1 \gamma_2 [amide]_0 \left( 1 - \frac{k_1}{k_1 - k} e^{-k[OH]t} + \frac{k}{k_1 - k} e^{-k_1[OH]t} \right)
\]

Equation S10: Evolution of HNCO as a function of time when HNCO is a product of both formamide oxidation and the parent amide oxidation (two sources)

\[
\frac{d[HNCO]}{dt} = \gamma_2 k_1[formamide][OH] + \gamma_3 k[amide][OH]
\]
Equation S11: Analytical solution for the evolution of HNCO from two different sources (Note: not used to fit the experimental data in this study. Presented for reference purposes.)

\[
[HNCO]_t = \gamma_1 \gamma_2 [amide]_0 \left( 1 - \frac{k_1}{k_1 - k} e^{-k[OH]t} + \frac{k}{k_1 - k} e^{-k_1[OH]t} \right) - \gamma_3 [amide]_0 e^{-k[OH]t}
\]

3.8.3 Calibration curves

Graph 3-2: Calibration curve for isocyanate on the ion chromatograph
Graph 3-3: Calibration curve for HNCO on the PTR-MS

\[ y = 0.0113x - 0.0092 \]
\[ r^2 = 0.885 \]

Graph 3-4: Plot of Equation 1 for acetamide where the linear regression is forced through the origin.

\[ \text{slope} = 0.0885 \pm 0.0006 \]
3.8.4 Extended product study

Scheme 3-2: Postulated mechanism for the atmospheric fate of the N-methylformamide peroxyl radical O₂CH₂NHCHO. Note that there is no NOₓ in our experimental setup, but this mechanism may be possible under RO₂ chemistry in our oxidation of N-methylformamide experiments.

Figure 3-8: Oxidative decay of N-methylacetamide (fitted by Equation S4) and its major products, formamide (fitted by Equation S6), m/z 60 which may represent acetamide or N-methylformamide (fitted by Equation S6) and HNCO (fitted by Equation S9). The dots represent 10-second PTR-MS data and the solid lines represent modelled kinetics of the N-methylacetamide decay and its products.
Figure 3-9: Oxidative decay of propanamide and its major products, formamide (Eq S4) and HNCO (Eq S6). The dots represent 10-second PTR-MS data and the solid lines represent modelled kinetics of the propanamide decay and its products.

3.8.5 Extended theoretical energy diagrams

Figure 3-10: Theoretical energy diagram for N-methylformamide + OH from the N–H site. Energies are 0 K enthalpies in kcal mol$^{-1}$, at the G3X-K level of theory.
Figure 3-11: Theoretical energy diagram for acetamide + OH. Energies are 0 K enthalpies in kcal mol$^{-1}$, at the G3X-K level of theory.

Figure 3-12: Theoretical energy diagram for N-methylacetamide + OH. Energies are 0 K enthalpies in kcal mol$^{-1}$, at the G3X-K level of theory.
Figure 3-13: Theoretical energy diagram for the \textit{N}-methylacetamide alkoxyde rearrangement. Energies are 0 K enthalpies in kcal mol\(^{-1}\), at the G3X-K level of theory.

Figure 3-14: Theoretical energy diagram for propanamide + OH. Energies are 0 K enthalpies in kcal mol\(^{-1}\), at the G3X-K level of theory.
### 3.8.6 SAR analysis of amines

<table>
<thead>
<tr>
<th>Amines</th>
<th>Rate Coefficient (k)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanamine ( H_3C\cdot NH_2 )</td>
<td>( (1.73 \pm 0.11) \times 10^{-11} )</td>
<td>Carl et al.</td>
</tr>
<tr>
<td>Dimethylamine ( H_3C\cdot N\cdot CH_3 )</td>
<td>( (6.49 \pm 0.64) \times 10^{-11} )</td>
<td>Carl et al.</td>
</tr>
<tr>
<td>Trimethylamine ( H_3C\cdot N\cdot CH_3 )</td>
<td>( (3.58 \pm 0.22) \times 10^{-11} )</td>
<td>Carl et al.</td>
</tr>
<tr>
<td>Ethanamine ( H_3C\cdot NH )</td>
<td>( (2.38 \pm 0.50) \times 10^{-11} )</td>
<td>Carl et al.</td>
</tr>
<tr>
<td>N-Methylethanamine ( H_3C\cdot N\cdot CH_3 )</td>
<td>( (7.3 \pm 0.7) \times 10^{-11} )</td>
<td>Nielsen et al.</td>
</tr>
<tr>
<td>N,N-Dimethylethanamine ( H_3C\cdot N\cdot CH_3 )</td>
<td>( k = \text{unknown} )</td>
<td>Nielsen et al.</td>
</tr>
<tr>
<td>Propan-1-amine ( H_3C\cdot NH )</td>
<td>( k = \text{unknown} )</td>
<td>Nielsen et al.</td>
</tr>
<tr>
<td>N-Methylpropan-1-amine ( H_3C\cdot N\cdot CH_3 )</td>
<td>( (8.3 \pm 0.9) \times 10^{-11} )</td>
<td>Nielsen et al.</td>
</tr>
<tr>
<td>N,N-Dimethylpropan-1-amine ( H_3C\cdot N\cdot CH_3 )</td>
<td>( k = \text{unknown} )</td>
<td>Nielsen et al.</td>
</tr>
</tbody>
</table>

Figure 3-15: Summary of homologous amines to the amide series presented in Figure 3-7, with examples of rate coefficients with OH radicals from Carl et al. and Nielsen et al.\(^{42,46}\)
Graph 3-5: Estimated rate coefficients using EPA’s EPI Suite as a function of experimentally measured rate coefficients for nine amines. The numbers represent the level of N-methylation on the N, so that 1° represents the primary amine, 2° represents the secondary amine and 3° represents the tertiary amine. The color coding matches Figure 3-15, so that the blue series represents methylamine and its methylated analogues, the red series represents ethylamine and its methylated analogues and the green series represents propanamine and its methylated analogues. The solid line is the 1:1 relationship, and the dotted lines have slopes differing by a factor of two from the 1:1 relationship.

3.8.7 AOPWIN notes

D.2.6. Nitrogen Reaction Values for Amide [-N-C(=O)-C] Type Structures

AOP v1.55 uses a nitrogen reaction value 11.8 E-12 for the -N-C(=O)-C structure; this value was estimated from the 11.8 E-12 value assigned to the -N-C(=O)-S structure (Kwok et al, 1992). New experimental data (for N-methylacetamide, N-methylpropionamide, N,N-dimethylacetamide and N,N-dimethylpropionamide) indicate that new values should be assigned to -NH-C(=O) and >N-C(=O) as 5.5 and 15.0 E-12 respectively.
In addition, a value of 2.0 E-12 has been estimated for NH2-C(=O) based upon comparative ionization potentials (gas-phase) and OH radical rate constants in water for acetamide and the compounds above.

D.2.9. Hydrogen Abstraction from Aldehyde [O=CH-] Type Structures

Hydrogen abstraction from an aldehyde-type fragment (O=CH-) was derived from actual aldehydes where the O=CH- fragment is connected to a carbon atom. In AOP v1.55, the hydrogen abstraction value was assigned a value of zero if the O=CH- fragment was connected to an oxygen (as in O=CH-O-CH3)...this was based upon experimental data for various formates. AOP v1.60 (through v1.70) extends this zero assignment to O=CH- connected to nitrogens or sulfur because resulting estimates seem to be much too high if the zero assignment is not applied. For example, formamide (O=CH-NH2) is estimated as 173 E-12 by AOP v1.55 and as 2 E-12 by AOP v1.60; data for OH reaction rates in water suggest that the latter estimate is more realistic.
Chapter 4
Solubility and Reactivity of HNCO in Water: Insights into HNCO’s Fate in the Atmosphere

This chapter was submitted to Atmospheric Chemistry and Physics on July 24th, 2015 with the coauthor list as follows: Borduas, N., Place, B., Wentworth, G. R., Abbatt, J. P. D., and Murphy, J. G.

4 Chapter 4
4.1 Abstract

A growing number of ambient measurements of isocyanic acid (HNCO) are being made, yet little is known about its fate in the atmosphere. To better understand HNCO’s loss processes and particularly its atmospheric partitioning behavior, we measure its effective Henry’s Law coefficient \( K_{H}^{\text{eff}} \) with a bubbler experiment using chemical ionization mass spectrometry as the gas phase analytical technique. By conducting experiments at different pH values and temperature, a Henry’s Law coefficient \( K_{H} \) of \( 26 \pm 2 \text{ M atm}^{-1} \) is obtained, with an enthalpy of dissolution of \(-34 \pm 2 \text{ kJ mol}^{-1}\). Our approach also allows for the determination of HNCO’s acid dissociation constant, which we determine to be \( K_{a} = 2.1 \times 10^{-4} \text{ M at 298 K} \). Furthermore, by using ion chromatography to analyze aqueous solution composition, we revisit the hydrolysis kinetics of HNCO at different pH and temperature conditions. Three pH dependent hydrolysis mechanisms are in play and we determine the Arrhenius expressions for each rate to be \( k_{1} = 4.4 \times 10^{7} \exp(-50 \text{ kJ mol}^{-1} / (RT)) \text{ M s}^{-1} \), \( k_{2} = 8.9 \times 10^{6} \exp(-56 \text{ kJ mol}^{-1} / (RT)) \text{ s}^{-1} \) and \( k_{3} = 7.2 \times 10^{8} \exp(-91 \text{ kJ mol}^{-1} / (RT)) \text{ s}^{-1} \) where \( k_{1} \) is HNCO + H\(^{+} \) + H\(_{2}\)O \( \rightarrow \) NH\(_{4}\)\(^{+} \) + CO\(_{2}\), \( k_{2} \) is HNCO + H\(_{2}\)O \( \rightarrow \) NH\(_{3}\) + CO\(_{2}\) and \( k_{3} \) is NCO\(^{-} \) + 2 H\(_{2}\)O \( \rightarrow \) NH\(_{3}\) + HCO\(_{3}\)\(^{-}\). HNCO’s lifetime against hydrolysis is therefore estimated to be 10 days to 28 years at pH values, liquid water contents, and temperatures relevant to tropospheric clouds,
years in oceans and months in human blood. In all, a better parameterized Henry’s Law coefficient and hydrolysis rates of HNCO allow for more accurate predictions of its concentration in the atmosphere and consequently help mitigate exposure of this toxic molecule.

4.2 Introduction

Until recently, the interest in studying HNCO was from a fundamental science perspective with research conducted on its structure, preparation and physical properties and on its theoretical rovibrational spectra.\(^1,2\) Both theoretical and experimental data indicate that HNCO is the most stable CHNO isomer with a near-linear \(\pi\)-bond system.\(^3-5\) In 2010, Roberts et al. reported detection of HNCO using negative ion proton transfer chemical ionization mass spectrometry (CIMS) from laboratory biomass burning and later determined its emission factor to be 0.25 – 1.20 mmol per mol of CO for different types of biomass fuels.\(^6\) Shortly afterwards, the same authors reported the first ambient atmospheric measurements of HNCO in Pasadena, California, reaching 120 pptv and raising concerns of HNCO exposure due to its toxicity.\(^7\) Indeed, HNCO has been observed to cause protein carbamylation leading to cardiovascular disease, rheumatoid arthritis and cataracts.\(^8-11\)

Since Roberts et al.’s initial measurements, ambient HNCO has also been measured in Boulder and in Fort Collins, Colorado, in Toronto, Ontario and in Calgary, Alberta.\(^12-14\) HNCO has also been detected simultaneously in the gas phase and in cloud water in La Jolla, California.\(^15\) From these studies, typical urban concentrations range from below detection limits to approximately 100 pptv, whereas concentrations as high as 1.2 ppbv, enough to be of health concern, have been measured in air masses impacted by biomass burning in Boulder, Colorado.\(^7,12,14\)

HNCO has a variety of anthropogenic and biogenic sources to the atmosphere. HNCO has been quantified from diesel engine exhaust\(^13,16\) and light duty vehicles\(^17\) as well as from biogenic sources such as biomass burning.\(^6,7,14,18\) There also exist secondary sources of HNCO to the atmosphere, including the gas phase oxidation of amines and amides by OH radicals producing HNCO via H-abstraction mechanisms.\(^19-21\) Evidence of secondary sources of HNCO has also been demonstrated in the field, with peak HNCO concentrations occurring during daytime.\(^7,14,15\)

The sinks of HNCO however remain poorly constrained. HNCO has a lifetime of decades towards OH radicals in the atmosphere as estimated by extrapolating high temperature rate coefficients to
atmospheric temperatures.\textsuperscript{22-24} It is also not expected to photolyze in the actinic region since its first UV absorption band is observed below 280 nm wavelengths.\textsuperscript{25-27} Nonetheless, HNCO has served as a benchmark system in understanding photodissociation decomposition pathways such as direct and indirect dissociation processes and remains an area of active research (see ref. 28 and earlier references therein).\textsuperscript{28} HNCO is most likely removed from the atmosphere by wet and/or dry deposition. HNCO’s gas-to-liquid partitioning is therefore an important thermodynamic property that can be used to predict its atmospheric fate. Specifically, the Henry’s Law coefficient \(K_H\) for the solubility of HNCO represents the equilibrium ratio between its gas phase and aqueous phase concentrations at infinite dilutions according to Equation 1.\textsuperscript{29,30} The Henry’s Law coefficient for HNCO has only recently been measured by Roberts and coworkers but their experimental set up was limited to a single pH measurement.\textsuperscript{7} As HNCO is a weak acid with a pK\textsubscript{a} of 3.7, its Henry’s Law coefficient is expected to have a large pH dependence as described in Equation 2. Furthermore, the enthalpy of dissolution for HNCO is currently unknown. In lieu of measurements, modelling studies on HNCO have used formic acid’s enthalpy of dissolution to model the temperature dependence of HNCO’s Henry’s Law coefficient.\textsuperscript{31,32} In our present study, we measure the effective Henry’s Law coefficient of HNCO at a range of pH and temperatures to determine its enthalpy of dissolution for the first time.

\textbf{Equation 1:} \(K_H = \frac{C_{\text{HNCO}}}{p_{\text{HNCO}}}\)

\textbf{Equation 2:} \(K_{H}^{\text{eff}} = K_H \left(1 + \frac{K_a}{[H^+]}\right)\)

HNCO reacts irreversibly with water in the aqueous phase, an unusual property for an atmospheric molecule. Once HNCO partitions to the aqueous phase, three mechanisms for its hydrolysis are possible. The first (1) is acid-catalysed and is therefore termolecular whereas the second (2) and third (3) are bimolecular reactions involving either the protonated or deprotonated form of HNCO (Scheme 4-1).\textsuperscript{2,33,34} In 1958, Jensen determined the hydrolysis rate of the three mechanisms through addition of AgNO\textsubscript{3} to buffered solutions at different time points to precipitate unreacted isocyanate as AgNCO, followed by back titration of excess AgNO\textsubscript{3} with NH\textsubscript{4}SCN.\textsuperscript{33} Considering the importance of these mechanisms in evaluating the fate of HNCO in the atmosphere, we follow up on the study by Jensen with our own experiments using ion chromatography to determine the pH and temperature dependencies of the overall rate of hydrolysis of HNCO.
Quantitative knowledge of the propensity of HNCO to partition to the aqueous phase and its subsequent reactions with water allows for an accurate understanding of the chemical fate of HNCO in the atmosphere (Figure 4-1). In this study, we therefore provide laboratory measurements of HNCO’s Henry’s Law coefficient and enthalpy of dissolution as well as its three rates of hydrolysis and their respective activation energies.

\[
\begin{align*}
(1) & \quad H_3N=CO + H^+ + H_2O \xrightarrow{k_1} NH_4^+ + CO_2 \\
(2) & \quad H_3N=CO + H_2O \xrightarrow{k_2} NH_3 + CO_2 \\
(3) & \quad -N=CO + 2 H_2O \xrightarrow{k_3} NH_3 + HCO_3^-
\end{align*}
\]

**Scheme 4-1**: The three mechanisms involved in HNCO’s hydrolysis.

**Figure 4-1**: The fate of HNCO in the atmosphere includes its partitioning between the gas and aqueous phases and its hydrolysis through three different mechanisms governed by \(k_1\), \(k_2\), and \(k_3\).

4.3 Experimental methods

4.3.1 Henry’s Law coefficient experiments

4.3.1.1 Acetate reagent ion CIMS

The quadrupole chemical ionization mass spectrometer (CIMS) was built in house and is described in detail elsewhere.\textsuperscript{35} We opted to use acetate as the reagent ion which has been shown to be sensitive for the detection of acids.\textsuperscript{18,36} For this experimental set up, the reagent ion was generated by flowing 20 sccm of nitrogen over a glass tube containing acetic anhydride (from Sigma-Aldrich
and used as is) and maintained at 30 °C. This flow was subsequently mixed with a nitrogen dilution flow of 2 L min⁻¹ and passed through a polonium-210 radioactive source. All flows were controlled using mass flow controllers. The data acquisition was done under selected ion mode where 10 m/z ratios were monitored with dwell times of 0.2 s each and each duty cycle was 4 s. The inlet flow of the CIMS was 0.5 L min⁻¹, governed by a pin hole, and a N₂ dilution flow of 0.4 L min⁻¹ into the inlet was used to avoid depletion of the acetate reagent ion by high HNCO concentrations. The CIMS monitors NCO⁻ at m/z 42.

4.3.1.2 Experimental set up for measurement of \( K_H \)

To obtain the Henry’s Law coefficient, \( K_H \), we monitored the decrease in gas phase HNCO exiting a buffered aqueous solution for a range of volume flow rates through the buffer. Thus, a bubbler column experimental set up is used with online gas phase detection. This method is employed to measure HNCO’s partitioning and take into account the concurrent hydrolysis of HNCO in the buffer solution at high time resolution. Our experimental setup is based on previous work\(^7,37,38\) and so our apparatus is comprised of one fritted bubbler with an approximate volume of 70 mL which contained 15 mL of a citric acid/Na₂HPO₄ buffer at varying pH. The 15 mL volume was chosen to reduce HNCO equilibration times and to simultaneously ensure that the bubbler’s frit was submerged. Experiments performed in 30 mL of buffer yielded identical results. The bubbler was held in a temperature-controlled bath of approximately 1:1 mixture of deionized water and ethylene glycol. Upstream of the bubbler was a valve and a tee connection where the HNCO flow could be connected and disconnected during the experiments. Downstream of the bubbler was another tee which connected to both the exhaust and the acetate reagent ion chemical ionization mass spectrometer (CIMS). Conveniently, the absolute concentration of gas-phase HNCO is not required in this approach since it relies on since it relies on the decay of the signal, \([\text{HNCO}]_t/[\text{HNCO}]_0\).

HNCO was produced using a permeation source which sublimes solid cyanuric acid at 250 °C in a flow of nitrogen.\(^{21}\) The buffer solutions were made with solid citric acid, disodium phosphate and deionized water with citric acid concentrations ranging from 0.02 M to 0.0035 M to access a pH range of 2.5-4.0.

Each experiment began with gaseous HNCO flowing through a fresh buffer solution until a reasonably stable signal (> 0.01 ncps) was obtained by the CIMS. The solution does not need to
reach equilibrium for the experiment to proceed and so lower temperatures and higher pHs (when the equilibration time is longest and may reach over 4-5 hours) were feasible. Once a normalized signal (i.e. relative to the reagent ion signal) of at least 0.025 for HNCO was obtained, the flow of HNCO through the bubbler was turned off, and only pure nitrogen continued to flow through. The HNCO signal then decayed exponentially as a function of time due to partitioning as well as hydrolysis. This decay was monitored until it had decreased to less than one quarter of the original signal. This method also has the advantage of extracting an effective Henry’s Law coefficient without needing to monitor the aqueous phase HNCO concentration.

4.3.2 Hydrolysis rate experiments

4.3.2.1 Ion chromatography

The measurements for the hydrolysis of HNCO were made using a Dionex IC-2000 Ion Chromatography (IC) System. An IonPac (AS19) anion column consisting of a quaternary ammonium ion stationary phase with diameter and length dimensions of 4 mm and 25 mm respectively was employed. Sample runs used a concentration gradient of the eluent KOH ranging from 2 mM to 20 mM. An optimized elution program was written for each pH range measured (between 25-60 minutes for each injection). Samples were injected using a Dionex (AS40) automated sampler into a 25 μL loop for pre-injection. The use of a loop rather than a concentrator was important and ensured that the total HNCO/NCO⁻ concentrations were being measured. The IC was calibrated using matrix-matched standards of known HNCO/NCO⁻ concentrations prepared from serial dilutions of KOCN (Sigma-Aldrich, 96% purity).

4.3.2.2 Hydrolysis kinetics experiments

The kinetics of the hydrolysis reactions in the pH range of 1-2 are very fast; complete decays occur in a matter of minutes. The decay of HNCO at these low pH values is therefore too quick for the 25 min IC method to capture. To circumvent this issue, we used a quenching method. Specifically, we prepared an aqueous solution of 50 mL of sulphuric acid at the desired pH. 5 mL of this acidic solution was subsequently added to a 0.02 M solution of KOCN in eight different falcon tubes to initiate the rapid hydrolysis reaction. Each reaction was then quenched at different times by a 0.1 M aqueous solution of KOH. Increasing the pH to more than 10 slowed the hydrolysis kinetics by orders of magnitude and allowed for subsequent IC measurements. Replacing sulphuric acid by
nitric acid and/or KOH by NaOH yielded identical hydrolysis rates and ensured the results were reproducible with different acids and bases.

Buffer solutions in the pH range of 3-5 were prepared by using appropriate molar ratios of citric acid and disodium phosphate whereas buffer solutions in the pH range of 9-10 used sodium carbonate and sodium bicarbonate. For the room temperature set of kinetic experiments, the experiment was initiated by the addition of 0.1 g of KOCN to 50 mL of the desired buffer solution. The solution was further diluted by a factor of 500 and then split into 8 samples for analysis at succeeding intervals on the anion IC.

Hydrolysis reactions were run at different temperatures to assess the activation energies of each of the three hydrolysis mechanisms. Room temperature reactions were conducted inside the IC autosampler AS40 (with a cover) and monitored by a temperature button (iButtons, Maxim Integrated, San Jose, CA with 0.5 °C resolution)). Colder temperature reactions were done in a water ice bath and monitored by a thermometer. Finally, warmer temperature reactions for high pH samples were run in a temperature-controlled water bath. These reactions took days to weeks to reach completion, and so 5 mL samples from the reaction mixtures were taken out of the water bath and measured on the IC at appropriate time intervals.

4.4 Results and discussion

4.4.1 Henry’s Law coefficient $K_H$

HNCO’s effective Henry’s Law solubility coefficient $K_{H}^{\text{eff}}$ expressed in M atm$^{-1}$ was determined based on the exponential decay of gaseous HNCO exiting a bubbler containing a buffered solution. The observed decay of HNCO is caused by its partitioning from the aqueous phase to the gas phase as well as its competing hydrolysis reaction. Equation 3 represents the rate law for the disappearance of HNCO during the experiment where the first term represents the loss to partitioning of HNCO within the experimental set up (derived from $pV = nRT$) and the second term represents the loss due to hydrolysis. Equation 4 is the integrated rate law.

Equation 3: \[-\frac{d[HNCO]}{dt} = [HNCO] \frac{\varphi}{K_{H}^{\text{eff}} V RT} + [HNCO] k_{hyd}\]

Equation 4: \[ln \frac{[HNCO]_t}{[HNCO]_0} = - \left[ \frac{\varphi}{K_{H}^{\text{eff}} VRT} + k_{hyd} \right] t\]
Where \([\text{HNCO}]_t\) is the HNCO concentration at time \(t\), \([\text{HNCO}]_0\) is the initial HNCO concentration (at time \(t = 0\)), \([\text{HNCO}]_t/\text{[HNCO]}_0\) is the HNCO concentration in the gas phase downstream of the bubbler measured by the CIMS, \(\phi\) is the volumetric flow rate (cm\(^3\) s\(^{-1}\)), \(K_{\text{eff}}^H\) is the effective Henry’s Law coefficient for solubility (mol L\(^{-1}\) atm\(^{-1}\)), \(V\) is the liquid volume of the buffer (cm\(^3\)), \(R\) is the ideal gas constant (8.21 × 10\(^{-2}\) L atm mol\(^{-1}\) K\(^{-1}\)), \(T\) is the temperature (K), \(k_{\text{hyd}}\) is HNCO’s overall rate of hydrolysis (s\(^{-1}\)) and \(t\) is the time (s). To extract the value of \(K_{\text{eff}}^H\) from the experimental decay curves, we first plot the natural logarithm of change in HNCO concentration versus time for different flow rates ranging from 175 to 800 sccm as shown in Graph 4-1A. The slope of each experiment is then plotted as function of the ratio of the flow rate and volume depicted in Graph 4-1B. The slope of Graph 4-1B leads to a value representing \((K_{\text{eff}}^H RT)^{-1}\) and so \(K_{\text{eff}}^H\) can be calculated.

These dynamic experiments were repeated with a range of buffer solutions ranging from pH 2.5-4.0 to determine the pH-independent Henry’s Law coefficient, \(K_H\), of HNCO. Experiments at temperatures of 273-298 K were also conducted to determine HNCO’s enthalpy of dissolution, \(\Delta H_{\text{diss}}\).

**Graph 4-1:** A) The concentration decay curves as a function of time according to Equation 4 for each flow rate shown; B) The slopes of each fit in Figure 4-2A plotted as a function of the ratio of the flow rate to the volume. The symbols in both figures represent the same flow rate shown.
4.4.1.1 pH dependence of $K_{H}^{\text{eff}}$

The pH dependence of the effective Henry’s Law coefficient $K_{H}^{\text{eff}}$ of a weak acid like HNCO depends on its $pK_a$ as well as on the pH according to Equation 2. Throughout our experiments, we measure the value of $K_{H}^{\text{eff}}$ and employ Equation 2 to plot $K_{H}^{\text{eff}}$ as a function of the inverse of the proton concentration, $[H^+]$, and thus to extract HNCO’s Henry’s Law coefficient for solubility, $K_H$. Graph 4-2A depicts this linear relationship and yields a value of $26 \pm 2$ M atm$^{-1}$ for $K_H$. Our $K_H$ value compares well with the only other published value of $21$ M atm$^{-1}$ determined solely at pH 3.\textsuperscript{7} Graph 4-2B on the other hand shows experimentally determined $K_{H}^{\text{eff}}$ at different pH values and at a constant temperature of $298.0 \pm 0.2$ K. Error bars in both Graph 4-2A and 4-2B represent the standard deviation of the slope as in Graph 4-1B. The slope in Graph 4-2A also allows us to determine HNCO’s acid dissociation constant, $K_a$, which at 298 K is $2.1 \pm 0.2 \times 10^{-4}$ M. Our $K_a$ value also agrees well with previously reported $K_a$ for HNCO.\textsuperscript{2,34}

Graph 4-2: A) The fit according to Equation 2 of the experimental $K_{H}^{\text{eff}}$ values which allows for the determination of $K_H$ and $K_a$ at 298 K. B) The experimental $K_{H}^{\text{eff}}$ values as a function of pH at 298 K. The black line is the modelled dependence of $K_{H}^{\text{eff}}$ according to Equation 2 based on the determined value of $K_H$ and a value for $K_a$ of $2.1 \pm 0.2 \times 10^{-4}$ M. The inset shows the range of $K_{H}^{\text{eff}}$ across the full range of pH.
4.4.1.2 Temperature dependence

The temperature dependence of HNCO’s solubility was established by running experiments at varying temperatures from 273 to 298 K. Since $K_{\text{H}}^{\text{eff}}$ is very sensitive to pH changes, all experiments were conducted with a buffer solution from the same batch and same volumetric flask within a few days. Plotting the natural logarithm of the effective Henry’s Law coefficient as a function of the inverse of temperature yields the ratio of the enthalpy of dissolution, $\Delta H_{\text{diss}}$, to the gas constant, R (Graph 4-3). We report a value of $-34 \pm 2$ kJ mol$^{-1}$ for HNCO’s enthalpy of dissolution, where the uncertainty stems from the deviation from the slope depicted in Graph 4-3. This value is somewhat smaller than similar weak acids like HONO ($-40$ kJ mol$^{-1}$) and HCN ($-42$ kJ mol$^{-1}$), and differs most from the value of formic acid ($-47$ kJ mol$^{-1}$) which was the value assumed for HNCO in the Young et al. and the Barth et al. modelling studies.$^{30-32}$

Graph 4-3: The temperature dependence of experimentally measured $K_{\text{H}}^{\text{eff}}$ at pH 3.08.

4.4.2 Rate of hydrolysis $k_{\text{hyd}}$

There are three mechanisms by which HNCO can react with water described in Scheme 4-1 (1-3) and depicted in Figure 4-1. The disappearance of HNCO in the aqueous phase can therefore be described by the rate law shown as Equation 5. The pH dependence of HNCO’s hydrolysis
manifests itself in the first term of equation 5 as the hydrogen ion concentration as well as in the concentration of the dissociated/non-dissociated acid in each term.

Equation 5: $- \frac{d[HNC0]}{dt} = k_1[HNC0][H^+] + k_2[HNC0] + k_3[NCO^-]$

To mathematically integrate this rate law, the concentration of HNCO needs to be expressed as the sum of undissociated HNCO and of isocyanate ion NCO$^-$ in solution, which is denoted in Equation 6 as $[HNCO]_{tot}$. HNCO’s acid dissociation constant $K_a$ relates the concentration of HNCO and NCO$^-$ as shown in Equation 6. The $K_a$-dependant expression of Equation 6 is then substituted into the rate law of Equation 5, and subsequently integrated. The $K_a$ value of HNCO has a slight temperature dependence with a heat of dissociation previously measured by Amell of 5.4 kJ mol$^{-1}$, which for the temperature range of 273 to 298 K represents a 25% change. We therefore use Amell’s heat of dissociation value throughout our analysis to account for $K_a$’s temperature dependence in the van’t Hoff equation. Furthermore, Belson et al.’s evaluation of the $K_a$ of HNCO literature recommends $2.0 \times 10^{-4}$ M at 298 K. Finally, our own work on the pH dependence of Henry’s Law coefficient of HNCO, suggests a $K_a$ value of $2.1 \pm 0.2 \times 10^{-4}$ M at 298 K, consistent with the recommended value (Graph 4-2A).

Equation 6: $[HNCO] = [HNCO]_{tot} - [NCO^-] = \frac{[H^+][NCO^-]}{K_a} = \frac{[HNCO]_{tot}[H^+]}{K_a+[H^+]}$

By integrating Equation 5 with the appropriate substitutions, the resulting expression is Equation 7, where $k_{hyd}$ represents the observed first-order rate loss of hydrolysis of HNCO and depends on the individual reaction rates $k_1$, $k_2$ and $k_3$ according to Equation 8.

Equation 7: $\frac{[HNCO]_t}{[HNCO]_0} = e^{-k_{hyd}t}$

Equation 8: $k_{hyd} = \frac{k_1[H^+]^2+k_2[H^+]+k_3K_a}{K_a+[H^+]}$

The aim of our hydrolysis experiments is to measure $k_{hyd}$ at different pH values to subsequently solve for the values of the individual hydrolysis rate coefficients $k_1$, $k_2$ and $k_3$. To measure $k_{hyd}$, we employ ion chromatography (IC) which allows for quantitative measurement of the total isocyanic acid in solution as NCO$^-$ using an anion chromatography column. The key to making $[HNCO]_{tot}$ measurements was to use a loop injection port for the IC instead of a concentrator column, since
the latter retains only ions and would not measure any protonated HNCO in solution. Appropriate buffer solutions were made to conduct experiments over a range of pH values from 1.7 to 10.4. The decay of [HNCO]_{tot} was monitored by IC over time and plotting the natural logarithm of the decay as a function of time as in Graph 4-4 yields the $k_{hyd}$ specific to that temperature and pH. Hydrolysis experiments are listed in Table 4-2 in Appendix C.

Graph 4-4: Example of a hydrolysis experiment at pH 5.4 and at 25 °C where the [HNCO]_{tot} is measured by loop injections on the IC.

4.4.2.1 Determining $k_1$ and $k_2$

At a pH below 3, the third hydrolysis mechanism (Scheme 4-1 (3)) will contribute minimally to the overall $k_{hyd}$. Indeed, the third term in Equation 8, $k_3K_a/(K_a+[H^+])$ will become very small because $[H^+] >> K_a$. Furthermore, very little of the HNCO is present as NCO⁻ at low pH. This assumption (which we verify retroactively) simplifies the $k_{hyd}$ expression to Equation 9 with only two unknowns, $k_1$ and $k_2$. We can now solve for $k_1$ and $k_2$ from two $k_{hyd}$ values derived from experiments conducted at two different pH values but at the same temperature. For example, solving for $k_1$ and $k_2$ at 295 K using the $k_{hyd}$ in Table 4-2 in Appendix C, we obtain a value of $(6.73 ± 0.27) \times 10^{-2}$ M s⁻¹ for $k_1$ and of $(1.04 ± 0.04) \times 10^{-3}$ s⁻¹ for $k_2$. We do this calculation once per temperature. The uncertainties associated with these measurements come from the fit of the decay of aqueous phase HNCO measured by IC.

Equation 9: $k_{hyd@pH<2.7} = \frac{k_1[H^+]^2+k_2[H^+]}{K_a+[H^+]}$
4.4.2.2 Temperature dependence of $k_1$ and $k_2$

Hydrolysis experiments of HNCO at three different temperatures further enables us to solve for the temperature dependence of $k_1$ and $k_2$. We chose three temperatures relevant to tropospheric air masses: 270, 283 and 295 K. Graph 4-5 represents the slope of the natural logarithm of the rate coefficient of hydrolysis as a function of the inverse of the temperature which according to the Arrhenius equation shown in Equation 10 yields the activation energy specific to each hydrolysis mechanism. We obtain activation energies of $50 \pm 2$ kJ mol$^{-1}$ and $56 \pm 4$ kJ mol$^{-1}$ for $k_1$ and $k_2$ respectively. Furthermore, the y-intercept of these linear plots yields the value of ln($A$) in Equation 10 and so the A factors of each hydrolysis mechanism can also be obtained, providing Arrhenius expressions of $k_1 = (4.4 \pm 0.2) \times 10^7 \exp(-6000 \pm 240 / T) \text{ M s}^{-1}$ and $k_2 = (8.9 \pm 0.9) \times 10^6 \exp(-6770 \pm 450 / T) \text{ s}^{-1}$. The uncertainties stem from the fit to the data points in Figure 6 (and their error bars comes from the slope of the decay of aqueous phase HNCO measured by IC).

Equation 10: $k = A e^{-E_a/RT}$

Graph 4-5: The linear plots of the natural logarithm of each hydrolysis rate coefficient $k_1$, $k_2$ and $k_3$ as a function of the inverse of temperature to yield the activation energies of each mechanism.
4.4.2.3 Determining $k_3$ and its temperature dependence

At high pH levels, the third hydrolysis mechanism (Scheme 4-1 (3)) will dominate the observed $k_{\text{hyd}}$, however, the first two mechanisms may still have a non-negligible contribution to $k_{\text{hyd}}$ and can therefore not be disregarded. We can solve for $k_3$, knowing $k_1$ and $k_2$ and their respective temperature dependencies, using Equation 8. The $k_{\text{hyd}}$ values measured at pH above 9 and at 40 °C are used (Table 4-2, Appendix C), and $k_3$ is determined for each pH. The average of our three measurements at 40 °C is $(5.77 \pm 0.35) \times 10^{-7}$ s$^{-1}$. The temperature dependence of $k_3$ is determined in an analogous way to $k_1$ and $k_2$ and is also depicted in Graph 4-5. We obtain a value of $91 \pm 12$ kJ mol$^{-1}$ which translates to an Arrhenius expression of $k_3 = (7.2 \pm 1.5) \times 10^8 \exp(-10900 \pm 1400 / T)$ s$^{-1}$.

Equipped with the values of $k_1$, $k_2$ and $k_3$ and their temperature dependencies, a map of the expected total hydrolysis rate, $k_{\text{hyd}}$, as a function of temperature and pH can be generated using Equations 8 and 10 and is plotted as Graph 4-6. For reference, the colour scale of Graph 4-6 also reads in hydrolysis lifetime of HNCO in hours. It is clear that HNCO’s lifetime in the aqueous phase has a large temperature and pH dependence.

4.4.2.4 Comparing the rate of hydrolysis $k_{\text{hyd}}$ through different methods

The individual rate coefficients of the three hydrolysis mechanisms (Scheme 4-1 (1-3)) have only been evaluated one other time in the literature.$^{33}$ Our IC experimental method differs substantially from Jensen’s back titration method, and yet we obtain similar values for $k_1$, $k_2$ and $k_3$ as well as for their respective activation energies. The values are summarized in Table 4-1. Again, the colour scale of Graph 4-6 is generated from Equation 8 using our obtained values for $k_1$, $k_2$ and $k_3$ and for $E_{a1}$, $E_{a2}$ and $E_{a3}$, and we superimpose all our $k_{\text{hyd}}$ measurements from Table 4-2 (Appendix C) as circles. We further add Jensen’s published raw data for comparison as triangles.$^{33}$ The agreement is good and is consistently within the same order of magnitude (Graph 4-6).

**Table 4-1: HNCO’s Henry’s Law coefficient, acid dissociation constant and hydrolysis constants**

<table>
<thead>
<tr>
<th>Physical parameter</th>
<th>Value</th>
<th>Energy</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry’s Law coefficient, $K_H$</td>
<td>26 ± 2 M atm$^{-1}$</td>
<td>$\Delta H_{\text{diss}} = -34 \pm 2$ kJ mol$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>21 M atm$^{-1}$</td>
<td>$-$</td>
<td>Roberts et al. 2011</td>
</tr>
</tbody>
</table>
Acid dissociation constant, \( K_a \)

<table>
<thead>
<tr>
<th>( K_a )</th>
<th>( \Delta H_{\text{diss}} )</th>
<th>( E_a )</th>
<th>Reference</th>
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<tbody>
<tr>
<td>( 2.1 \pm 0.2 \times 10^{-4} ) M</td>
<td>(-5.4 ) kJ mol(^{-1})</td>
<td>+50 ± 2 kJ mol(^{-1})</td>
<td>This work</td>
</tr>
<tr>
<td>( 2.0 \times 10^{-4} ) M</td>
<td></td>
<td>+63 kJ mol(^{-1})</td>
<td>Amell 1956</td>
</tr>
</tbody>
</table>

Hydrolysis rate coefficient, \( k_1 \)

<table>
<thead>
<tr>
<th>( k_1 )</th>
<th>( E_a )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 7.6 \pm 0.3 \times 10^{-2} ) s(^{-1})</td>
<td>+56 ± 4 kJ mol(^{-1})</td>
<td>This work</td>
</tr>
<tr>
<td>( 1.1 \times 10^{-1} ) s(^{-1})</td>
<td>+63 kJ mol(^{-1})</td>
<td>Jensen 1958</td>
</tr>
</tbody>
</table>

Hydrolysis rate coefficient, \( k_2 \)

<table>
<thead>
<tr>
<th>( k_2 )</th>
<th>( E_a )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.4 \pm 0.1 \times 10^{-3} ) s(^{-1})</td>
<td>+56 ± 4 kJ mol(^{-1})</td>
<td>This work</td>
</tr>
<tr>
<td>( 1.8 \times 10^{-3} ) s(^{-1})</td>
<td>+83 kJ mol(^{-1})</td>
<td>Jensen 1958</td>
</tr>
</tbody>
</table>

Hydrolysis rate coefficient, \( k_3 \)

<table>
<thead>
<tr>
<th>( k_3 )</th>
<th>( E_a )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 8.1 \pm 1.7 \times 10^{-8} ) s(^{-1})</td>
<td>+91 ± 12 kJ mol(^{-1})</td>
<td>This work</td>
</tr>
<tr>
<td>( 1.2 \times 10^{-8} ) s(^{-1})</td>
<td>+100 kJ mol(^{-1})</td>
<td>Jensen 1958</td>
</tr>
</tbody>
</table>

* at 298K

In addition, our Henry’s Law coefficient experiment provides a complimentary way to determine \( k_{\text{hyd}} \) at different temperatures and pH values. Indeed, the intercept of the line which fit the data of \( \frac{\text{dln}(C_t/C_0)}{\text{dt}} \) versus \( \varphi/V \) yields \( k_{\text{hyd}} \), representing the value for the loss process in the solution of the bubbler column experiment (an example is given in Graph 4-1B). We show these values as squares in Graph 4-6. Roberts et al. also determined \( k_{\text{hyd}} \) through this method at pH 3 and at 25 °C and this value is appended to Graph 4-6 as a diamond. The agreement is good from all four cases.

We can conclude that the lifetime of HNCO against hydrolysis in dilute aqueous solutions spans seconds to years depending on pH and temperature. The lifetime of HNCO against hydrolysis in cloud water of pH 3-6 will be shorter and range from 10 hours to ~ 20 days in the troposphere. On the other hand, HNCO’s hydrolysis in ocean waters of pH ~ 8.1 and temperatures below 30 °C will be very slow, translating to a lifetime of 1-2 years if we assume no other reactive chemistry is taking place. Finally, in the context of exposure, if HNCO is present in human blood at physiological pH and temperature, its lifetime to hydrolysis will be as high as several months. On the other hand, if HNCO is present in the stomach, which is more acidic, we would expect its lifetime to drop to minutes or hours.
Graph 4-6: $k_{\text{hyd}}$ as function of temperature and pH generated from Equation 8 using our obtained values for $k_1$, $k_2$ and $k_3$ and for $E_{a1}$, $E_{a2}$ and $E_{a3}$. All available $k_{\text{hyd}}$ measurements for HNCO in the literature and from this work are superimposed and colour coded appropriately. As a guide, the colour scale also represents the lifetime in hours for HNCO in dilute aqueous solutions.

4.5 Atmospheric implications

HNCO is a toxic molecule and can cause cardiovascular and cataract problems through protein carbamylation.\textsuperscript{8,9,11} Recently reported ambient measurements of HNCO in North America raise concerns of exposure particularly from biomass burning, diesel and gasoline exhaust and urban environments.\textsuperscript{7,12-15,17} With the values for HNCO’s Henry’s Law coefficient and hydrolysis rates reported here, a better understanding of HNCO’s removal rate from the atmosphere can be determined, and hence HNCO’s atmospheric lifetime can be estimated. Note however that our HNCO lifetime estimates do not consider dry deposition and therefore represent a higher limit, particularly since Young et al. found that dry deposition can be significant for HNCO.\textsuperscript{31}
Specifically, the lifetime of HNCO in the atmosphere will depend on its partitioning to the aqueous phase $K_{H}^{\text{eff}}$, the temperature $T$, the pH and liquid water content (LWC) of the aerosol/droplet and finally the hydrolysis of HNCO $k_{\text{hyd}}$ once in solution. We can calculate HNCO’s lifetime against hydrolysis based on Equation 11 where $\tau$ is the lifetime in seconds, $L$ is the fraction of air volume occupied by liquid water (dimensionless) and $R$ is the gas constant. Graph 4-7A and 4-7B depict outputs of Equation 11 with different fixed variables. Graph 4-7A holds the LWC to 1 g m$^{-3}$, a value representative of cloud water, highlighting the dependence of HNCO’s lifetime on temperature and pH.$^{39}$ At atmospherically relevant pH of 2 to 6 and at temperatures below 30 °C, HNCO has a lifetime on the order of 10 days to hundreds of years. Alternatively, Graph 4-7B holds the pH at 4 and varies the LWC on the x-axis. Water concentrations relevant to wet aerosol (1-100 μg m$^{-3}$) are too small to act as a significant sink for gas phase HNCO. However, Graph 4-7B highlights the strong dependence of HNCO lifetime on LWC in clouds, again ranging from days to hundreds of years. It therefore appears that if HNCO is incorporated into cloud water, it is more likely to be rained out or revolatilized than to hydrolyse given typical times in clouds of minutes to hours. There is also the possibility that HNCO has other currently unknown sinks in cloud water that may be competitive with its hydrolysis and further work on HNCO’s aqueous phase chemistry is certainly warranted. Finally, HNCO will partition readily in oceans at pH ~8, but will take years to hydrolyze.

Equation 11: $\tau = 1/K_{H}^{\text{eff}}RTLk_{\text{hyd}}$

Zhao et al. observed higher concentrations of HNCO in the cloud water in La Jolla, California than predicted by its Henry’s Law coefficient at 298 K.$^{15}$ This observation remains puzzling but may point towards other sources of HNCO than simple partitioning chemistry. The Barth et al. 2013 modeling study concluded that fog, low-level stratus clouds or stratocumulus clouds were the most efficient cloud conditions at removing HNCO from the gas phase, particularly in polluted scenarios where the cloud water was more acidic. The authors highlighted the high dependence of HNCO’s fate on liquid water pH and temperature, consistent with our findings.$^{32}$ The Young et al. study, which modelled global HNCO budgets, assumed the aqueous loss of the weak acid occurred only when the cloud liquid water content was greater than 1 mg m$^{-3}$. Based on Graph 4-7B, 1 mg m$^{-3}$ is low for HNCO to significantly partition into the aqueous phase and rather requires water mass concentrations 1000 times greater for HNCO’s lifetime to drop to days. The model may have overestimated the ability for LWC to act as a sink for HNCO. HNCO may be a longer lived species
than previously thought and exposure of this toxic molecule may pose a threat to regions with HNCO point sources like biomass burning and engine exhaust, as pointed out by Young et al. and by Barth et al.\textsuperscript{31,32}

Graph 4-7: A) The lifetime of HNCO in days as a function of temperature and pH at 1 g m\textsuperscript{-3} of LWC and B) the lifetime of HNCO in days as a function of temperature and LWC at pH 4.

4.6 Conclusions

In summary, we provide laboratory measurements of HNCO’s important thermochemical properties related to its behavior in water. We measured its Henry’s Law coefficient using a bubbler column experiment to be 26 ± 2 M atm\textsuperscript{-1} with an enthalpy of dissolution of -34 ± 2 kJ mol\textsuperscript{-1}. Using ion chromatography, we determined the Arrhenius expression of HNCO’s three hydrolysis mechanisms: \( k_1 = (4.4 ± 0.2) \times 10^7 \exp(-6000 ± 240 / T) \) M s\textsuperscript{-1}, \( k_2 = (8.9 ± 0.9) \times 10^6 \exp(-6770 ± 450 / T) \) s\textsuperscript{-1} and \( k_3 = (7.2 ± 1.5) \times 10^8 \exp(-10900 ± 1400 / T) \) s\textsuperscript{-1}. These values will provide better constrains on the sinks and thus lifetime of HNCO in the atmosphere with the aim of minimizing exposure of this toxic molecule.

References


### 4.7 Appendix C

Table 4-2: Compilation of $k_{hyd}$ experiments at different pH and temperatures

<table>
<thead>
<tr>
<th>pH</th>
<th>T (K)</th>
<th>$k_{hyd}$ (S$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.75</td>
<td>270</td>
<td>$(8.30 \pm 0.64) \times 10^{-4}$</td>
</tr>
<tr>
<td>1.75</td>
<td>295</td>
<td>$(2.22 \pm 0.06) \times 10^{-3}$</td>
</tr>
<tr>
<td>1.81</td>
<td>283</td>
<td>$(1.17 \pm 0.06) \times 10^{-3}$</td>
</tr>
<tr>
<td>2.23</td>
<td>270</td>
<td>$(1.92 \pm 0.16) \times 10^{-4}$</td>
</tr>
<tr>
<td>2.23</td>
<td>295</td>
<td>$(1.39 \pm 0.02) \times 10^{-3}$</td>
</tr>
<tr>
<td>2.26</td>
<td>283</td>
<td>$(5.13 \pm 0.28) \times 10^{-4}$</td>
</tr>
<tr>
<td>2.30</td>
<td>295</td>
<td>$(1.09 \pm 0.04) \times 10^{-3}$</td>
</tr>
<tr>
<td>3.40</td>
<td>297</td>
<td>$(9.90 \pm 0.25) \times 10^{-4}$</td>
</tr>
<tr>
<td>3.91</td>
<td>296</td>
<td>$(3.74 \pm 0.03) \times 10^{-4}$</td>
</tr>
<tr>
<td>4.27</td>
<td>296</td>
<td>$(2.99 \pm 0.02) \times 10^{-4}$</td>
</tr>
<tr>
<td>5.00</td>
<td>296</td>
<td>$(6.55 \pm 0.21) \times 10^{-5}$</td>
</tr>
<tr>
<td>5.40</td>
<td>298</td>
<td>$(2.10 \pm 0.05) \times 10^{-5}$</td>
</tr>
<tr>
<td>9.26</td>
<td>313</td>
<td>$(5.39 \pm 0.26) \times 10^{-7}$</td>
</tr>
<tr>
<td>9.46</td>
<td>313</td>
<td>$(6.07 \pm 0.28) \times 10^{-7}$</td>
</tr>
<tr>
<td>10.20</td>
<td>313</td>
<td>$(6.03 \pm 0.33) \times 10^{-7}$</td>
</tr>
<tr>
<td>10.36</td>
<td>333</td>
<td>$(4.84 \pm 0.09) \times 10^{-6}$</td>
</tr>
<tr>
<td>10.37</td>
<td>325</td>
<td>$(1.70 \pm 0.09) \times 10^{-6}$</td>
</tr>
</tbody>
</table>
Chapter 5
Gas Phase Mechanisms of the Reactions of Organic Nitrogen Compounds with OH Radicals

Contributing authors: Borduas, N., da Silva, G., Murphy, J. G., and Abbatt, J. P. D.

5 Chapter 5
5.1 Abstract

Research on the fate of organic nitrogen compounds in the atmosphere has gained momentum since the scale up of carbon capture and storage (CCS) technology which employs amine-based solvents on an unprecedented scale. Amines are known to have short gas phase lifetimes, on the order of a few hours against OH radicals, and typically form amides as oxidation products. Less is known about the fate of amides, but recent studies suggest they have longer lifetimes, on the order of days to weeks and may be oxidized to form isocyanates. In this chapter, we use ab initio methods to investigate the gas phase mechanisms governing the reactions of amines, amides, isocyanates and carbamates with OH radicals. We identify a reactive pathway in amides, the formyl C–H abstraction, not currently considered in current structure-activity relationship (SAR) models. Furthermore, we determine that N–H abstraction is only a viable mechanistic pathway for amines and is negligible in other organic nitrogen compounds. We also show that the addition of OH radicals to nitrogen in amines, amides, isocyanates and carbamates is consistently endothermic with a high activation energy, and hence is never a competitive pathway. We then use our acquired knowledge to calculate new SAR factors more representative of the plausible mechanisms and present our preliminary efforts for amide SAR factors. In all, we evaluate comprehensively the mechanisms involved in the atmospheric oxidation of amines, amides, isocyanates and carbamates.
by OH radicals, highlight discrepancies in current SAR models, and propose new SAR factors for appropriate prediction of the fate of organic nitrogen compounds in the atmosphere.

5.2 Introduction

Organic nitrogen compounds, that is molecules containing at least one carbon and one nitrogen, are of importance in the study of air quality and climate change. Molecules with functional groups such as amines, amides, imines, isocyanates, carbamates, cyanates, nitrosamines and nitramines are prominent examples of organic nitrogen compounds. These molecules have a wide range of biogenic and anthropogenic sources to the atmosphere. Recent large scale use of amines as solvents in carbon capture and storage (CCS) technologies, as well as their role in aerosol formation and growth has warranted increased attention to the understanding of their fate. It is known that the current benchmark solvent for CCS, monoethanolamine (MEA), if emitted to the atmosphere, has a short lifetime, approximately 2 h, governed by its reactivity towards the OH radical. Other sources of organic nitrogen molecules to the atmosphere include direct emissions from industrial solvents, biomass burning, cigarettes, and animal husbandry as well as due to secondary oxidative chemistry of amines. Indeed, the gas phase oxidation of MEA produces amides as well as toxic isocyanates.

The sinks for the majority of organic nitrogen compounds are reactions with oxidants like OH radicals, NO\textsubscript{3} radicals and ozone, and because most amines, amides and isocyanates do not absorb photons of wavelengths in the actinic window they are not photolysed in the atmosphere. Another important sink for some organic nitrogen compounds is loss to aerosols. For example, amines may act as bases and nucleate particles as well as contribute to particle growth, thereby impacting climate directly through light scattering and indirectly through acting as cloud condensation nuclei. Organic nitrogen compounds are also thought to be responsible for the colouring in brown carbon aerosols, again impacting climate through their light-absorbing properties. Organic nitrogen compounds may also be toxic and raise concerns of population exposure near point sources. In particular, methyl isocyanate and isocyanic acid may pose serious health effects if inhaled in mixing ratios above 1 ppbv. In addition, nitrosamines and nitramines, oxidation products of amines reacting with NO\textsubscript{x}, are carcinogens. Generally, organic nitrogen compounds are not important radiative forcing agents due to their small gas phase
concentrations. However, the current record holder for the highest global warming potential of any compounds detected in the atmosphere is an amine, perfluorotributylamine.\textsuperscript{16}

A number of laboratory experiments, theoretical calculations and field studies have aimed to better understand the fate of organic nitrogen compounds and were recently reviewed in the context of their use and/or production in CCS plants.\textsuperscript{2,6,10,11} However, their chemical mechanisms are mostly based on experimental product studies. There is computational chemistry literature on amines in the context of CCS,\textsuperscript{17-22} as well as recent studies on amide oxidation mechanisms.\textsuperscript{8,23} To better understand the overall atmospheric fate of organic nitrogen compounds, we evaluate through computational chemistry the mechanisms involved in their gas phase oxidation with OH radicals. We then compare their mechanisms to highlight the impact that adjacent functionalities to the nitrogen atom have on reactivity. In particular, we focus our attention on amines, amides, isocyanates, since their lifetimes are strikingly different, ranging from hours to years depending on the functional group.\textsuperscript{2,11} We opted to study the simplest molecule of each class, i.e. methylamine, formamide and isocyanic acid for relevance and calculation simplicity. We also evaluate a model carbamate molecule, $N$-methyl methylcarbamate since structure-activity relationship (SAR) analyses for many organic nitrogen compounds stem from the evaluation of carbamate rate coefficients.\textsuperscript{24} Our mechanistic approach is comprehensive as we consider all possible reaction sites on each functionality including C−H and N−H abstractions, carbonyl-additions and N-additions to demonstrate the importance of previously neglected, as well as incorrectly assumed, mechanistic pathways.

\section*{5.3 Computational Method}

To investigate the mechanism of the reaction of organic nitrogen molecules with OH radicals, computational ab initio methods were employed using the Gaussian 09 code.\textsuperscript{25} Structures of the reactants were first optimized using the M06-2X density functional with the 6-31G(2df,p) basis set. Then, they were further evaluated using the G3X-K composite theoretical method which combines a series of Hartree-Fock, Møller-Plesset perturbation and coupled cluster theory calculations.\textsuperscript{26,27} G3X-K theory is used here since it was specifically designed for thermochemical kinetics and reproduces barrier heights in the DBH24/08 database with an average accuracy of 0.6 kcal mol\textsuperscript{-1}.\textsuperscript{27} The energies reported are 0 K and are calculated from the sum of the electronic energy
and the zero point energy. The accuracy of the energies stated is expected to be within 1 kcal mol\(^{-1}\).\(^{27}\)

Throughout this work, we describe transition state energy, used interchangeably with barrier height energy, as the energy difference between the transition state and the sum of the reactants’ energies. Along the same lines, we assume that the pre-complex formation of the organic nitrogen molecule with OH radicals is not a deep enough well for the pre-complex to get caught and so does not require additional kinetic energy than the entrance level energy of the reactants to overcome the transition states. In addition, we relate transition state energy with measured rate coefficients for a particular organic nitrogen molecule with OH. One must keep in mind however, that between molecules this comparison does not always hold. In fact, the pre-exponential factor, \(A\), in the Arrhenius equation may be different between small versus large molecules.\(^{28}\) For example, the number of successful collisions may be smaller for larger molecules with less reactive sites.

### 5.4 Results

#### 5.4.1 Methylamine + OH

We begin our mechanistic analysis of organic nitrogen compounds with methylamine, the simplest of amines. Scheme 5-1 shows the three possible mechanisms for the OH radical to react with methylamine in the gas phase. Both H-abstraction mechanisms are competitive for this alkylamine with barriers to reaction close to the entrance level energies of the reactants and within a 1 kcal mol\(^{-1}\) difference. Both reactions are exothermic, as expected due to the formation of water as a by-product. The third mechanism investigated is the OH addition to the nitrogen atom, which is clearly endothermic with an inaccessible transition state energy. The implications are discussed further in the following sections.

Methylamine’s gas phase reaction has been experimentally investigated before by Atkinson et al., by Carl et al. and by Onel et al.\(^{17,29,30}\) These authors find a room temperate rate coefficient consistent with \(2 \times 10^{-11}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\), in agreement with a low transition state energy. In each study, two mechanisms are considered for reaction with OH radicals, the C–H abstraction and the N–H abstraction.\(^{17,29,30}\) Onel et al. also investigated this reaction by ab initio methods and found transition states for both H-abstraction mechanisms slightly below the entrance level energies of
the reactants.\textsuperscript{17} Our results are consistent, albeit slightly higher in energies, a difference attributable to the different level of theory and basis set employed.

![Scheme 5-1: Theoretical energy diagram for methylamine + OH. Energies are 0 K enthalpies in kcal mol\textsuperscript{−1}, at the G3X-K level of theory.](image)

5.4.2 Formamide + OH

Amides are known to be products of amine oxidation but our understanding of their fate in the atmosphere is limited.\textsuperscript{2,5,11,31} Their functionality differs from amines in that amides have a carbonyl moiety adjacent to the nitrogen. The nitrogen’s lone pair is thus delocalized in the carbonyl’s \(\pi\)-system, making amides poor nucleophiles compared to amines. This effect translates to poor reactivity with electrophilic OH radicals which explains amides’ longer atmospheric lifetimes.\textsuperscript{8,31}
Scheme 5-2 depicts the energy diagram of formamide’s four possible mechanisms of reaction with OH radicals. The lowest energy transition state is the formyl C–H abstraction, 6 kcal mol$^{-1}$ lower than the next lowest transition state energy, meaning this pathway governs the majority of formamide’s reactivity. This mechanism is also quite exothermic compared to the N–H abstraction. In contrast to amines, amides may also react with OH radicals by adding to the carbonyl moiety. We find that this pathway is 9.9 kcal mol$^{-1}$ above the entrance level energy of the reactants but is exothermic. Similarly to amines, the OH addition to the nitrogen in amides is high in energy and endothermic.

From previous work, we measured the room temperature rate coefficient of formamide and OH radicals to be $4.44 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$, which we also supported by ab initio calculations. We solely focused on the H-abstraction mechanisms, which are indeed the most relevant. The formyl C–H abstraction produces a C-centered formyl radical which can go on to react with O$_2$ and form isocyanic acid. Interestingly, the formyl C–H abstraction is also competitive for N-alkylated amides as seen for N,N-dimethylformamide in Scheme 5-5 in Appendix D, for example. This mechanism is further discussed in the context of modelling in the following sections. To complement our previous ab initio work on the reactivity of amides with OH radicals, we also investigated the mechanistic pathways of N,N-dimethylacetamide, N,N-dimethylpropanamide and N-methylpropanamide in Schemes 5-6, 5-7 and 5-8 respectively in Appendix D.
Scheme 5-2: Theoretical energy diagram for formamide + OH. Energies are 0 K enthalpies in kcal mol\(^{-1}\), at the G3X-K level of theory.

5.4.3 Isocyanic acid + OH

Isocyanates differ from the amide functionality by being hybridized sp\(^2\) at the nitrogen and sp at the adjacent carbon. In isocyanic acid, the nitrogen’s lone pair is entirely delocalized in the \(\pi\)-system. Isocyanic acid’s energy diagram is presented in Scheme 5-3. Three mechanisms are plausible for OH radicals to react with isocyanic acid: N−H abstraction and OH additions to the carbonyl or the nitrogen. All three mechanisms are high in energy and are therefore expected to be very slow at room temperature (Scheme 5-3). Indeed, the experimental rate coefficient for the reaction of isocyanic acid with OH radicals has been measured only at high temperatures and if extrapolated to room temperature would be \(\sim 10^{-15}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\), translating to a lifetime of decades.\(^{14,32}\) The OH-addition to the carbonyl (barrier height of +9.1 kcal mol\(^{-1}\)) and the N−H
abstraction (barrier height of +19.4 kcal mol\(^{-1}\)) pathways are exothermic compared to the OH-addition to the nitrogen which is consistently endothermic in amines, amides and isocyanates. No pre-complex could be isolated in our ab initio calculations between isocyanic acid and OH as all the mechanisms have a transition state energy significantly above that of the reactants. Since the mechanistic pathways depicted in Scheme 3 are all significantly above the entrance level energy of the reactants, we do not expect OH reactivity to be a sink for isocyanic acid. Rather, it will likely partition to the aqueous phase and undergo further reactions including hydrolysis (see Chapter 4).

![Theoretical energy diagram for isocyanic acid + OH. Energies are 0 K enthalpies in kcal mol\(^{-1}\), at the G3X-K level of theory.]

Scheme 5-3: Theoretical energy diagram for isocyanic acid + OH. Energies are 0 K enthalpies in kcal mol\(^{-1}\), at the G3X-K level of theory.
5.4.4 \textit{N}-Methyl methylcarbamate + OH

The difference between carbamate and amide is the presence of an extra oxygen atom, which enhances the reactivity of the molecule towards OH radicals. This conclusion is supported by the presence of transition state energies lower than the entrance energies of the reactants compared to amides. We rationalize this observation by the fact that the oxygen’s lone pair can delocalize in the carbonyl group thereby increasing the electron density in the N–H bond and making it more reactive towards the electrophilic OH radical. Indeed, through ab initio calculations, we find that the transition state energy of the N–H abstraction in \textit{N}-methylformamide is 1 kcal mol\(^{-1}\) higher than in \textit{N}-methyl methylcarbamate.\(^8\) We opted to use \textit{N}-methyl methylcarbamate as our carbamate substrate rather than the simpler methylcarbamate in this chapter as it does not yet have a reported rate coefficient in the literature. Scheme 5-4 shows the theoretical energy diagram of the five mechanistic pathways relevant to the reaction of \textit{N}-methyl methylcarbamate with OH. The two C–H abstraction transition state energies are below the energies of the reactants and are expected to dominate the reactivity of carbamates. Kwok et al. have measured the room temperature rate coefficient of \textit{N}-methyl methylcarbamate to be \(4.3 \times 10^{-12}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\), which represents a lifetime on the order of one day, about as fast as its analogue \textit{N}-methylacetamide (see Figure 5-1).\(^8,24\) Note here that this rate coefficient is slower than that of methylamine \((2 \times 10^{-12}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\)) despite having calculated lower transition state energies, but each molecule has a different, and consequently not directly comparable, pre-exponential factor \(A\) to also take into consideration. The N–H abstraction transition state lies above the reactant energies but is exothermic. On the other hand, both OH addition mechanisms, i.e. to the carbonyl or to the nitrogen, require high energy to proceed and are also both endothermic reactions.

\[
\begin{align*}
\text{\textit{N}-methyl methylcarbamate} & : \quad H_3C\begin{array}{c}O\end{array}\text{-}N\text{-}CH_3 \quad \text{TS} = +2.5 \text{ kcal mol}^{-1} \\
\text{\textit{N}-methyl acetamide} & : \quad H_3C\begin{array}{c}O\end{array}\text{-}N\text{-}CH_3 \quad +3.4 \text{ kcal mol}^{-1}
\end{align*}
\]

\textbf{Figure 5-1: Comparison in N–H abstraction transition state energies between carbamates and amides.}
5.5 Mechanistic Discussion

By comparing the calculated transition state energies in Schemes 5-1 to 5-8, we gain insight into the mechanisms governing the reactivity of four subclasses of organic nitrogen compounds, namely amines (Scheme 5-1), amides (Scheme 5-2, 5-5, 5-6, 5-7 and 5-8), isocyanates (Scheme 5-3) and carbamates (Scheme 5-4). We now use this insight to evaluate current structure-activity relationships (SAR) models in the hope of developing more accurate SAR group rate constants and substituent factors for organic nitrogen and of better predicting their fate in the atmosphere.

5.5.1 SAR models

Structure-activity relationships (SAR) are used in atmospheric chemistry to estimate the lifetime of organic compounds and their initial oxidation products.\textsuperscript{33,34} SAR group rate constants and SAR
substituent factors were developed as a predictive tool for estimating the room temperature rate coefficient and hence the atmospheric lifetime of organic compounds against the OH radical and later for other atmospheric oxidants.\textsuperscript{33-35} The general approach of the SAR model consists of predicting an overall rate coefficient by summing the individual rates constants of every reactive site on a molecule of interest. Mechanisms currently incorporated that are relevant to OH radicals include H-abstraction, addition to unsaturated carbon-carbon bonds and addition to heteroatoms.\textsuperscript{33}

The SAR method includes two types of factors relevant to our organic nitrogen analysis. First, there is the SAR group rate constants for H-abstractions from any atom (C, N, O, etc.), denoted by a $k$ value with a subscript denoting the site (or functional group) of the H-abstraction. Three main SAR group rate constants relevant to C−H abstractions exist for each type of carbon centre: a primary ($k_{\text{prim}}$), secondary ($k_{\text{sec}}$) or tertiary ($k_{\text{ter}}$) carbon center. Second, specifically for C−H abstractions, the SAR group rate constant ($k_{\text{prim}}$, $k_{\text{sec}}$, or $k_{\text{ter}}$) is then multiplied by a substituent factor denoted as $F(X)$ to obtain an overall rate constant specific for the functional group’s reactivity. Sample equations for C−H abstractions are given below.

$$k_{\text{overall}}(\text{CH}_3 - X) = k_{\text{prim}}F(X)$$

$$k_{\text{overall}}(Y - \text{CH}_2 - X) = k_{\text{sec}}F(X)F(Y)$$

$$k_{\text{overall}}(Z > \text{CH} - X) = k_{\text{ter}}F(X)F(Y)F(Z)$$

There are published SAR group rate constants for N−H abstractions for amines, carbamates and thiocarbamates as well as SAR substituent factors for C−H abstractions occurring adjacent to an amine, a carbamate or a thiocarbamate functionality derived from experimental rate coefficients.\textsuperscript{24,33,34,36} There are currently no SAR group rate constants for amides or isocyanates. To circumvent this problem, the U.S. Environmental Protection Agency’s (EPA) Estimation Program Interface (EPI) Suite model for example, uses estimated values based on the available amine, carbamate or thiocarbamate factors to predict the atmospheric fate of the majority of organic nitrogen compounds.\textsuperscript{37} In this section, we examine each mechanism computed by our ab initio method of each organic nitrogen subclass to in order to improve upon past SAR analyses of these classes of compounds.
5.5.2 C−H Abstraction

The C−H abstraction mechanisms, when present, dominate the reactivity of organic nitrogen compounds. This observation is expected as the C−H bond is the least polarized bond compared to heteroatom−H bonds, making it more prone to break homolytically and react with the electrophilic OH radical. There are also statistically more C−H bonds than N−H bonds in amines, amides and carbamates. There are differences in reactivity based on the type of carbon on which the C−H abstraction is occurring. Relevant to organic nitrogen, the N-CH\textsubscript{3} group imparts significant reactivity. In fact, the C−H abstraction from an N-CH\textsubscript{3} group is more facile than from an O-CH\textsubscript{3}, which can be reasoned by the ability of the nitrogen to donate more electron density into the C−H bond. Hence, in carbamates, the OH radical will preferentially react with the N-CH\textsubscript{3} moiety with a transition state lower by \(\sim 1.5\) kcal mol\(^{-1}\). Current SAR models represent this factor as \(F(-N)\) and it is worth a value of 9.3 regardless of whether the nitrogen has one, two or three substituents.\(^{33}\) This \(F(-N)\) factor, multiplied by \(k_{\text{prim}}\), like for methylamine, gives a value of \(1.26 \times 10^{-12}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\), a value which would only account for \(\sim 6\%\) of methylamine’s reactivity. Based on our calculations in Scheme 1, this C−H abstraction pathway is competitive with the N−H abstraction and would be expected to contribute more than 6% of methylamine’s reactivity. We conclude that a value of 9.3 is biased low for \(F(-N)\). The same reasoning applies to amides, and more specific substituent factors should be introduced depending on the substituents on the nitrogen.

Current SAR models do not attribute any factor to the formyl C−H bond in amides, when in fact it dominates the reactivity of formamide.\(^8\) We therefore also propose including a new group rate constant \(k_{\text{HC(O)NR}_2}\) to represent the importance of this reactive site in amides like formamide (Scheme 5-2).

5.5.3 N−H Abstraction

The N−H abstraction mechanism is only a relevant pathway in amines. The increasing trend observed for transition state energies of this N−H abstraction mechanism is as follows: amine < carbamate < amide < isocyanate. Indeed, only for the N−H abstraction in amines is the calculated barrier height below the entrance level energy of the reactants, indicating a rapid and favorable reaction. In other words, the group rate constant for N−H abstraction, \(k_{\text{NH}_2}, k_{\text{NH}−}\), and \(k_{>\text{N}−}\), is solely valid for amines. Currently the SAR model includes a variety of organic nitrogen group rate
constants like $k_{NH2C(O)}$, $k_{NHC(O)}$, and $k_{>NC(O)}$ which are overestimated because the N-H abstractions and addition to the N atom are unlikely to occur. We also believe that SAR substituent factors $F_S(X)$ specific to N–H abstractions could be developed.

As a case study, Kwok et al. use the group rate constant $k_{NHC(O)O}$ which represents, “the rate constant for OH radical addition to the -NHC-(O)O- structural unit”. They solve their system of SAR equations, which also included terms for C–H abstractions (i.e. $k_{prim} \times F(-OC(O)NHR)$ and $k_{prim} \times F(-NHC(O)OR)$), and attributed half of the N-methyl methylcarbamate’s reactivity, i.e. $2.7 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$ (out of a measured rate coefficient of $4.3 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$) to the addition term (i.e. $k_{NHC(O)O}$, refer to Appendix D for detailed SAR equations). In reality, $k_{NHC(O)O}$ should be at least an order of magnitude less than $2.7 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$ because our calculations indicate that the OH radical cannot add to this functional group and that N–H abstraction is negligible (Scheme 5-4). This incorrect attribution of reactivity to the -NHC-(O)O-moiety also causes the other factors to be underestimated. N-methyl methylcarbamate has a transition state energy of 2.5 kcal mol$^{-1}$ for the N–H abstraction mechanism (Scheme 5-4, Figure 5-1), and in the context of room temperature rate coefficients on the order of $10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$, a 1 kcal mol$^{-1}$ difference in activation energy translates to approximately a factor of 5 difference in rate coefficients using the Arrhenius equation. Based on this analysis, we propose setting an upper limit for the N–H abstraction by OH to a value of $10^{-13}$ cm$^3$ molec$^{-1}$ s$^{-1}$ for amides and carbamates as well as a value of $10^{-15}$ cm$^3$ molec$^{-1}$ s$^{-1}$ for isocyanates using the same logic.

The issue of misrepresenting N–H abstractions in SAR models is heightened by the fact that these factors (like the ones derived from the carbamate analysis) are also used as estimates for other organic nitrogen compounds, namely amides, propagating the error. SAR models do a fair job of representing the lifetime of amides, but for perhaps incorrect reasons (underestimating the C–H abstraction and overestimating the N-H abstraction).

5.5.4 Carbonyl-addition

The addition of OH radicals to unsaturated bonds is a common mechanistic pathway for alkenes and alkynes. For completeness, we also explored this mechanism for carbonyls, as they exist in organic nitrogen compounds. Although this mechanism is exothermic in formamide and isocyanic acid, it is very slightly endothermic for N-methyl methylcarbamate. Nonetheless, it possesses a high energy barrier to reaction and thus is not expected to be competitive with C–H or N–H
abstraction pathways. However, in the case of isocyanic acid, this mechanism dominates its reactivity, despite the fact that this mechanism is still slow enough to be negligible in the context of isocyanic acid’s atmospheric fate.

5.5.5 N-Addition

The fourth mechanism investigated is the OH addition to the nitrogen atom. This mechanism has been proposed by Atkinson et al. and is currently incorporated in SAR models. At the time of the SAR model development, it was assumed that the reactivity of OH with amines was analogous to the reactivity of organic sulfides, which has been proposed to proceed with OH addition to the sulfur moiety. We show in Schemes 5-1 to 5-4 that for nitrogen, this mechanism is consistently high in energy and endothermic for all classes of organic nitrogen studied. Currently, the SAR factor for N−H abstractions also incorporated this N-addition mechanism, and is typically called the “group rate constant for hydrogen abstraction and radical reaction”. However, this mechanism should be worth an SAR factor of zero in all cases and is quite distinct from the analogous reaction with organic sulfide species.

5.5.6 New SAR factors for organic nitrogen compounds

In an attempt to propose more appropriate SAR factors for the general class of organic nitrogen compounds, we start by calculating SAR factors specific to amides. Nine simply alkylated amides (see Chapter 3) have known experimental rate coefficients and we employ this data set to determine four different SAR factors, the group rate constant $k_{\text{HC(O)NR}_2}$, the substituent factors for hydrogen abstractions, $F(-\text{C(O)NR}_2)$ and $F(-\text{NR(CO)R})$, and the group rate constant $k_{-\text{NHR}_2}$ which we set to $10^{-13}$ cm$^3$ molec$^{-1}$ s$^{-1}$ based on our discussion above (Figure 5-2). We purposely omit the carbonyl and N-addition mechanisms based on the energy diagram depicted in Scheme 5-2. With a set of nine equations and three unknowns, we can solve for each unknown. The solutions obtained are $k_{\text{HC(O)NR}_2} = 5.6 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$, $F(-\text{C(O)NR}_2) = 4.0$ and $F(-\text{NR(CO)R}) = 35$. An SAR factor of 35 is large and unprecedented compared to the current list of substituent factors. However, these values correctly represent the fact that no reactivity occurs through the N−H abstraction or the N-addition mechanisms, and are therefore more representative for organic nitrogen.
Figure 5.2: The developed amide SAR group rate constants and substituent factors where the highlighted hydrogen is the reactive site represented by the SAR factor.

Next, we examine the utility of the SAR factors determined above for predicting rate coefficients for amides more complex than those substituted with simple linear alkyl functional groups. We choose N-methylpyrrolidinone, a simple alkylated amide but with a five-membered ring, to test our SAR group rate constants and substituent factors. It is indeed predicted to within a factor of 2.4 and is illustrated on Graph 5.1 as a black square. With these preliminary results, we hope to expand this approach to revisit the SAR factors for all organic nitrogen compounds.

Graph 5.1: Predicted rate coefficients using the SAR factors determined in this work as a function of experimentally measured rate coefficients for nine amides. The numbers represent the level of N-methylation on the amide, so that 1° represents primary amides, 2° represents monomethylated amides and 3° represents dimethylated amides. The color
coding represents amide subclasses, so that the blue series represents formamide and its alkylated analogues, the red series represents acetamide and its alkylated analogues and the green series represents propanamide and its alkylated analogues. The black square represents N-methylpyrrolidinone. The solid line is the 1:1 relationship, and the dotted lines have slopes differing by a factor of two from the 1:1 relationship.

5.6 Conclusion

In summary, we employed quantum chemical techniques to investigate the mechanism of organic nitrogen compounds with OH radicals to better understand their fate in the atmosphere. We specially looked at four subclasses of organic nitrogen compounds which included amines, amides, isocyanates and carbamates and identified four types of mechanisms, C−H abstractions, N−H abstractions, carbonyl additions and N additions. In all cases, if a C−H bond is present, it will dominate the reactivity of the organic nitrogen molecules. N−H abstractions are only competitive in amines and should be worth negligible SAR values for the analyses of amides, carbamates or isocyanates. This previous attribution to the importance of N−H abstraction mechanisms in most organic nitrogen compounds has led to an underestimate of the contribution of C−H abstractions adjacent to nitrogen atoms. We calculated the barrier height energies for carbonyl addition mechanisms and although high in energy, this mechanism dominates the reactivity of isocyanates where no C−H bonds are present. Finally, the activation energies for the mechanisms of OH adding to a nitrogen atom were calculated to be > 30 kcal mol\(^{-1}\) and the reactions are endothermic, and should therefore be disregarded from contributing to reactivity of organic nitrogen molecules. Our goal is now to take this mechanistic knowledge and to develop more representative SAR factors for this class of compounds for incorporation into SAR models.

5.7 References


29. Carl, S. A.; Crowley, J. N. Sequential two (blue) photon absorption by NO$_2$ in the presence of H$_2$ as a source of OH in pulsed photolysis kinetic studies: Rate constants for reaction of


### 5.8 Appendix D

#### 5.8.1 Extended theoretical energy diagrams

**Scheme 5-5:** Theoretical energy diagram for \(N,N\)-dimethylformamide + OH. Energies are 0 K enthalpies in kcal mol\(^{-1}\), at the G3X-K level of theory.

**Scheme 5-6:** Theoretical energy diagram for \(N,N\)-dimethylacetamide + OH. Energies are 0 K enthalpies in kcal mol\(^{-1}\), at the G3X-K level of theory.
Scheme 5-7: Theoretical energy diagram for N,N-dimethylpropanamide + OH. Energies are 0 K enthalpies in kcal mol$^{-1}$, at the G3X-K level of theory.
Scheme 5-8: Theoretical energy diagram for N-methylpropanamide + OH. Energies are 0 K enthalpies in kcal mol\(^{-1}\), at the G3X-K level of theory.

5.8.2 SAR equations:

Methylamine:

\[
\text{H}_3\text{C}^-\text{NH}_2 \quad k_{overall} = k_{NH_2} + k_{prim}F(-NH_2)
\]

Formamide:

\[
\text{HC(O)N}_2 \quad k_{overall} = k_{HC(O)NR_2} + k_{-NHR_2}
\]

N-methylformamide:

\[
\text{HC(O)NCH}_3 \quad k_{overall} = k_{HC(O)NR_2} + k_{prim}F(-NRC(O)R) + k_{-NHR_2}
\]

N,N-dimethylformamide:

\[
\text{HC(O)NCH}_3 \quad k_{overall} = k_{HC(O)NR_2} + 2k_{prim}F(-NRC(O)R)
\]
acetamide:

\[ k_{overall} = k_{prim}F(-C(O)NR_2) + k_{-NHR2} \]

\[ \begin{array}{c}
  \text{H}_3\text{C} \\
  \text{O} \\
  \text{NH}_2 \\
  \end{array} \]

\[ \text{H}_3\text{C} \\
  \text{N} \\
  \text{CH}_3 \\
  \text{CH}_3 \\
  \text{CH}_3 \\
\]

\[ N\text{-methylacetamide:} \]

\[ k_{overall} = k_{prim}F(-C(O)NR_2) + k_{prim}F(-NRC(O)R) + k_{-NHR2} \]

\[ \begin{array}{c}
  \text{H}_3\text{C} \\
  \text{O} \\
  \text{NH} \\
  \text{CH}_3 \\
  \text{CH}_3 \\
\end{array} \]

\[ \text{H}_3\text{C} \\
  \text{N} \\
  \text{CH}_3 \\
  \text{CH}_3 \\
  \text{CH}_3 \\
\]

\[ N,N\text{-dimethylacetamide:} \]

\[ k_{overall} = k_{prim}F(-C(O)NR_2) + 2k_{prim}F(-NRC(O)R) \]

\[ \begin{array}{c}
  \text{H}_3\text{C} \\
  \text{O} \\
  \text{NH}_2 \\
  \text{CH}_3 \\
\end{array} \]

\[ \text{propanamide:} \]

\[ k_{overall} = k_{prim}F(-CH_2-) + k_{sec}F(-C(O)NR_2)F(-CH_3) + k_{-NHR2} \]

\[ \begin{array}{c}
  \text{H}_3\text{C} \\
  \text{O} \\
  \text{NH}_2 \\
  \text{CH}_3 \\
\end{array} \]

\[ \text{N\text{-methylpropanamide:} } \]

\[ k_{overall} = k_{prim}F(-CH_2-) + k_{sec}F(-C(O)NR_2)F(-CH_3) + k_{prim}F(-NRC(O)R) + k_{-NHR2} \]

\[ \begin{array}{c}
  \text{H}_3\text{C} \\
  \text{O} \\
  \text{NH}_2 \\
  \text{CH}_3 \\
\end{array} \]

\[ \text{N,N\text{-dimethylpropanamide:} } \]

\[ k_{overall} = k_{prim}F(-CH_2-) + k_{sec}F(-C(O)NR_2)F(-CH_3) + 2k_{sec}F(-NRC(O)R) \]

\[ \begin{array}{c}
  \text{H}_3\text{C} \\
  \text{O} \\
  \text{NH}_2 \\
  \text{CH}_3 \\
  \text{CH}_3 \\
\end{array} \]

\[ \text{N\text{-methyl methylcarbamate:} } \]

\[ k_{overall} = k_{prim}F(-OC(O)NR_2) + k_{prim}F(-NRC(O)OR) + k_{-NHC(O)O} \]

where \( k_{prim} \) and \( k_{sec} \) are the group rate constants for H-atom abstraction from \(-\text{CH}_3\) and \(-\text{CH}_2-\) respectively for a standard substituent and where \( k_{overall} \) is the predicted rate coefficient of the organic nitrogen compound.}\(^{34}\)
Chapter 6
The Fate of Nicotine in the Environment

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6 Chapter 6
6.1 Abstract

Smoking cigarettes is widely recognized as having harmful health effects for the smoker and for people breathing second-hand smoke. In an atmospheric chemistry context, little is known about the speciation and fate of organic nitrogen compounds present in cigarette smoke. Indeed, the atmospheric oxidation of nicotine, one of the major nitrogen-containing components of cigarette smoke, has yet to be investigated, and we present the first rate coefficient measurement of nicotine with OH radicals at 298 ± 3 K, \((8.38 \pm 0.28) \times 10^{-11}\) cm³ molec⁻¹ s⁻¹. We use online mass spectrometry techniques to quantify nicotine’s oxidation products, including formamide and isocyanic acid (HNCO). Mechanistic pathways for the oxidation of nicotine by OH radicals were further investigated by ab initio calculations and we find that there are many competitive H-abstraction sites on nicotine. To better assess the implication of nicotine oxidation in the context of cigarette smoke, we used authentic sidestream cigarette smoke inside an environmental smog chamber and exposed the gas and particle phase components to OH radicals. We monitored the evolution of the organic nitrogen compounds in the smoke, namely the disappearance of nicotine and the production of formamide and isocyanic acid (HNCO). In today’s emerging scene of e-cigarettes, known to emit less particles and thus more gas phase nicotine, a comprehensive assessment of nicotine’s fate in the atmosphere is warranted.
6.2 Introduction

Smoking has well-documented serious negative health consequences for populations worldwide, including cancer, pulmonary diseases and cardiovascular diseases. Exposure pathways of concern include mainstream smoke, inhaled by the smoker, sidestream smoke (or second-hand smoke), inhaled in the presence of a smoker, and third-hand smoke, inhaled near surfaces previously exposed to cigarette smoke. Both mainstream and second-hand smoking increase cardiovascular disease risk by promoting atherosclerosis and blood clot formation. There are at least 69 known carcinogens in tobacco smoke, of which 20 are known to cause lung tumors, leading to lung cancer. Children born to women who smoke during pregnancy are at higher risk of hereditary disorders, cancer, respiratory disease, and sudden death.

Sidestream emissions greatly exceed mainstream emissions, thus from an environmental point of view, it is important to accurately characterise the former. Nicotine is the major organic nitrogen compound emitted from burning tobacco cigarettes. It can be present at levels up to 3 mg per cigarette depending on the cigarette brand, in other words, nicotine can account for ~1.5% of a cigarette’s weight. Nicotine is a known health hazard and causes addiction, but is also used as a therapeutic for Parkinson’s and Alzheimer’s disease as well as a probe drug for phenotyping cytochrome P450 2A6 (CYP2A6).

The atmospheric fate of nicotine has been assumed to be governed by its deposition to surfaces. Based on the current literature, gas-phase nicotine is expected to be rapidly removed by sorption to indoor surfaces, and re-emitted during ventilation, leading to concentrations up to ~10% of those observed during the smoking phase indoors. Nicotine adsorption rates to surfaces in an indoor environment range from 1.5 – 6 hours\(^{-1}\) and it is partitioned 95-99% in the sorbed phase at equilibrium. Surprisingly, its rate coefficient with OH radicals has yet to be investigated. Nicotine’s reactivity with OH radicals may be less relevant in indoor environments where lower OH radical concentrations are present, but may still compete with deposition and air exchange rates. In an outdoor context, nicotine emissions may be increasing through the use of electronic cigarettes where fewer particles are generated, allowing for more nicotine to be present in the gas phase. It may also be relevant in the context of exposure in designated smoking areas like in a secluded room or outdoors on a patio.
Sidestream smoke and nicotine exposures are of concern, but the aging of both the smoke and nicotine may also have negative health impacts. Nicotine has been found to contribute significantly (with yields of 4-9%) to the formation of secondary organic aerosol (SOA) through reaction with ozone.\textsuperscript{11} SOA formation has also been observed for sorbed nicotine from cellulose, cotton and paper surfaces reacting with ozone in the presence of NO\textsubscript{x} and varying RH.\textsuperscript{12} In addition, residual nicotine from tobacco smoke sorbed to indoor surfaces may react with ambient nitrous acid (HONO) to form carcinogenic tobacco-specific nitrosamines.\textsuperscript{13} These recent studies raise concerns about exposures to the tobacco smoke residue, known as third-hand smoke.

In an effort to contribute to the growing knowledge of cigarette smoke from an environmental chemistry perspective, we provide the first measurement of nicotine’s rate coefficient with OH radicals at room temperature. We quantify formamide and HNCO as oxidation products of this alkaloid and further support nicotine’s oxidation mechanism with ab initio calculations. Finally, we conducted a lab study involving real cigarette sidestream smoke to better characterize nicotine’s decay and oxidation products in the context of its primary source to the environment.

6.3 Methods

6.3.1 Experimental method

6.3.1.1 Kinetic and product study of nicotine

The kinetics of nicotine was measured using a previously described experimental setup for amines and amides also described in chapters 2 and 3.\textsuperscript{14,15} It consists of a proton-transfer-reaction mass spectrometer (PTR-MS) (Ionicon Analytik GmbH, Innsbruck Austria)\textsuperscript{16} connected to a 1 m\textsuperscript{3} Teflon FEP film (American Durafilm) bag (Ingeniven) and mounted on a Teflon-coated frame. The chamber is also surrounded by a total of twelve UVB lamps (Microlites Scientific) used to photolyse hydrogen peroxide as the OH radical source. The PTR-MS’s inlet is a ~1 m long 1/16” ID silco-coated steel inlet (Ionicon’s standard transfer line) heated to 50 °C with ~ 100 sccm flow and linked to an FEP tubing that sampled from the middle of the chamber. The signals of the compounds of interest were normalized to the H\textsubscript{3}\textsuperscript{18}O\textsuperscript{+} ion, m/z 21.

Nicotine was purchased from Sigma-Aldrich and used as is. For the calibration of the PTR-MS, known volumes of a 0.7 M aqueous solution of nicotine were injected into the chamber through a glass tube connection. A flow of pure air from an AADCO 737-series generator passed through
the glass tube adding nicotine to the chamber in mixing ratios up to ~700 ppbv. Nicotine was monitored at its protonated molecular ion m/z 163, and had a linear calibration with a sensitivity of 2 ncps/ppbv. Formamide was calibrated similarly to nicotine, injecting known amounts of a 0.5 M aqueous solution into the chamber and has a sensitivity of 17 ncps/ppbv. Isocyanic acid (HNCO) by PTR-MS was calibrated using our previously reported method in Chapter 3 and has a sensitivity of 23 ncps/ppbv. Briefly, it involves the thermolysis of cyanuric acid as the source of HNCO which is then captured in an aqueous solution in a bubbler and quantified using ion chromatography analysis. Other VOCs, such as methanol, acetaldehyde, acetonitrile and acetone were quantified inside the chamber using a range of flows from an EPA TO-15 method certified VOC canister with standard concentrations of ~40 µg m⁻³ quantified by GC-MS. The yields reported are the quotient of moles of product produced divided by the moles of nicotine that decayed away at the end of the reaction, i.e. when the lights surrounding the chamber were turned off. Furthermore, the m/z 44 and m/z 46 PTR-MS signals assigned to HNCO and formamide respectively are background corrected using ¹³C natural abundance at m/z 43 and m/z 45 as previously described in Chapter 3.

A typical oxidation experiment is also described elsewhere. We use 1,3,5-trimethylbenzene (TMB) as the reference compound for the relative rate kinetics, which is detected by the PTR-MS at m/z 121. An aqueous solution of 30 % hydrogen peroxide introduced into the chamber acts as the OH radical precursor and the latter is generated upon UVB light exposure inside the chamber. At the end of the experiments, the chamber is purged with clean air and further cleaned weekly with the addition of hydrogen peroxide with the lights turned on.

### 6.3.1.2 Cigarette smoke study

A laboratory study of aged sidestream cigarette smoke was also conducted to assess the fate of tobacco-derived nicotine. We used a house-built smoking machine which had a pump pulling periodically on a lit cigarette, from a leading Canadian brand, at a flow of 1.05 L min⁻¹, according to the ISO/FTC protocol (35 mL puff volume, 2 s puff duration, and one puff every 60 s) (Figure 6-1). A flow of pure air from an AADCO 737-series generator of 1 L min⁻¹ was constantly flowing over the cigarette and introducing the smoke into the chamber via a 1.5 m long FEP ¼ inch tubing. Only 2-4 puffs were introduced into our 1 m³ chamber, since they produced enough particles and VOCs to be easily detected. Connected to the chamber with ¼ inch FEP tubing was
a quadrupole PTR-MS operated in MID mode (500 ms dwell time), a house-built chemical ionization mass spectrometer (CIMS)\textsuperscript{20} operated also in MID mode (250 dwell time) and using acetate as its reagent ion (fully described in Chapter 4) as well as Thermo Scientific gas monitors for O\textsubscript{3}, NO\textsubscript{x} (= NO + NO\textsubscript{2}), SO\textsubscript{2}, CO and CO\textsubscript{2} (Figure 6-1). Furthermore, we conducted elemental analysis on the cigarette and tobacco using a 2400 Series II CHNS Analyzer.

Once the sidestream smoke was introduced into the chamber and the VOC and particle signals had stabilized, a flow of $\sim$ 1 L min$^{-1}$ of pure air was bubbled through a 30\% aqueous hydrogen peroxide solution into the chamber. After approximately 1 hour, the UVB lights surrounding the chamber were turned on to generate OH radicals and age the cigarette smoke. The experiments were typically left to run between 1-3 hours.

Three types of experiments were conducted: filtered smoke (no particles), denuded particle smoke (no gas phase) and whole smoke (particles and gas phase species). In the filtered smoke experiments, a Teflon filter was placed downstream of the cigarette just before the chamber entrance. By PTR-MS we detected no nicotine, likely since organic nitrogen compounds and especially amines are known to stick on surfaces, e.g. the particle-loaded filter. Upon oxidation of the filtered smoke however, formamide was produced above background levels, indicating the presence of some organic nitrogen precursors in the chamber that had passed through the filter. In the denuded particle smoke experiments, a sidestream smoke puff was passed through a Carulite\textsuperscript{®} denuder to remove the NO and NO\textsubscript{2} that are also generated in the combustion and a Charcoal denuder to remove gaseous volatile organic compounds (VOCs). In these experiments, nicotine was also not detected, suggesting that our PTR-MS is not detecting particle phase nicotine. The experiments where we detected nicotine and quantified oxidation product yields were conducted with whole smoke.
Figure 6-1: Experimental set up for the measurement of aging sidestream cigarette smoke inside an environmental chamber.

6.3.2 Theoretical method

To investigate the mechanism of gas-phase nicotine with OH radicals, computational ab initio methods were employed using the Gaussian 09 code.\textsuperscript{21} Structures of the reactants and transition states were optimized using the M06-2X density functional method with the 6-31G(2df,p) basis set.\textsuperscript{22} The energies reported are 0 K enthalpies and are calculated from the sum of the electronic energy and the zero point energy.

Transition state energy in this chapter (as in Chapter 5) represents the energy difference between the transition state and the sum of the reactants’ energies. The assumption is that the energy of the pre-complex formation of nicotine with OH radicals does not affect the rate of the reaction, i.e. we report transition state energy relative to the energy of the reactants as an indication of whether the mechanism is likely to occur readily.

6.4 Results and Discussion

6.4.1 Kinetics results

The rate coefficient for nicotine’s gas phase reaction with OH radicals was measured using the relative rate kinetics method.\textsuperscript{23} Nicotine was detected in the chamber, but required the use of hundreds of ppbv of the analyte for detectable decays. Compared to our previous experience with monoethanolamine (MEA) (see Chapter 2), the chamber did not require prior conditioning for a
reproducible nicotine signal to be observed. On the other hand, the nicotine PTR-MS signal did typically require ~ 5 mins to stabilise, making this amine slightly less well-behaved than amides inside our chamber (see Chapter 3). Plotting the natural logarithm of the decay of nicotine as a function of the natural logarithm of the decay of the reference compound, TMB, yields a linear regression in which the slope represents the ratio of the nicotine’s rate coefficient to TMB’s rate coefficient (Graph 6-1). Hence, based on TMB’s previously reported room temperature rate coefficient of \((5.73 \pm 0.53) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\),\(^{24}\) we obtain a value of \((8.38 \pm 0.28) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) for nicotine + OH radicals at \(298 \pm 3 \text{ K}\) where the standard deviation represents the variability between experiments. If we assume an indoor environment with an OH radical concentration of \(5 \times 10^5 \text{ molec cm}^{-3}\),\(^{25}\) nicotine would have a lifetime of 6.6 hours, and a shorter lifetime outdoors where higher OH concentrations are expected. The room temperature rate coefficient measured for nicotine is similar to other amines’ reactivity towards OH radicals. Indeed, the majority of alkylamines have rate coefficients between \(6-9 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\).\(^{26}\)

Graph 6-1: Plot of the natural logarithm of the decay of nicotine against the natural logarithm of the decay of the reference compound TMB. Each point was taken at ~ 5 s intervals by the PTR-MS and the linear regression is represented as the black line and is forced through the origin.

6.4.2 Product study

Since nicotine reacts quickly in the presence of OH radicals, it becomes important to understand the formation of its oxidation products to better assess its impact specifically in the context of
indoor air. Graph 6-2 depicts the evolution of nicotine and its products as a function of time as measured by the quadrupole PTR-MS. The major product detected is acetaldehyde and its yield is approximated to be 15%. Acetaldehyde is also the most abundant VOC reported to be found in second-hand smoke.\textsuperscript{27} The major oxidation products containing nitrogen that could be unambiguously identified were formamide and HNCO. If we assume that all the nicotine injected was oxidized, we can report lower limit yields of 5 ± 2% for both formamide (not corrected for its own sink with OH radicals) and HNCO after 2 h of photo-oxidation. The yield of formamide is similar here to previously calculated yields from other amines like monoethanolamine (MEA).\textsuperscript{14} m/z 42 was assigned to acetonitrile and detected with a yield of ~ 1%. Acetonitrile is typically known as a biomass tracer in ambient air and is expected to be formed from the oxidation of organic nitrogen.\textsuperscript{28} Other oxidation products detected include m/z 31, m/z 59 and m/z 58 which we assigned to methanol, acetone + propanal and methyl isocyanate (CH$_3$NCO), respectively.

The organic nitrogen oxidation products like formamide and HNCO are only small fragments of the larger nicotine molecule. Indeed, plotting the mixing ratios of formamide and HNCO over time as a function of the decaying nicotine mixing ratio as in Graph 6-3, it is clear that these products are not first order generation. In fact, the exponential curve in Graph 6-3 suggests they are at least second or third generation products, implying a complex mechanism of formation. Our method does not unfortunately allow us to unambiguously identify potential first generation products which could include two nitrogen atoms, as they would appear at an odd m/z in our quadrupole PTR-MS. The natural relative abundances of $^{15}$N is not useful for product identification by PTR-MS as it would give a signal 0.004% of the molecular ion signal, too low to detect. We do however see a small signal at m/z 74 which could correspond to $\text{N}_2\text{N}$-dimethylformamide, but again the resolution of our PTR-MS does not allow for unambiguous assignment.
Graph 6-2: The evolution of nicotine and its oxidation products upon exposure to OH radicals at time 0.0 s. The m/z with their assignments are m/z 163 (nicotine), m/z 44 (isocyanic acid), m/z 46 (formamide), m/z 45 (acetaldehyde), m/z 42 (acetonitrile), m/z 33 (methanol), m/z 59 (acetone/propanal) and m/z 58 (methylisocyanate).

Graph 6-3: The mixing ratio of formamide (m/z 46) and HNCO (m/z 44) as a function of the mixing ratio of nicotine. This graph shows the non-linearity of this relationship.
6.4.3 Mechanism of oxidation

To explore the mechanism of oxidation of nicotine, as well as to better characterize the production of formamide and HNCO, we employ computational chemistry to calculate the transition state energies of nicotine + OH radicals relative to the energies of the reactants. The most likely reactive position on nicotine towards OH is its benzylic position as pictured in Figure 6-2. Nicotine’s benzylic position is a tertiary C−H bond and is therefore the most electron rich C−H bond of the molecule, and its abstraction has been observed as the primary pathway in nicotine’s aqueous phase oxidation.\(^{29}\) We calculate a nicotine-OH radical pre-complex at 4.8 kcal mol\(^{-1}\) below the entrance energies of the reactants with a transition state only 0.4 kcal mol\(^{-1}\) above the energy of the pre-complex (Figure 6-2). These energies translate to a facile C−H abstraction and are consistent with the fast rate coefficient we measured.

Nonetheless, there exist fourteen different C−H bonds in nicotine which could react with OH radicals, plus OH-addition mechanisms on the pyridine ring. To identify which C−H abstraction governs nicotine’s reactivity, we iteratively calculated each C−H bond’s transition state energy. Figure 6-3 depicts these transition state energies which are colour coded in blue if the transition state is below the reactants’ entrance level energies or in red if the transition state is above the reactants’ entrance level energies.

Furthermore, we highlight a unique reactive site on nicotine’s pyridine ring. On aromatic rings, and in particular on pyridine rings, OH addition mechanisms typically dominate reactivity,\(^{30,31}\) however, we calculate a transition state energy of -3.6 kcal mol\(^{-1}\) below the reactants’ energy for the pyridine C−H\(_1\) bond abstraction in nicotine. This energy is significantly lower than the OH addition transition state energy of +0.8 kcal mol\(^{-1}\). To understand this difference, we flipped the pyridine ring by 180° and calculated that the C−H\(_{\text{para}}\) bond also had a low transition state energy (-3.0 kcal mol\(^{-1}\) and in green) compared to when it was further from the alkyl N−CH\(_3\) group (left side of Figure 6-3). We find that the OH radical sits nicely underneath the N−CH\(_3\) group, H-bonding to the nitrogen atom thereby significantly decreasing the barrier height for activation.

Figure 6-3 also suggests that many C−H abstraction mechanisms are competitive for reaction with OH radicals. Thus, the oxidation mechanisms of nicotine appear to be complex and occur at several competitive C−H abstraction sites (based on ten calculated transition state energies below the entrance level energy of the reactants denote in blue in Figure 6-3). It becomes difficult to assign
a single mechanistic pathway for the production of formamide and even HNCO. We estimate that at least two non-radical intermediates are likely prior to formamide production based on calculations of subsequent reactions of the benzylic radical product in Figure 6-2 (See Figure 6-4 in Appendix E). We also cannot differentiate if the nitrogen in formamide originates from the N–CH₃ group or the pyridine ring N. Further studies with isotopically labelled nitrogen might help in elucidating and differentiating different mechanisms leading to formamide and HNCO.

Figure 6-2: Theoretical energy diagram for nicotine + OH. Energies are 0 K enthalpies in kcal mol⁻¹, at the M06-2X level of theory and 6-31G(2df,p) basis set.
Figure 6-3: The transition state (TS) energies associated with each reactive site towards OH radicals for nicotine. Negative values are in blue and represent TS energy below the energy of the reactants. Positive values are in red and represent TS energy above the energy of the reactants. Green value for the para-C–H bond represent the TS energy of the pyridine flipped 180° around the aryl C–C bond. Energies are 0 K enthalpies in kcal mol⁻¹, at the M06-2X level of theory and 6-31G(2df,p) basis set.

6.4.4 Cigarette smoke experiment

Taking what we learned from the oxidation of pure nicotine, we apply this knowledge to a more relevant context and the primary source of nicotine to the environment: cigarette smoke. We conducted experiments where sidestream smoke was introduced into our 1 m³ chamber and subsequently exposed to OH radicals for 1-2 hours. Our goal was to understand the behaviour of tobacco-derived nicotine as well as to identify cigarette smoke’s primary emissions and its oxidation products, with a particular interest in quantifying HNCO yields.

Upon introduction of the sidestream smoke into the chamber (grey shaded area in Graph 6-4), acetonitrile and a wide range of VOCs could be detected in mixing ratios of hundreds of ppbv. Nicotine’s signal on the PTR-MS took longer to appear than other VOC signals like acetonitrile and acetaldehyde likely due to some tubing partitioning but was then stable in the chamber until oxidation. Next, hydrogen peroxide was added during the time corresponding to the blue shaded area in Graph 6-4 and at time 0.0, the UVB lights were turned on, exposing the smoke to OH radicals (yellow shaded area in Graph 6-4). A normalized signal difference plot of before and after photo-oxidation was obtained while operating the PTR-MS in scan mode (Graph 6-5A & B). This
The oxidation of sidestream smoke initiated by OH radicals degraded nicotine at a rate that can be modelled reasonably well by pseudo-first order kinetics with our measured rate coefficient. The modelled decay is depicted as the dotted black line in Graph 6-4 and was obtained by estimating an OH radical concentration of $10^7$ molec cm$^{-3}$ from previous characterization of our chamber.$^{14,15}$ This OH radical concentration is an upper limit, as there are many more VOCs present acting as sinks for OH radicals in these sidestream cigarette smoke than in our previous chamber characterization experiments. We note that the signal of nicotine doesn’t decay back to its background signal, suggesting that partitioning either from the particle phase or the chamber walls is occurring to same extent. In addition, we believe the results for nicotine obtained with the Canadian low tar brand are representative of other cigarette brands, since it was reported in an early study that tar and nicotine levels in sidestream smoke are comparable regardless of whether they come from medium-, low-, or ultra-low tar cigarettes.$^{32}$

By PTR-MS, we observed a small signal following the introduction of the sidestream smoke at m/z 46 which we attribute to formamide. However, upon oxidation, a much larger signal was observed which indicates that formamide is mostly a secondary pollutant of cigarette smoke. Formamide from pure nicotine oxidation was generated in 5 % yield, however, in the cigarette smoke experiments, the production of formamide exceeds 300 % if taken uniquely from the decay of nicotine. Three plausible scenarios are hypothesized. First, there could be many more organic nitrogen compounds present in the cigarette smoke which we have not quantified/identified that are being oxidized to produce formamide. Second, our technique is sensitive only to nicotine in the gas phase, and so more nicotine could be present on the smoke particles and oxidize heterogeneously, thereby forming formamide which then partitioned to the gas phase. Third, sorbed nicotine could be released to the gas phase from particles/walls as the gas-phase nicotine is oxidized away, leading to a small nicotine signal, but a large formamide production. We note that the time trace for formamide plateaus in this experiment (see Graph 6-4), but in the nicotine-only experiment (see Graph 6-2) it continues to increase even once the nicotine is gone. We speculate that formamide could be formed as an earlier generation product from other precursors in tobacco smoke, which would be consistent with formamide stemming from other nitrogen-containing compounds (first hypothesis).
HNCO, on the other hand, exhibited continuous production behaviour, representing a later gas-phase oxidation product and potentially also arising from surface chemistry (Graph 6-4). Our preliminary attempts to quantify the HNCO measurements made by the acetate CIMS suggests that ~ 6 ppbv was formed during the oxidation of nicotine in Graph 6-4. The production of HNCO is significant as it is a toxic molecule and has been measured in ambient air in mixing ratios up to 1 ppbv, enough to raise concern for human health (also see Chapter 4 for a discussion on HNCO’s health impact). Our experiment shows that HNCO is not a primary emission from cigarette smoke, as previously believed, but rather a secondary pollutant, being formed upon oxidation of organic nitrogen precursors. HNCO is a weak acid however, and could have been lost to the surface or the tubing on its way to the chamber. To address this hypothesis, we conducted a control experiment where a cigarette was smoked into the lab air with the PTR-MS’s inlet next to the sidestream smoke. We were unable to detect any HNCO, suggesting that oxidation is required for its production.

The oxidation also produces nitrous acid (HONO) very quickly as seen by the acetate CIMS (Graph 6-4) but whether its formation is due to gas phase or heterogeneous chemistry requires further investigation through control experiments. Nonetheless, a control experiment without hydrogen peroxide but with UVB light irradiation showed no abrupt increase in nitrous acid, suggesting its formation is by photo-oxidation. The production of nitrous acid in an indoor environment is of significance as a source of OH radicals and further studies on nitrous acid production from nicotine and cigarettes smoke are warranted.

Other m/z ratios qualitatively detected during the photo-oxidation of the sidestream smoke are shown in Graph 6-5. We attribute m/z 97 to dimethylfuran, a known cigarette smoke tracer and m/z 83 to methylfuran. m/z 47 and m/z 61 are likely formic acid and acetic acid production. Loss of m/z 57 may be due to the reaction of acrolein, another common emission specie from cigarette smoke.

Elemental analysis of the cigarette (paper + tobacco) yielded 37.14% C, 5.53 % H and 1.13 % N. The individual elemental analysis of the paper and tobacco revealed that the nitrogen-containing compounds predominantly come from the tobacco rather than the cigarette’s paper. Knowing the percentage of nitrogen present in the cigarette, we can estimate the amount of nitrogen emitted from 0.27 g of a smoked cigarette. If this mass was converted into sidestream smoke (a large
overestimation as some mass was lost to ashes, mainstream smoke and tubing), it would lead to 3050 μg/m³ of N into the chamber. 3050 μg/m³ of N is equivalent to 4.6 ppmv of N in the chamber. Nicotine, which contains two nitrogen atoms, was measured at levels up to 150 ppbv during experiments. This back-of-the-envelope calculation helps us estimate that a significant amount of the mass balance of N is either as other nitrogen-containing products, or in the particle phase or lost to the walls.

Graph 6-4: Time traces of sidestream cigarette smoke oxidation by OH radicals (starting at time 0.0 h). The top panel shows traces measured in MID mode by the CIMS running with acetate reagent ion and the bottom panel shows traces measured in MID mode of the PTR-MS. The dotted black line represents the modelled decay of nicotine based on its measured rate coefficient. All these signals follow first order decay rate following purging of the chamber. The grey, blue and yellow shaded areas correspond to time periods of cigarette smoke addition, of H₂O₂ addition and of UVB light irradiation, respectively.
Graph 6-5: (A) The mass spectrum obtained before (in blue) and after 2 h (in orange) of photo-oxidation of sidestream smoke. (B) The normalized signal difference plot of m/z 25-165 based on the shown two mass spectra. The green bars represent m/z ratios produced and the red bars represent m/z ratios decayed.
6.5 Conclusion

In summary, we provide the first measurement of the room temperature rate coefficient of nicotine with OH radicals, a value of \((8.38 \pm 0.28) \times 10^{-11}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\) at 298 \(\pm\) 3 K corresponding to a lifetime of 6.6 h in the presence of an OH radical concentration of \(5 \times 10^5\) molec cm\(^{-3}\). Using online PTR-MS and acetate-CIMS, formamide and HNCO were quantified from nicotine’s oxidation with yields of \(5 \pm 2\%\) each. These products appear to be at least second or third generation products of nicotine. We also employed computational chemistry to calculate the transition state energies of every reactive site of nicotine towards OH radicals, including C–H abstractions and OH additions. We show that most barrier heights are below the entrance level energy of the reactants and therefore are competitive with one another, complicating the mechanism analysis, but consistent with a rapid rate coefficient. Sidestream cigarette smoke aging experiments were also conducted to better understand the fate of nicotine and other organic nitrogen compounds as primary versus secondary tobacco-related pollutants. We find that formamide and HNCO are produced upon photo-oxidation of the sidestream cigarette smoke, suggesting that second-hand smoke is a concern for exposure to these toxic compounds.

6.6 References


6.7 Appendix E

[Diagram of chemical reactions and structures, including benzyl H abstraction and barrierless processes]
Figure 6-4: Additional theoretical diagrams calculated for the benzylic C–H abstraction mechanism of nicotine + OH radicals. Energies are 0 K enthalpies in kcal mol$^{-1}$, at the M06-2X level of theory and 6-31G(2df,p) basis set.
Chapter 7
Conclusions and Outlook on Organic Nitrogen

7 Chapter 7

Throughout the PhD research presented in this thesis, I sought to address key uncertainties in the fate of organic nitrogen compounds in the environment. I measured the kinetics of amines and amides with important atmospheric oxidants like OH radicals and ozone. I identified oxidation products and quantified their product yields. I show experimentally and theoretically that amines are oxidized to amides which are themselves oxidized to isocyanates. I also studied the fate of isocyanic acid in the aqueous phase which ultimately hydrolyses to ammonia. Therefore, I argue that the fate of gas phase amines leads in part to ammonia via the intermediacy of amides and isocyanates and I support this claim using ab initio calculations. I have also investigated how to incorporate this knowledge into structure-activity relationship (SAR) models and show preliminary analyses for new SAR factors governing the fate of organic nitrogen in the atmosphere.

Our research efforts presented in Chapters 2 through 6 are contributing to the advancement of knowledge on nitrogenated compounds, but gaps in knowledge remain. Our work also raises new questions about our mechanistic understanding of organic nitrogen reactivity. In this chapter, I place into context our contributions to the field of organic nitrogen and highlight directions the field may be pursuing based on new and unanswered questions.

7.1 Chemistry of amines, amides and isocyanates

Presented in Table 7-1 are the rate coefficients for amines and amides reacting with OH radicals (and ozone) that I measured throughout this thesis and that other authors have measured before and after my contributions. Table 7-2 (also presented in Chapter 4) shows the physical parameters I measured compared to other published values.

<table>
<thead>
<tr>
<th>Organic nitrogen</th>
<th>Rate coefficient (k \times 10^{12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})</th>
<th>authors</th>
<th>year</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA + OH</td>
<td>92 \pm 11</td>
<td>Karl et al.</td>
<td>2011</td>
</tr>
<tr>
<td></td>
<td>76.1 \pm 7.6</td>
<td>Onel et al.</td>
<td>2012</td>
</tr>
</tbody>
</table>
Table 7-2: HNCO’s Henry’s Law coefficient, acid dissociation constant and hydrolysis constants

<table>
<thead>
<tr>
<th>Physical parameter</th>
<th>Value at 298 K</th>
<th>Energy</th>
<th>Authors</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry’s Law coefficient, $K_H$</td>
<td>26 ± 2 M atm$^{-1}$</td>
<td>$\Delta H_{\text{diss}} = -34 \pm 2$ kJ mol$^{-1}$</td>
<td>Borduas et al.</td>
<td>2015$^\Delta$</td>
</tr>
<tr>
<td></td>
<td>21 M atm$^{-1}$</td>
<td>–</td>
<td>Roberts et al.</td>
<td>2011</td>
</tr>
<tr>
<td>Acid dissociation constant, $K_a$</td>
<td>$2.1 \times 10^{-4}$ M</td>
<td>–</td>
<td>Borduas et al.</td>
<td>2015$^\Delta$</td>
</tr>
<tr>
<td></td>
<td>$2.0 \times 10^{-4}$ M</td>
<td>$\Delta H_{\text{diss}} = -5.4$ kJ mol$^{-1}$</td>
<td>Amell</td>
<td>1956</td>
</tr>
<tr>
<td>Hydrolysis rate coefficient, $k_1$</td>
<td>$7.6 \times 10^{-2}$ s$^{-1}$</td>
<td>$E_{a1} = +50 \pm 2$ kJ mol$^{-1}$</td>
<td>Borduas et al.</td>
<td>2015$^\Delta$</td>
</tr>
<tr>
<td></td>
<td>$1.1 \times 10^{-1}$ s$^{-1}$</td>
<td>$E_{a1} = +63$ kJ mol$^{-1}$</td>
<td>Jensen</td>
<td>1958</td>
</tr>
<tr>
<td>Hydrolysis rate coefficient, $k_2$</td>
<td>$1.4 \times 10^{-3}$ s$^{-1}$</td>
<td>$E_{a2} = +56 \pm 4$ kJ mol$^{-1}$</td>
<td>Borduas et al.</td>
<td>2015$^\Delta$</td>
</tr>
<tr>
<td></td>
<td>$1.8 \times 10^{-3}$ s$^{-1}$</td>
<td>$E_{a2} = +83$ kJ mol$^{-1}$</td>
<td>Jensen</td>
<td>1958</td>
</tr>
<tr>
<td>Hydrolysis rate coefficient, $k_3$</td>
<td>$8.1 \times 10^{-8}$ s$^{-1}$</td>
<td>$E_{a3} = +91 \pm 12$ kJ mol$^{-1}$</td>
<td>Borduas et al.</td>
<td>2015$^\Delta$</td>
</tr>
<tr>
<td></td>
<td>$1.2 \times 10^{-8}$ s$^{-1}$</td>
<td>$E_{a3} = +100$ kJ mol$^{-1}$</td>
<td>Jensen</td>
<td>1958</td>
</tr>
</tbody>
</table>

$^\Delta$ This paper is submitted.

We provided the first rate coefficient of MEA with ozone in Chapter 2. Although other amines have been observed to react with ozone at similar rates, the mechanism remains very speculative. Nielsen et al. propose the addition of ozone to the nitrogen atom to form an $N$-oxide compound. These mechanisms have yet to be investigated using computational chemistry, which would be a valuable tool for studying these types of mechanisms. Reactivity of amines with ozone is not expected to dominate their atmospheric fates but may be important at higher latitudes in the winter time. Studying this mechanism would also give insight on a fundamental chemical level for the
difference between oxidation by OH radicals and by ozone, paving the way to new reactivities and new reactions.

In Chapter 3, I observed the formation of formamide as a common photo-oxidation product from all four different alkylated amides studied. To make formamide from N-methylacetamide for instance, the acetyl C–C bond as well as the C–N bond must break. This retrosynthetic analysis remains puzzling and further studies on the mechanism of formamide formation is warranted including studies on whether this process is occurring in the gas phase or heterogeneously. Indeed, a challenge arising with smog chamber experiments is the degree to which heterogeneous reactions are competing with gas phase processes.

The chemistry of imines as a class of organic nitrogen compounds remains unknown. We (in Chapter 2) and others have proposed the formation of imines as intermediates of amine oxidation by OH radicals. However, imines have yet to be identified in ambient air. Our attempts to identify imines by PTR-MS and CIMS were unsuccessful. Furthermore, no rate coefficients have been measured in kinetic studies to determine how reactive they are against the atmosphere’s oxidants. There exists the inherent problem that imines are not stable molecules and thus cannot be purchased. If their experimental fate in the atmosphere was to be investigated, the in situ synthesis of these compounds would need to be accomplished. One way to achieve this synthesis would add a photolabile group on an amine type of functionality which upon photolysis, would generate an imine. One recent study used computational methods to study the formation of imines via the oxidation of amines by O$_2$ and NO$_2$. Nonetheless, this elusive group of organic nitrogen compounds will be important to tackle in future investigations of amine oxidation pathways. It will also be interesting to determine how imines may be reacting in our atmosphere.

Isocyanic acid (HNCO) is currently a molecule of great interest to atmospheric chemists as it is toxic at levels previously measured in ambient air.$^{3-5}$ We measured isocyanic acid’s pH-dependant hydrolysis rates as it forms ammonia. We now know that amines oxidize to form amides, which in turn oxidize to from isocyanates and that isocyanic acid hydrolyzes to form ammonium. This cycle leads me to link the ultimate fate of some amines to the production of ammonia in the atmosphere. An interesting question is then raised; does organic nitrogen processing have an impact on the ammonia budget? Also, our experimental study presented in Chapter 4 suggests that isocyanic acid may partition very little to aqueous atmospheric particles (pH 2-6) but will partition
readily to oceans. However, once in the aqueous phase at pH higher than ~ 3, isocyanic acid will hydrolyse slowly. It is therefore likely that competing reactions could be important sinks for aqueous phase isocyanic acid. For instance, ammonia is known to react with isocyanic acid to form urea, but the kinetics have yet to be quantified. In the context of ocean water, there is a multitude of organic molecules present in the sea surface microlayer that could react with isocyanic acid. Hence, the aqueous phase chemistry of isocyanic acid warrants further investigation. In addition, throughout our chamber studies, I observed production of isocyanic acid from photo-oxidation of the chamber walls during control experiments. There is evidently important heterogeneous chemistry to be considered in understanding the sources of isocyanic acid. I conducted preliminary studies (not discussed in this thesis) on the exposure of amino-polymers to high ozone concentrations in a flow tube experimental set up and observed the production of formamide and isocyanic acid. Further studies investigating the mechanism of production as well as quantifying the formation of isocyanic acid will be useful. Also, is there formation of isocyanic acid in or on atmospheric particles? If so, how important is this source of isocyanic acid versus its gas phase formation?

Aerosol processing of organic nitrogen compounds have been shown to contribute to brown carbon, an important climate forcer due to its light absorbing features. It is important to identify and quantify the organic nitrogen molecules involved in brown carbon and some research has already done so. Do hydrolysis reactions within brown carbon particles also lead to the formation of ammonia and does this nitrogenated compound partition out to the gas phase?

Finally, our kinetic work has already made an impact in modelling. In Chapter 2, I measured the room temperature rate coefficients of monoethanolamine (MEA) against OH radicals and ozone. The importance of measuring these rates with appropriate uncertainties is to enable their incorporation into chemical transport models (CTM). Karl et al. recently used our measured rates in the Weather Research and Forecasting model coupled to chemistry (WRF-Chem) to predict the impact of MEA fugitive emissions on surrounding environments and human exposures. Their model inputs also included the rate coefficient for oxidation of formamide to isocyanic acid as well as its production yield. Karl et al. find that the release of MEA into the atmosphere from a model CCS plant would indeed impact the background level concentrations of HNCO, but may not lead to exceedances of the 1 ppbv threshold for human health exposure concerns. Future work in this
area will likely include other amines relevant to carbon capture and then comparing the impact against other carbon capture technologies.

7.2 SAR of organic nitrogen

In the analysis of structure-activity relationship (SAR) models for organic nitrogen compounds, I identified existing discrepancies in the values presented in Table 1-1.\textsuperscript{14,15} From our mechanistic interpretation of the theoretical results presented in Chapter 5, we now know that the contribution of the N-H abstraction mechanism is negligible for the majority of organic nitrogen, excepting amines. I also highlighted unaccounted for reactivity in amides via the formyl C–H abstraction, and showed that N-addition mechanisms must be completely neglected in SAR models. With this understanding, I plan to review available rate coefficients for organic nitrogen and develop new SAR group rate constants and new SAR substituent factors. These factors will hopefully be incorporated into SAR models like EPI Suite to more accurately predict the lifetime of this class of molecules. In addition, some SAR factors for organic nitrogen were developed based on the assumption that the analogous organic sulfur compound reacted the same way. It would be important to show computationally that OH additions do occur on sulfur atoms but not on nitrogen atoms and elucidate this difference in reactivity. There is further interest in studying the photo-oxidation of sulfides and thiols as they are relevant to particle nucleation over the oceans and have significant impact on climate through acting as cloud condensation nuclei as well as affecting our planet’s radiative balance.

7.3 Chemistry of cigarette smoke

In Chapter 6, I provide preliminary results in determining the fate of tobacco-derived nicotine and find that cigarette smoke analysis is complicated by the presence of gas phase, particle phase and wall chemistry. It would be valuable to set up experiments to simplify the analysis so that each phase would be investigated separately. Larger environmental chambers may be useful in examining the gas phase chemistry by increasing the volume to surface ratio. Moving to electronic cigarettes may also help in studying gas phase chemistry of nicotine, since fewer particles are being generated. Filter-based analyses could be valuable in studying the particle phase chemistry of cigarette smoke. In addition, a flow tube experimental set up would allow for the characterization of surface chemistry, simulating the wall chemistry observed in our environmental chamber.
To further characterize the products of cigarette smoke, commercially available $^{15}\text{N}$ isotopically labelled nicotine might help elucidate and differentiate mechanisms leading to formamide and isocyanic acid. The large production of formamide remains unexplained, and studies into its precursors are warranted, where the use of high mass resolution mass spectrometry would be helpful. It would also be of interest to quantify nicotine in the gas versus the particle phases. Furthermore, the rate coefficient for the reaction of nicotine with ozone has yet to be measured. Studying the formation of nitrous acid (HONO) from cigarette smoke will be significant as nitrous acid is currently an important precursor for indoor OH radicals. From our preliminary experiments in Chapter 6, nitrous acid is being produced by photo-oxidation, but whether it is from the particle phase, from sorbed nitrogenated species on the walls of the chamber or from nitrogen oxide chemistry is unclear. Reverting back to nicotine-only experiments might help elucidate the source of nitrous acid as would conducting experiments in a flow tube set up specifically designed to look at surface chemistry.

7.4 Outlook

The importance of organic nitrogen compounds in air quality and climate is being acknowledged and their chemistry is beginning to be incorporated into models. Evidently, there remain gaps in our understanding of the fate of nitrogenated compounds and it is encouraging that research groups worldwide are beginning to think about the chemistry and physics of this class of compounds. Further, instrument development for the detection of gas phase and particle phase organic nitrogen molecules such as amines and amides will undoubtedly continue to be important. These molecules tend to be present in small ambient concentrations and suffer from sampling problems due to their surface-active nature. Laboratory investigations will also be an important pillar in trying to understand the field measurements in a more controlled manner. Finally, much work is still required in incorporating not only organic nitrogen, but also ammonia and nitrogen oxides into chemical transport models to predict ambient measurements from known underlying chemical processes occurring in our atmosphere. The three pillars of atmospheric chemistry will continue to stand tall.

7.5 References

2. Tang, Y.; Nielsen, C. J. A systematic theoretical study of imines formation from the atmospheric reactions of $R_n\text{NH}_2\text{N}$ with $O_2$ and $NO_2$ ($R = \text{CH}_3$ and $\text{CH}_3\text{CH}_2$; $n = 1$ and 2). *Atmos. Environ.* **2012**, 55, 185-189.


