Field and Smog Chamber Studies of Agricultural Emissions and Reaction Products

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FIELD AND SMOG CHAMBER STUDIES OF AGRICULTURAL
EMISSIONS AND REACTION PRODUCTS

by

Derek J. Price

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Chemistry

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2010
ABSTRACT

Field and Smog Chamber Studies of Agricultural Emissions and Reaction Products

by

Derek J. Price, Master of Science

Utah State University, 2010

Major Professor: Dr. Robert S. Brown
Department: Chemistry and Biochemistry

Agricultural emissions are an important contributor to atmospheric aerosol. These emissions include nitrogen containing organic compounds, primarily as amines, which have not been well investigated to date. Although there have been several studies that have looked at the emission of gas phase amines, there are only a few studies that have focused on ambient amine-based aerosol. There have also only been a handful of smog chamber studies that have investigated amine aerosol chemistry. Kinetic studies have looked at the reactions of amines with OH and ozone. However, amine reactions with nitrate radical (NO₃) are not well understood. Several years of measuring atmospheric particulate matter in Cache Valley, Utah, using an aerosol mass spectrometer (AMS), has shown the presence of amine aerosol in significant concentrations (0.5-6 μg/m³). Furthermore, the concentration of amine aerosol peaks at night when NO₃ is the dominant oxidant. This thesis details experiments aimed at obtaining a better understanding of the underlying reactions that lead to aerosol formation in Cache Valley
and is focused on amine reactivity studies, employing both field and laboratory experiments.

There were two field studies performed near agricultural facilities in California. These studies provide a good comparison to the ambient chemistry observed in Utah. The detection of a small amount of amine aerosol was important in showing that amine aerosol is not unique to Utah. The results of these studies add to the previous knowledge base of ambient chemistry in California. This should help future researchers performing similar field studies in California and other locations.

Smog chamber-based laboratory experiments included amine reactions with common oxidants, such as ozone and NO₃. While small amounts of aerosol formation occurred with ozone (~10 µg/m³), reaction with NO₃ produced the most aerosol (up to 135 µg/m³). The smog chamber studies show the importance of amine/NO₃ chemistry in the formation of ambient aerosol. Researchers can use this work to aid in further understanding the ambient atmospheric chemistry occurring at various locations. The smog chamber studies also provide a knowledge base that should help guide future work into this area of research.

(100 pages)
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I appreciate and give thanks to the people at the University of California, Riverside for allowing me to make use of their smog chamber facilities (especially since the compounds of interest were typically quite pungent). Thanks go out to Dr. David Cocker, Quentin Malloy, Li Qi, and Bethany Warren, who not only made me feel welcome, but also provided me with an understanding of the instrumentation and methods of smog chamber experiments. Thanks should also be given to the National Science Foundation for providing the funds for this research.

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ABBREVIATIONS

40 CFR 50: Code of federal regulations, title 40, part 50

AMS: Aerosol Mass Spectrometer

CPC: Condensation Particle Counter

DBA: Dibutylamine

DBA*: Dibenzylamine

DEA: Diethylamine

DMA: Dimethylamine

DMA*: Differential Mobility Analyzer

DPA: Dipropylamine

DPA*: Diphenylamine

EPA: Environmental Protection Agency

eV: Electron volts

FEP: Fluorinated ethylene propylene

FPS: Filter-based Particle Samplers

H₂SO₄: Sulfuric acid

HNO₃: Nitric acid

HOA: Hydrocarbon-like Organic Aerosol


MCF: Mass conversion factor

m/z: Mass-to-charge ratio

NAAQS: National Ambient Air Quality Standard
NH₃: Ammonia
NO: Nitric oxide
NO₂: Nitrogen dioxide
NO₃: Nitrate radical
NOAA-NESDIS: National Oceanic and Atmospheric Administration – National Environmental Satellite, Data, and Information Service
NOₓ: Combination of NO and NO₂
O₃: Ozone
OH: Hydroxyl radical
OOA: Oxygenated Organic Aerosol
OPC: Optical Particle Counter
PAH: Polycyclic Aromatic Hydrocarbon
PM₁: Particulate matter less than 1 μm in aerodynamic diameter
PM₂.₅: Particulate matter less than 2.5 μm in aerodynamic diameter
PM₁₀: Particulate matter less than 10 μm in aerodynamic diameter
POA: Primary Organic Aerosol
Psig: Pound-force per square inch gauge
PTR-MS: Proton Transfer Reaction – Mass Spectrometer
RH: Relative humidity
SMPS: Scanning Mobility Particle Spectrometer
SO₂: Sulfur dioxide
SOA: Secondary Organic Aerosol
TBA: Tributylamine
TEA: Triethylamine
Tg N: Teragrams of nitrogen
TMA: Trimethylamine
TSP: Total suspended particulate
UCR: University of California, Riverside
VOC: Volatile Organic Compounds
CHAPTER 1

INTRODUCTION

Background

Cache Valley is an agricultural area with a small urban influence that is located on the border between Utah and Idaho. The human population of the valley (Cache County, Utah and Franklin County, Idaho) is just over 125,000 according to the U.S. Census Bureau’s 2008 population estimates (1). As of 2004, there were about 111,500 cows (2) and just over 80,000 registered vehicles (3). The valley floor averages about 1400 meters above sea level and is surrounded by mountains that reach heights greater than 2700 meters above sea level to the east and around 1650 meters above sea level to the west (4). The valley’s largest city, Logan, Utah, (pop. 48,657) is a university town that provides a population influx during the school year.

The valley is prone to temperature inversions in winter, especially the months of January through March (5). Normal temperature trends in the troposphere show decreasing temperature with increasing altitude. During a temperature inversion, a layer of warm air overlaps a layer of cool air, which halts the vertical mixing of the cooler air mass. When such a temperature inversion occurs, the valley’s bowl shape prevents the cool air mass, and all the pollutants released into that cool air mass, from escaping.

Atmospheric pollutants come in two main forms, gas-phase and aerosol. Aerosols are defined as solids or liquids suspended in a gas. Atmospheric aerosols are divided into separate categories based on their aerodynamic diameter. Fig. 1.1 summarizes the size distribution categories for particulate matter. Aerosols larger than 2.5 μm in diameter are designated course particulate matter. These aerosols are generally emitted directly from
Figure 1.1 Atmospheric aerosol size distribution schematic showing three ranges. The two modes sometimes observed in the accumulation range are also shown (adapted from ref 6).
the source, such as wind blown dust, ocean sea salt, volcanic ash, and plant particulate. Most of the atmospheric aerosol mass is found in the course particulate matter range. Aerosols smaller than 2.5 \( \mu m \) in diameter are designated fine particulate matter (PM\(_{2.5}\)). PM\(_{2.5}\) can either be emitted directly from the source, known as primary aerosol, or it can be formed in the atmosphere (secondary aerosol) after conversions from gas to particle phase. PM\(_{2.5}\) is divided into two ranges, the accumulation range (0.08 – 2.5 \( \mu m \)), and the transient nuclei range (<0.08 \( \mu m \)). Most of the surface area for atmospheric aerosol is found in the accumulation range. The accumulation range has been observed to be bi-modal at times. These modes are known as the condensation mode (0.1 – 0.4 \( \mu m \)) and the droplet mode (0.45 – 1.0 \( \mu m \)). The condensation mode is attributed to aerosol formation from the gas phase, while the droplet mode is attributed to oxidative reactions occurring in the aqueous phase (7, 8). The largest number of atmospheric aerosol is found in the transient nuclei range.

Past research has shown that high concentrations of PM\(_{2.5}\) have negative impacts on human health (9-11) as well as reduced visibility (12, 13). Fig. 1.2 illustrates the impacts of aerosol on visibility in Cache Valley. Other impacts include changes in climate, as it has been shown that atmospheric aerosol can affect Earth’s radiative forcing (change in net irradiance of the tropopause) by directly reflecting radiation back into space or indirectly through cloud condensation, thereby producing a cooling effect (14, 15).

Due to these health concerns, PM\(_{2.5}\) has been classified as a criteria pollutant by the environmental protection agency (EPA). Currently, the EPA has set the 24-hr
Figure 1.2 A visual comparison of ambient air in Cache Valley on a clean air quality day (Oct. 14, 2007) and a bad air quality day (Feb. 21, 2008).

National Ambient Air Quality Standard (NAAQS) for PM$_{2.5}$ at 35 $\mu$g/m$^3$ \(^{(16)}\). The 24-hr value is measured from midnight to midnight. Each year is regulated on the 98th percentile, which is the 24-hr (daily) value out of a year of PM$_{2.5}$ monitoring data below which 98 percent of all daily values fall (the 7 highest values are disregarded). The average of the past three years is then used to determine if an area is in violation of the NAAQS (termed nonattainment area).

When Cache Valley experiences an inversion episode, the PM$_{2.5}$ levels can frequently exceed the NAAQS limit. Severe inversion periods occurred in the winters of 2004 and 2005. As an example, during the months of January and February of 2004, the...
PM$_{2.5}$ concentrations in Logan reached values of 130-140 $\mu$g/m$^3$ (5). The pollution levels during the winters of 2003, 2006, and 2007 were relatively mild in comparison, reaching mass concentration levels of only about 15-20 $\mu$g/m$^3$. Recent years (2008 – 2010), however, have seen a return to high mass concentration levels (~80 $\mu$g/m$^3$). As a result, on Dec. 14, 2009, Cache Valley was officially designated a nonattainment area for PM$_{2.5}$ by the EPA.

**Ambient Measurements**

Over the past several years a quadrupole aerosol mass spectrometer (AMS, Aerodyne Research, Inc.) has been employed to sample the ambient air of Cache Valley during the normal winter month inversion period from January to March (17). The AMS has been described in detail in previous studies (18-20). The AMS obtains continuous quantitative size and chemical composition information on the non-refractory components of particulate matter. The AMS detects particles within the range of ~50 nm – 1.0 $\mu$m in size. The air to be sampled is introduced through an aerodynamic focusing lens that forces the aerosols into a beam. The beam passes through a time of flight region. A spinning chopper allows through only small bursts of particles, which are separated based on size. The AMS uses a high temperature vacuum oven (650-820°C) to vaporize the introduced aerosol particles and employs the impact of energetic electrons (70eV) to ionize the vaporized material. The ions are then separated by a quadrupole mass spectrometer.

The data collected from the AMS reveals the valley air to be composed mainly of ammonium salts (predominantly as ammonium nitrate) and organic aerosol. Ammonium
nitrate typically made up 50-80% of the particle mass, while organic aerosol constituted another 15-25%. Organic aerosol can be divided into two types: primary organic aerosol (POA) and secondary organic aerosol (SOA). A common source of POA is vehicle emissions, which contain large hydrocarbon compounds. These compounds are referred to as hydrocarbon-like organic aerosol (HOA). In the case of SOA, volatile organic compounds (VOCs) can react in the gas phase with oxidants such as ozone, hydroxyl radical (OH), or nitrate radical (NO₃) to produce semi-volatile or non-volatile compounds known as oxygenated organic aerosol (OOA). The AMS can distinguish between these different organic aerosol types, as discussed in Zhang et al. (21). Hydrocarbon species form chain like patterns separated by 14 amu that continue through higher mass-to-charge peaks, which correlates to successive losses of CH₂. A common mass-to-charge peak used as a marker for HOA is \( m/z \) 57 (\( \text{C}_4\text{H}_9^+ \)). The relatively simple pattern of HOA becomes more complicated for the OOA as there are additional possible fragment ions containing oxygen. The mass-to-charge marker for OOA is \( m/z \) 44 (\( \text{CO}_2^+ \)).

Among the organic aerosol detected in Logan were HOA, OOA, and nitrogen containing aerosol. The fragmentation pattern of the nitrogen aerosol is distinct from either HOA or OOA. The mass spectrum consists of even valued \( m/z \) ion fragments, including \( m/z \) 58, 86, 100, and 114. These mass-to-charge peaks are typically used as markers for amine compounds (22). Fig. 1.3 shows the temporal intensity profiles for these amine markers during the inversion period of 2005. It can be seen that there are different temporal profiles among the various amine markers. This suggests two amine sources or chemical reaction mechanisms are responsible for the generation of amine aerosol in the valley’s air. Linear regression analysis (Fig. 1.4 and 1.5) showed a positive
Figure 1.3 Time trends of certain mass-to-charge ions that act as markers for amines as measured in Cache Valley, Utah, during February 2005.
Figure 1.4 Comparison plot of two amine ions (m/z 58 and m/z 114) with best-fit line and regression analysis.

Figure 1.5 Comparison plot of two amine ions (m/z 86 and m/z 100) with best-fit line and regression analysis.
correlation between the temporal profiles for mass-to-charge peaks 58 and 114 ($R^2 = 0.783$). A similar positive correlation was observed for the temporal profiles of mass-to-charge peaks 86 and 100 ($R^2 = 0.836$). However, the temporal profiles for the two sets of $m/z$ ion pairs do not correlate with each other ($m/z$ 58:86 gives $R^2 = 0.050$).

Fig. 1.6 shows the mass concentration of the observed ambient aerosol during the months of February and March of 2005. A clear diurnal cycle can be seen in Fig. 1.3 and 1.6. The maximum concentrations of aerosol were reached in the early morning hours between 2:00 – 5:00 a.m. and the minimum concentrations were reached by the afternoon hours of 3:00 – 6:00 p.m. Several probable explanations exist for these diurnal cycles. One is a temperature/humidity effect in which compounds, such as ammonium nitrate, will stay in particle phase at lower temperatures (higher relative humidity) then partition to gas phase at higher temperatures (lower relative humidity). Another explanation could

![Figure 1.6](image_url)  
**Figure 1.6** Mass concentration of the chemical composition as measured in Cache Valley, Utah, during February 2005.
be nighttime reactions with radicals, such as nitrate radical (NO₃), leading to aerosol formation. The alternate is that aerosol is being depleted during the day through photochemical degradation pathways. One final explanation could be changes in the boundary layer. However, this is less likely, as not every mass-to-charge ion shows this diurnal pattern, which would be the case with a boundary layer change.

A typical (log scale) mass spectrum of Cache Valley ambient aerosol (taken in Feb. of 2005) is shown in Fig. 1.7. As with other years, nitrate (m/z 30 and 46) was detected and was usually the most abundant compound. Amines were present during most inversion episodes. The mass spectra taken during time periods with significant hydrocarbon-like organic character can be subtracted from the mass spectra taken during time periods with a more mixed chemical composition to form a difference mass spectrum as can be seen in Fig. 1.8. The difference mass spectrum more clearly highlights the hydrocarbon ion signals related to the organic aerosol (1.8B), while the nitrate, sulfate, and amine related ion signals are seen in the more typical spectrum (1.8A). The HOA burst seen in the difference mass spectrum (1.8B) was most likely due to diesel exhaust and/or other vehicle emissions.

Field and Smog Chamber Studies

Agricultural emissions are an often neglected source of VOCs that can lead to the production of SOA. Despite the number of studies that have monitored gas-phase amines in the field (ambient studies), there are only a handful of these studies that report amine aerosol (23-27). Similarly, there have only been a few smog chamber based studies that have examined the reactivity of amines (28, 29). However, these smog
Figure 1.7 Aerosol mass spectrum as measured in Cache Valley, Utah, during February 2005.
Figure 1.8 The difference of two mass spectra as measured in Cache Valley, Utah. A) Mass spectrum taken during February 27, 2006 (typical composition). B) Mass spectrum taken during February 28, 2006 (organic composition).
chamber studies mainly focused on the gas-phase reactions of amines. The objective of this thesis is to better understand the atmospheric chemistry occurring in Cache Valley, Utah, specifically in regards to amine compounds. This thesis is divided into two chapters that discuss two separate sets of experiments.

Chapter 2 details a set of collaborative experiments with the Space Dynamics Laboratory (at Utah State University) that were designed to measure particulate emissions from tillage processes and other operations at dairy and cotton farms in California. Both farm locations are similar to Cache Valley in that they combine significant agricultural activities with an urbanized environment. The same AMS that was used to sample in Cache Valley was employed in these California studies. An optical particle counter (OPC) and a set of AirMetric MiniVol portable air samplers were collocated with the AMS. The OPC obtains particle number distribution information for aerosol of certain size ranges including PM$_1$, PM$_{2.5}$, PM$_{10}$, and total suspended particulate (TSP). A laser diode is used to illuminate a beam of particles and the scattered light is measured using off-axis photo detectors. The MiniVols are filter based particle samplers (FPS). The FPS pump draws the air sample through a particle size separator (impactor) and the particles are then collected on a 47 mm Teflon filter. The filters are both pre- and post-weighed according to federal regulations (40 CFR 50). The FPS can separate particles into PM$_{10}$ or PM$_{2.5}$ size ranges based on the choice of impactor. TSP can also be measured by removing the impactor section. In addition to being a good comparison to ambient measurements in Cache Valley, the general results of these studies add to the previous knowledge base of ambient chemistry in California.
A series of smog chamber experiments were also conducted in collaboration with the University of California, Riverside (UCR). Past collaborative work at UCR examined the oxidative reactions of a set of alkyl tertiary amines: trimethylamine (TMA), triethylamine (TEA), and tributylamine (TBA). Chapter III of this thesis examines the results from an expanded study involving a series of alkyl and aromatic secondary amines. These included: dimethylamine (DMA), diethylamine (DEA), dipropylamine (DPA), dibutylamine (DBA), dibenzylamine (DBA*), and diphenylamine (DPA*).

Several additional instruments were employed in these experiments. Among these were a high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS), a proton transfer reaction mass spectrometer (PTR-MS), and an in-house built scanning mobility particle spectrometer (SMPS). The HR-TOF-AMS (Aerodyne, Inc) is divided into three differentially pumped chambers. These include the sampling chamber, the particle time-of-flight chamber, and the analysis chamber. A sample of air is drawn through an aerodynamic lens that focuses the particles within that sample into a beam. The particle beam is then accelerated through the particle time-of-flight region before impacting an oven (600ºC). The non-refractory components are vaporized and sent through a beam of electrons (70eV) for ionization. The ions are sorted by a time-of-flight mass analyzer and detected by an MCP detector. The HR-TOF-AMS can alternate between two flight paths. The shorter flight path (V-mode) allows for higher ion throughput and therefore a higher sensitivity. The longer flight path (W-mode) allows for a better separation of the ions at the expense of lower sensitivity.

The PTR-MS (Iconicon Analytik) is a real-time instrument that measures the non-dissociative proton transfer reactions of H$_3$O$^+$ ions with ambient volatile organic
compounds (VOCs) that have a proton affinity greater than that of H₂O (Eq. 1.1).

\[ \text{VOC} (g) + \text{H}_3\text{O}^+ (g) \rightarrow \text{VOCH}^+ (g) + \text{H}_2\text{O} (g) \]  

(1.1)

The instrument is divided into four main compartments: an ion source, a drift tube, a quadrupole mass spectrometer, and an ion detector. High concentrations of H₃O⁺ are produced with pure water vapor in the hollow cathode ion source and then passed into the drift tube via a Venturi-type inlet. The air sample is introduced into the drift tube and the previously discussed VOCs are ionized. These ions are mass analyzed by the quadrupole mass spectrometer and measured by a scanning electron multiplier detector.

The SMPS is composed of a TSI model 3077 ⁸⁵Kr neutralizer, a TSI model 3081 long column cylindrical differential mobility analyzer (DMA*), and a TSI model 3760A condensation particle counter (CPC). The DMA* measures particle size distribution and the CPC is used to measure number concentration. The SMPS collects particle size distribution information from 28 nm to 730 nm.

These smog chamber experiments explore in more depth the aerosol chemistry of amines, which have not been studied to date in great detail. It is hoped that these amine studies will provide researchers better insight into alternative reaction pathways that may be contributing to the atmospheric pollution both here in Cache Valley and at other locations.

References

(1) U.S. Census Bureau, American FactFinder Website; http://factfinder.census.gov/home/saff/main.html?_lang=en

(2) USDA National Agricultural Statistics Service Website; http://www.nass.usda.gov/index.asp


CHAPTER 2
AGRICULTURAL EMISSION FIELD STUDIES

Introduction

Agricultural emissions are an often overlooked contributor to atmospheric aerosol pollution. A handful of studies have monitored the emissions and aerosol products of agricultural facilities at locations where urban emissions are also significant (1-5). Atmospheric aerosols are of concern due to their negative impacts on human health (6-8) as well as visibility (9, 10).

The two maps in Fig. 2.1 (11) display the ammonia (NH$_3$) and NO$_x$ emissions in the San Joaquin Valley, California, during a typical pollution season day according to the National Oceanic and Atmospheric Administration’s National Environmental Satellite, Data, and Information Service (NOAA-NESDIS). Agricultural facilities are the most common source of NH$_3$ emissions, accounting for 37.4 Tg N/yr (12). NO$_x$ (NO and NO$_2$) is emitted from vehicle exhaust and is a highly reactive atmospheric species. The combination of these rural and urban chemical species in such a confined area has the potential to produce large amounts of ambient aerosol. For example, as discussed in Seinfeld and Pandis (12), the combination of NH$_3$ emissions with those of NO$_x$ can lead to the formation of ammonium nitrate aerosol by Eq. 2.1 and 2.2

\[
\text{NO}_2 (g) + \text{OH} \cdot (g) \xrightarrow{M} \text{HNO}_3 (g) \tag{2.1}
\]

\[
\text{HNO}_3 (g) + \text{NH}_3 (g) \rightleftharpoons \text{NH}_4\text{NO}_3 (s) \tag{2.2}
\]
Figure 2.1 Maps of San Joaquin Valley, California, showing both the NH₃ and NOₓ average emissions per ozone season day as measured by NOAA-NESDIS.
where M stands for neutral matter. Ammonium nitrate formation, however, is highly
dependent on temperature and relative humidity. The particle phase is favored at lower
temperatures and higher relative humidity.

Another common pollutant, which is emitted from coal-fired power plants and
found as a contaminant in fuels, is sulfur dioxide (SO₂). SO₂ also reacts with NH₃ to
form ammonium sulfate according to Eq. 2.3 – 2.7.

\[
\begin{align*}
\text{SO}_2 (g) + \text{OH}^\cdot (g) & \xrightarrow{M} \text{HOSO}_2^\cdot (g) \quad (2.3) \\
\text{HOSO}_2^\cdot (g) + \text{O}_2 (g) & \rightarrow \text{HO}_2^\cdot (g) + \text{SO}_3 (g) \quad (2.4) \\
\text{SO}_3 (g) + \text{H}_2\text{O} (l) & \rightarrow \text{H}_2\text{SO}_4 (aq) \quad (2.5) \\
\text{H}_2\text{SO}_4 (aq) + \text{NH}_3 (g) & \rightarrow \text{NH}_4\text{HSO}_4 (s) \quad (2.6) \\
\text{NH}_4\text{HSO}_4 (s) + \text{NH}_3 (g) & \rightarrow (\text{NH}_4)_2\text{SO}_4 (s) \quad (2.7)
\end{align*}
\]

The sulfate/ammonia chemistry is more favored than the nitrate/ammonia chemistry.
Therefore, there must be enough NH₃ to first neutralize SO₂ before ammonium nitrate
can be formed (13).

In addition to NH₃, agricultural facilities emit large amounts of volatile organic
compounds (VOC). The oxidation of VOC leads to the formation of secondary organic
aerosol (SOA), which can comprise up to 80% of organic particulate matter (14). These
facilities also contribute to primary organic aerosol (POA) as tractors and other
agricultural equipment emit hydrocarbon-like organic aerosol (HOA) and stir up dust and
coarse particulate matter (PM₁₀) from tillage and other operations. Studies in Utah and
other various locations have further shown that nitrogen-containing compounds, such as
amines, can be an important contributor to aerosol chemistry in agricultural areas (1, 4,
15-19).
In order to better understand the aerosol chemistry occurring near agricultural facilities, a collaborative experiment with the Space Dynamics Laboratory (SDL) at Utah State University was set up to measure particulate emissions from tillage processes and other operations at dairy and cotton farms in California. The dairy was located near the city of Hanford and the cotton farm was located near Los Banos. Hanford is approximately 90 miles southeast of Los Banos. Both cities are in the San Joaquin Valley, a traditional agricultural area with increasing urbanization. The San Joaquin Valley stretches 300 miles from the Sacramento-San Joaquin Delta in the North to the Tehachapi Mountains in the south. The valley is, on average, about 40 miles wide and is surrounded by the Diablo and Santa Ynez ranges in the west and the Sierra Nevada range to the east.

The Hanford dairy also produces crops at its facility. In addition to dairy emissions (measured from June 13 to June 21, 2008), two tillage processes, termed “conventional” and “conservation” (measured from May 14 through May 20, 2008), were studied at the Hanford location. Conventional tillage is a stepwise process in which the soil is turned up multiple times. This produces large amounts of coarse particulate matter (PM$_{10}$) as can be seen in Fig. 2.2. Conservation or strip tillage is a one step process where the tiller, fertilizer, and planter are connected in series. Madden et al. (20) has shown that conservation tillage can reduce PM$_{10}$ emissions by as much as 85%. Along with producing far less dust particulate (Fig. 2.3), conservation tillage also reduces the overall amount of diesel fuel needed to operate the tractors. The resulting reduction in vehicle exhaust produces lower PM$_{2.5}$ emissions of HOA.
Figure 2.2 Photo showing conventional tillage operation.
Figure 2.3 Photo showing conservation tillage operation. The USU-SDL air quality trailer is seen in the foreground.
Methods

The ambient particulate matter at both locations was sampled by an aerosol mass spectrometer (AMS, Aerodyne Research, Inc.). The AMS has been described in detail in previous studies (21-23). Briefly, the AMS obtains continuous quantitative size and chemical composition information on the non-refractory components of particulate matter. The AMS can detect particles within the range of ~50 nm – 1.0 μm in size. The air to be sampled is drawn through an aerodynamic focusing lens, which forces the particles into a beam. This particle beam then passes through a time-of-flight region, where particles are separated based on their size. The AMS uses a high temperature oven (750°C in Los Banos; 650-820°C in Hanford) to vaporize the particles before electron impact (70eV) ionization. The ions are then mass analyzed by a quadrupole mass spectrometer using an electron multiplier for ion detection.

Another instrument employed in this study was a MetOne 9722 optical particle counter (OPC). The OPC obtains particle number distribution information for aerosols of certain particle matter size ranges including PM$_1$, PM$_{2.5}$, PM$_{10}$, and TSP. A laser diode is used to illuminate a beam of particles and the scattered light is measured using off-axis photo detectors. The particle volume concentration can be calculated as explained in Zavyalov et al. (24). Collocated with the OPC were a series of MiniVol portable air samplers (AirMetrics, Inc.). The MiniVols are filter particle samplers (FPS). The FPS pump draws the air sample through a particle size separator (impactor) and the particles are then collected on a 47 mm Teflon filter. The filters are both pre- and post-weighed according to federal regulations (40 CFR 50). These FPS samplers are an EPA approved method for measuring particulate mass concentration. The FPS can separate particles.
into PM$_{10}$ or PM$_{2.5}$ size ranges based on the choice of impactor. TSP can also be measured by removing the impactor section. Comparison of the FPS data with the OPC allowed for the derivation of a mass concentration factor (MCF). Conversion of particle volume concentration to mass concentration using MCFs has been reported in the literature in detail (24, 25). The MCF for a certain particulate matter size range (k) is calculated by dividing the mass concentration (PM) obtained by the FPS with the volume concentration ($V_k$) measured by the OPC. These data are averaged over a day and a mean MCF$_k$ for that day is calculated for each PM$_k$ division (Eq. 2.8).

$$MCF_k = \frac{1}{N} \sum (PM_k/V_k)$$

(2.8)

In this study, MCFs were calculated for PM$_{2.5}$, PM$_{10}$, and TSP. Since there was no FPS for the PM$_1$ size range, a MCF could not be calculated. Therefore, the OPC PM$_1$ volume concentration was compared to the PM$_1$ mass concentration of the AMS. The OPC was set to sample every few seconds while the AMS was set to sample every 15 minutes. The OPC data was averaged to match the AMS sampling times.

All instrumentation was housed in a trailer designed for use in ambient air sampling. Several sampling ports and access to the roof allowed for multiple instruments to be run simultaneously. In both Los Banos and Hanford, the trailer was positioned in the field downwind of the agricultural operations being monitored.

Results and Discussion

Los Banos: Cotton Farm. The data collected from the AMS revealed the air to be composed of ammonium salts, including ammonium nitrate and sulfate, and several types of carbonaceous species. Carbon species detected included hydrocarbon-like organic
aerosol (HOA) (m/z 57) and oxidized organic aerosol (OOA) (m/z 44). Fig. 2.4 shows the chemical composition of the ambient air at the cotton farm. HOA tends to be from a primary aerosol source such as combustion emissions (fossil fuels, biomass burning). OOA, on the other hand, is secondary in nature, and is formed by photochemical and oxidative processes in the atmosphere.

The pie chart (Fig. 2.5) shows that organic particulate matter made up about 44.2% of the overall detected aerosol. This is consistent with previous studies at various locations (5, 14, 26, 27) that report organic compounds to be around 20-50% of the total PM$_{2.5}$ aerosol. The ammonium salts were the next largest contributors. After mole ratio calculations, it was discovered that complete neutralization occurred between the basic species (ammonium ion) and the acidic species (nitrate, sulfate, and chloride ions). Ammonium nitrate made up about 41.7% while ammonium sulfate made up 13.6%.

**Figure 2.4** Mass concentration of the chemical composition at a cotton farm near Los Banos, California.
The fragmentation mass spectra of carbonaceous species exhibit distinctive patterns that start at lower m/z and progress through the spectrum, as can be seen in the mass spectrum in Fig. 2.6. The HOA show m/z peaks separated by 14 amu, which correlates to successive losses of CH₂. The relatively simple pattern of HOA becomes more complicated for the OOA as there are additional possible fragment ions containing oxygen. A study by Zhang et al. (5), employing an AMS at a site in Pittsburgh, PA, found that OOA constituted about 66% of organic aerosol mass detected. A clear HOA pattern (m/z 55, 69, 83, etc.) can be seen in the mass spectrum, as well as some OOA (m/z 92, 96, 106). Some polycyclic aromatic hydrocarbons (PAHs) are observed at higher mass (m/z 129, 154, and 167).

The size distribution plot of nitrate (Fig. 2.7) shows that most of the particle mass detected fell within the 0.1 – 0.6 μm size range. This puts it within the accumulation
Figure 2.6 Mass spectrum obtained by the AMS for the cotton farm near Los Banos, California.
range (0.08 – 2 μm). The accumulation range can be broken down into two subsections known as the condensation mode (0.1 – 0.4 μm) and the droplet mode (0.45 – 1.0 μm). The condensation mode is attributed to aerosol formation from the gas phase, while the droplet mode is attributed to reactions occurring in the aqueous phase (12, 13). Previous studies have shown that nitrate can be bimodal in the accumulation phase (28, 29). The size distribution of nitrate from Los Banos indicates that a large portion of the reactions were gas phase conversions.

**Hanford: Dairy.** As with the Los Banos study, the AMS data revealed the air to be composed of ammonium salts, including ammonium nitrate and sulfate, and several types of carbonaceous species. In addition to HOA and OOA, nitrogen-containing aerosol was also detected. The fragmentation pattern of the nitrogen particles was unlike either HOA or OOA and consisted of even valued fragment ions. Fig. 2.8 shows the chemical composition of the ambient air during the dairy portion of the study.
Pie charts (Fig. 2.8 and 2.9) show that organic particulate matter made up about 65% of the overall detected aerosol. As was the case in Los Banos, the ammonium salts were the next largest contributors. Molar ratio calculations show that Ammonium nitrate constituted 21.2% and ammonium sulfate 7.1% of the total aerosol. Unlike the Los Banos study, there was an excess of basic species (ammonium ion) present at the Hanford site (Fig. 2.10). Approximately 36.7% of the ammonium ion was not neutralized by the acidic species (nitrate, sulfate, and chloride). This excess ammonium could be neutralized by an acidic species found in the organic aerosol fraction, such as carbonate (CO$_3^{2-}$). Most rainwater is slightly acidic due to the presence of carbonic acid (H$_2$CO$_3$), which is formed by reactions of CO$_2$ with water. NH$_3$ could be reacting with H$_2$CO$_3$ (Eq. 2.9 – 2.11) in much the same way that it reacts with H$_2$SO$_4$ (I3).

**Figure 2.8** Mass concentration of the chemical composition measured at a dairy near Hanford, California.
Figure 2.9 Pie chart showing the chemical composition measured at a dairy near Hanford, California.

Figure 2.10 The percent of detected ammonium ion that was neutralized by nitrate, sulfate, and chloride ions.
\[
\begin{align*}
\text{CO}_2 (g) + \text{H}_2\text{O} (l) & \rightleftharpoons \text{H}_2\text{CO}_3 (aq) \quad (2.9) \\
\text{H}_2\text{CO}_3 (aq) + \text{NH}_3 (g) & \rightleftharpoons \text{NH}_4\text{HCO}_3 (s) \quad (2.10) \\
\text{NH}_4\text{HCO}_3 (s) + \text{NH}_3 (g) & \rightleftharpoons (\text{NH}_4)_2\text{CO}_3 (s) \quad (2.11)
\end{align*}
\]

Similar to the Los Banos data, HOA and OOA ion fragmentation patterns are observed in some mass spectra collected at the Hanford site (Fig. 2.11). Certain mass-to-charge ratios act as markers for certain compounds. Typical \( m/z \) markers for HOA and OOA are \( m/z 57 \) (mostly \( \text{C}_4\text{H}_9^+ \)) and \( m/z 44 \) (mostly \( \text{CO}_2^+ \)), respectively (5). These two markers are among the most abundant in the mass spectrum, which was measured during a dust plume event in the dairy section of the study. Also observed are higher \( m/z \) ions from PAHs (\( m/z 129 \) and 155).

Fig. 2.12 shows the time trend of the size distribution of nitrate during the morning hours of May 14\(^\text{th} \). The plot also shows the mass concentration values over that time period. The mass spectrum taken during that time range is shown in Fig. 2.13. The spectrum shows that the ammonium salts, especially ammonium nitrate, were the dominant chemical species during this period of time. The HOA and OOA markers (\( m/z 44, 55, 57, \) and 69) were also present, but less abundant.

As discussed previously, fragmentation ions with certain mass-to-charge ratios are indicative of specific compounds. Even valued fragments, including \( m/z 58, 86, \) and 100, typically act as markers for amine compounds (30). Several studies have shown that agricultural facilities, such as dairies and animal feedlots, are a large emitter of atmospheric amines (2, 3, 31, 32). These studies, though, have focused on gas phase amines. Fig. 2.14 shows the time trend of the size distribution of \( m/z 58 \) during the dairy sampling period. In the corresponding mass spectrum (Fig. 2.15), \( m/z 58 \) is observed
Figure 2.11 Mass spectrum from the AMS taken at a dairy near Hanford, California.
Figure 2.12 Time trend of the size distribution of nitrate measured at a dairy near Hanford, California.
Figure 2.13 Aerosol mass spectrum corresponding to the size distribution plot of nitrate measured at a dairy near Hanford, California.
Figure 2.14 Time trend of the size distribution of m/z 58 (amine) measured at a dairy near Hanford, California.
Figure 2.15 Aerosol mass spectrum corresponding to the size distribution plot of $m/z$ 58 (amine) measured at a dairy near Hanford, California.
to make a relatively large contribution. Significant aerosol amine signals have been
detected in previous studies in Cache Valley, Utah (15). The detection of amine markers
in California, though at a lower level, is significant in that it provides evidence that amine
aerosols are not unique to Cache Valley.

Unlike Los Banos, the size distribution plots of nitrate (Fig. 2.16) and m/z 58
(amine – Fig. 2.17) for Hanford show that most of the particle mass detected falls within
the droplet mode (0.4 - 1.0 µm) of the accumulation range. This suggests that more
aqueous phase reactions were occurring in Hanford. This difference in particle formation
between the two sites, however, could be due to meteorological differences in the
sampling season. The Los Banos study was performed in autumn (October), while the
Hanford study took place in late spring / early summer (May and June).

Fig. 2.18 shows the PM$_1$ time trends as measured by both the AMS and OPC from
June 13 to June 18, 2008. Although the correlation is not perfect, the general trends of

![Figure 2.16 Size distribution of nitrate measured at a dairy near Hanford, California.](image-url)
Figure 2.17 Size distribution of $m/z$ 58 (amine) measured at a dairy near Hanford, California.

Figure 2.18 PM$_1$ time trends measured by the AMS and OPC.
the two instruments do agree well. During sampling on the evening of June 13th, a
series of dust plumes corresponding to tractor activity were observed and measured by
multiple instruments at the site, including the AMS and OPC. A different pattern of ions
can be observed in the mass spectrum (Fig. 2.19) for this dust event, including \( m/z \) 55, 63,
93, 129, and 148. That the AMS was able to detect these dust plumes is surprising, as
dust particles are commonly composed of refractory matter and the AMS detects non-
refractory components. This suggests that there are some non-refractory components to
the dust at the Hanford site. It is also possible, though less likely, that the AMS is
capable of detecting certain types of refractory material.

A diurnal pattern emerged among the ammonium salts with nitrate dominant in
the morning and sulfate dominant in the evening (Fig. 2.20 and 2.21). In each diurnal
plot, the cross markers show the mean for each hour. The mid-line shows the median
value, the top and bottom lines show the upper and lower quartiles (75th and 25th
percentiles), and the whiskers show the 95th and 5th percentile values for each hour. Fig.
2.22 gives the mass spectrum and corresponding pie chart for the morning hours of 4:30
to 11:15 AM on June 15, 2008. The nitrate \( m/z \) peaks are the largest in the mass
spectrum. Note that the amine marker \((m/z \ 58)\) is also observed in the mass spectrum.
Previous studies have shown that amines have a diurnal pattern similar to nitrate (15).
Fig. 2.23 gives the mass spectrum and corresponding pie chart for the afternoon hours of
2:45 to 7:30 PM on June 15, 2008. Though an organic peak \((m/z \ 44)\) is the largest in the
spectrum, the sulfate \( m/z \) peaks are more abundant than the nitrate peaks. These diurnal
patterns have been observed in previous studies (33). The nitrate diurnal pattern is
usually due to photochemistry of morning traffic emissions (NO/NO\(_2\)) to produce
Figure 2.19 Aerosol mass spectrum measured during a dust plume event at a dairy near Hanford, California.
Figure 2.20 Diurnal pattern of nitrate measured at a dairy near Hanford, California.

Figure 2.21 Diurnal pattern of sulfate measured at a dairy near Hanford, California.
Figure 2.22 Aerosol mass spectrum with corresponding chemical composition pie chart of ambient air measured at a dairy during the morning of June 15, 2008.

Figure 2.23 Aerosol mass spectrum with corresponding chemical composition pie chart of ambient air measured at a dairy during the afternoon of June 15, 2008.
HNO₃. Contributing factors to the nitrate pattern are possible temperature and relative humidity effects. The cooler temperatures and higher relative humidity favor the partitioning of gas phase ammonia and nitric acid into ammonium nitrate aerosol. The increase in sulfate is most likely due to the photochemical oxidation of SO₂ as previously discussed in this chapter. The afternoon maximum of sulfate correlates with the daily solar radiation peak.

There was also a diurnal pattern observed with the carbonaceous species (Fig. 2.24). A similar diurnal pattern was observed by Zhang et al. (5). This pattern is due to a combination of vehicle traffic (HOA) and photochemical oxidation (OOA). The sharp peak from 6:00 to 9:00 AM corresponds to morning rush hour, while the broad peak from about 11:00 AM to 6:00 PM is related to the incoming solar radiation.

Figure 2.24 Diurnal pattern of carbonaceous species measured at a dairy near Hanford, California.
These studies have demonstrated that comparable ambient aerosol chemistry is observed in both California and Utah. Both locations are similar in that they are rural agricultural areas with a limited urban influence. The detection of a small amount of amine aerosol during the California field sampling is important in demonstrating that amine aerosol generation is not unique to Utah. The overall results of these field studies add to the overall knowledge base of ambient chemistry in California.

References


(11) USGS, The national map viewer; http://nmviewogc.cr.usgs.gov/viewer.htm


CHAPTER 3
SMOG CHAMBER STUDIES

Introduction

Aerosols have been known to cause negative impacts on human health, visibility, and climate change (1-4). Among gas phase pollutants that potentially form aerosols, agricultural emissions of amines are an often under studied class of compounds. Although there are both anthropogenic and biogenic sources of amines, such as feedlots, vehicle exhaust, and biomass burning (5-7), a major source of atmospheric amines are animal feedlots. Recent studies have shown that volatile organic compounds (VOCs), such as amines, are important to secondary organic aerosol (SOA) formation (8-11).

Atmospheric amines are removed mainly through oxidative processes (12, 13). Common oxidants in the atmosphere include ozone, hydroxyl radical (OH), and nitrate radical (NO₃). Research has been done on the kinetics of amine oxidation by ozone and OH (9, 14-16). However, there have been few smog chamber studies looking at the kinetics of NO₃ oxidation (17). NO₃ is the dominant nocturnal oxidant and it has been shown experimentally that amine related aerosol concentrations increase at night (10).

With only a handful of studies looking at ambient and smog chamber aerosol amine reactions, the aerosol chemistry involving amines is not well understood. In order to better understand atmospheric amine reaction chemistry, a series of experiments were conducted in collaboration with the University of California, Riverside (UCR). Previous work at UCR had focused on the oxidation of aliphatic tertiary amines with ozone and...
NO\textsubscript{x} \cite{10,18}. These included trimethylamine (TMA), triethylamine (TEA), and tributylamine (TBA).

The rates of these reactions were very quick, as can be seen in Fig. 3.1. The decay rate of trimethylamine in the TMA/O\textsubscript{3} reaction (Fig. 3.1) was calculated to be 2.08x10\textsuperscript{8} molecules/cm\textsuperscript{3}·s. This value was obtained by taking the amine number concentration measured by a proton transfer reaction mass spectrometer (PTR-MS; in counts per second, cps) between the time of ozone and NO injection and finding the best fit line. The slope of that line equation (decay rate) was converted to a volume rate by assuming that 40 cps is equal to 1 ppbv (part per billion volume). Based on the molecular weight of TMA and assuming the reaction occurred at standard conditions (25° C, 1 atm), the mass and eventually molecular rates were determined. The calculated rate constant was 1.04x10\textsuperscript{-17} cm\textsuperscript{3}/molecule·s. This was determined by converting the concentration values of TMA and ozone at the time of ozone injection to their respective molecular

![Figure 3.1](image-url)  

**Figure 3.1** Time trends of m/z 60 (PTR-MS) and aerosol concentration (SMPS) for the reaction of trimethylamine with ozone/NO\textsubscript{x}.  

\[\text{counts per second (cps)}\]

\[\text{10:00 AM} \quad 12:00 PM \quad 2:00 PM \quad 4:00 PM\]

\[\text{0} \quad 1000 \quad 2000 \quad 3000 \quad 4000\]

\[\text{0} \quad 20 \quad 40 \quad 60 \quad 80\]

\[\mu m^3/cm^3\]
concentrations, and employing a second order rate constant equation. The calculated rate constant is comparable to the literature value of \(7.84 \times 10^{-18} \text{ cm}^3/\text{molecule-s}\) \((16)\).

This chapter expands on this previous work by investigating the reactions of ozone and NO\(_x\) with secondary amines. There were four aliphatic amines and two aromatic amines examined. The aliphatic amines were chosen to discover any differences or similarities with the reactions of the tertiary amines. It was decided to investigate aromatic amines for the purpose of understanding whether the N-H hydrogen can be abstracted during the reaction. The amines examined include dimethylamine (DMA), diethylamine (DEA), dipropylamine (DPA), dibutylamine (DBA), diphenylamine (DPA\(^*\)), and dibenzylamine (DBA\(^*\)). Table 3.1 summarizes several chemical properties of these amines and their chemical structures are shown in Fig. 3.2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Weight (g/mol)</th>
<th>Proton Affinity (kcal)</th>
<th>Vapor Pressure (Torr)</th>
<th>Water Solubility (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylamine</td>
<td>45.08</td>
<td>224.9</td>
<td>1292.0</td>
<td>3540</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>73.14</td>
<td>230.1</td>
<td>400.0</td>
<td>miscible</td>
</tr>
<tr>
<td>Dipropylamine</td>
<td>101.19</td>
<td>231.9</td>
<td>20.1</td>
<td>soluble</td>
</tr>
<tr>
<td>Dibutylamine</td>
<td>129.25</td>
<td>232.7</td>
<td>2.0</td>
<td>soluble</td>
</tr>
<tr>
<td>Diphenylamine c</td>
<td>169.24</td>
<td>217.5</td>
<td>1.0</td>
<td>slightly sol</td>
</tr>
<tr>
<td>Dibenzyline</td>
<td>197.28</td>
<td>-</td>
<td>0.0012</td>
<td>0.05</td>
</tr>
<tr>
<td>Benzyline d</td>
<td>107.15</td>
<td>218.2</td>
<td>0.65</td>
<td>soluble</td>
</tr>
<tr>
<td>Water</td>
<td>18.02</td>
<td>165.0</td>
<td>17.5</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) The molecular weight, vapor pressure, and water solubility were found in the MSDS of each compound. \(^b\) The proton affinities for the aliphatic amines and water were found in ref. 19. \(^c\) The proton affinity for diphenylamine was found in units of kJ/mol in ref. 20 and converted to kcal. \(^d\) The proton affinity for benzyline was found in units of kJ/mol in ref. 21 and converted to kcal.
Methods

The experiments described in this chapter were performed at the UCR Bourns College of Engineering – Center for Environmental Research and Technology (CE-CERT) Atmospheric Processes Laboratory. The Atmospheric Processes Laboratory is home to dual 90 m³ FEP Teflon film smog chambers. The two smog chambers are housed in a temperature-controlled enclosure that is continually flushed with purified air to prevent contamination from reactive ambient species. The Teflon bags are hung from a rigid frame that descends throughout the experiment to maintain a slight positive pressure between the bags and the chamber housing. The enclosure also includes a series of black lights and an argon arc lamp to simulate any photochemical processes that might result from solar radiation. The smog chambers allowed for the re-creation of ambient conditions in a controlled environment. More complete details regarding the design of these chambers have been discussed previously (22). The laboratory also houses a smaller, 20 m³ Teflon film smog chamber (see Fig. 3.3). This chamber is similar to the
Figure 3.3 Diagram of the 20 m³ smog chamber facility at the University of California, Riverside.
larger chambers with the exception of the rigid frame and radiation lamps. However, for those experiments designed to simulate nocturnal chemistry, the smaller chamber can also be used and provide comparable results to those obtained with the larger chambers.

Before the start of each experiment, the background concentrations of ozone and NOx were checked to make sure they were below 2ppb. Ozone concentration was monitored by a Dasibi Environmental Corp 1003-AH O3 analyzer and NOx concentration was monitored by a Thermal Environmental Instruments model 42C chemiluminescent NOx analyzer. All experiments were conducted without the use of the black lights or argon arc lamp so as to simulate nocturnal conditions. Each experiment was run under dry (RH, < 0.1%) conditions. A known volume of the amine to be studied (Sigma Aldrich, purity ≥ 99%) was introduced by either injecting the liquid amine into a small glass injection manifold or by introducing the gas phase amine into a calibrated bulb based on calculated partial pressures. The amine was then flushed into the chamber by passing N2 gas over the liquid or through the bulb. Ozone would then be introduced into the chamber by passing 20 psig of pure air through two UV ozone generators. After the wall-loss corrected concentration of aerosol created from the ozone oxidation had leveled off, (~3 hours after ozone injection), nitric oxide (NO) would then be introduced by means of a calibrated bulb. The experiments were concluded when the wall-loss corrected aerosol concentrations reached a constant level.

The gas phase species were monitored by a proton transfer reaction - mass spectrometer (PTR-MS, Iconicon Analytik). The design and operating details of this instrument have been discussed previously (23). The PTR-MS is a real-time instrument that measures the non-dissociative proton transfer reactions of H3O+ ions with ambient...
volatile organic compounds (VOCs) that have a proton affinity greater than that of H₂O (Eq. 3.1).

\[
\text{VOC (g) + H}_3\text{O}^+ (g) \rightarrow \text{VOCH}^+ (g) + \text{H}_2\text{O (g)}
\] (3.1)

The proton affinities of each of the amines investigated are reported in Table 3.1. The proton affinity of DBA* was not found in the literature, therefore, the proton affinity of benzylamine was reported in the table as it should be close to the proton affinity of DBA*. Each amine had a proton affinity greater than that of water. The PTR-MS can detect VOC concentrations as low as 50 parts per trillion volume. The ion traces from \(m/z\) 21 to \(m/z\) 200 were monitored in scan mode with a dwell time of 0.2 sec per mass.

The aerosol products of the amine reactions being studied were monitored using a high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS, Aerodyne Inc.). The HR-TOF-AMS has been described in detail by Decarlo et al. (24). The HR-TOF-AMS is divided into three differentially pumped vacuum chambers. These include the sampling chamber, the particle time-of-flight chamber, and the analysis chamber. Air from the smog chamber is drawn through an aerodynamic lens that focuses the aerosol particles being sampled into a collimated beam. The collimated particle beam is then passed through the particle tof region (where it can be sized) before impacting a high temperature oven (600ºC). The non-refractory components are vaporized and subsequently ionized in a 70eV impact ion source. The resulting ions are separated based upon their \(m/z\) values by a time-of-flight mass analyzer and detected by an MCP detector. The HR-TOF-AMS can alternate between two flight path configurations. A shorter flight path configuration (V-mode) allows for higher ion throughput and provides higher
instrument sensitivity. A longer flight path configuration (W-mode) allows for better separation of the ions (high mass resolution) but at the expense of lower sensitivity.

Another instrument that was used to monitor the size and concentration of the aerosol products of the amine reactions was an in-house built scanning mobility particle spectrometer (SMPS) discussed by Wang and Flagan (25). The SMPS is composed of a TSI model 3077 $^{85}$Kr neutralizer, a TSI model 3081 long column cylindrical differential mobility analyzer (DMA*), and a TSI model 3760A condensation particle counter (CPC). The DMA* measures particle size distribution and the CPC is used to measure number concentration. The SMPS collected particle size distribution information for particles from 28 nm to 730 nm in diameter. The measured particle number and volume were wall loss corrected and the particle mass concentrations were then calculated using density conversion equations (26).

**Results and Discussion**

Table 3.2 summarizes the initial conditions and final aerosol yields from the secondary amine reactions with ozone and NOx. In each experiment, it is the addition of NO that leads to substantial particle formation. Ozone and NO quickly react to form NO$_2$, the other component of NOx (Eq. 3.2). Ozone also reacts with NO$_2$ to form nitrate radical (NO$_3$) according to Eq. 3.3.

\[
\text{O}_3 (\text{g}) + \text{NO} (\text{g}) \rightarrow \text{NO}_2 (\text{g}) + \text{O}_2 (\text{g}) \quad (3.2)
\]

\[
\text{O}_3 (\text{g}) + \text{NO}_2 (\text{g}) \rightarrow \text{NO}_3 (\text{g}) + \text{O}_2 (\text{g}) \quad (3.3)
\]

Since ozone is injected first, however, the NO$_3$ is most likely reacting with the amine oxidation products. Nonetheless, it was shown in previous tertiary amine experiments...
Table 3.2 Initial conditions and results obtained from the reactions of secondary amines with \( O_3 \) and \( NO_x \).

<table>
<thead>
<tr>
<th>Amine</th>
<th>Amine Concentration (ppb)</th>
<th>( NO_x ) Concentration (ppb)</th>
<th>Ozone Concentration (ppb)</th>
<th>Final Aerosol Concentration (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylamine</td>
<td>100</td>
<td>50</td>
<td>300</td>
<td>135</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>100</td>
<td>50</td>
<td>300</td>
<td>60</td>
</tr>
<tr>
<td>Dipropylamine</td>
<td>100</td>
<td>50</td>
<td>300</td>
<td>32</td>
</tr>
<tr>
<td>Dibutylamine</td>
<td>100</td>
<td>50</td>
<td>300</td>
<td>120</td>
</tr>
<tr>
<td>Diphenylamine</td>
<td>100</td>
<td>50</td>
<td>300</td>
<td>8</td>
</tr>
<tr>
<td>Dibenzylamine</td>
<td>100</td>
<td>50</td>
<td>300</td>
<td>0.5</td>
</tr>
</tbody>
</table>

that when the amines are directly reacted with \( N_2O_5 \) (which thermally decomposes to \( NO_3 \) and \( NO_2 \)) similar aerosol formation is observed (18).

DMA Reaction. After the initial injection of ozone, some aerosol formed. The reactions were allowed to run for three hours, at which time the aerosol concentration had leveled off to about 7 µg/m³. After NO injection, rapid and more significant particle formation occurred, eventually leveling off at around 135 µg/m³ (Fig. 3.4). The particle levels then slowly began to decrease at the end of the experiment, finishing at around 110 µg/m³.

The gas phase parent ion of DMA (m/z 45) is also shown in Fig. 3.4. Some of the major gas-phase species detected included m/z 45 (acetaldehyde), m/z 44 (methyl-methyleneimine), m/z 58 (methyl-ethyleneimine), and m/z 91 (dimethylnitramine). Table 3.3 gives a summary of the major ion peaks detected by the PTR-MS during each of the amine reactions. Though there were nitramines (R₂N-NO₂) detected in most of the aliphatic secondary amine reactions, there were no nitrosamines (R₂N-NO) observed.
Figure 3.4 Time trends of gas phase parent ion and aerosol mass concentration from the dimethylamine reaction with ozone/NO\textsubscript{x} as measured by the PTR-MS and SMPS.
This is not surprising due to the saturation of NO with O₃ to form NO₂ and O₂. An alternative pathway to nitrosamine formation is outlined in Eq. 3.4 and 3.5 (12).

\[
2\text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HONO} + \text{HNO}_3 \tag{3.4}
\]

\[
\text{R}_2\text{NH} + \text{HONO} \rightleftharpoons \text{R}_2\text{NNO} + \text{H}_2\text{O} \tag{3.5}
\]

However, as the experiments were conducted under dry conditions (RH, < 0.1%), the formation of HONO was limited.

Fig. 3.5 shows a HR-TOF-AMS average spectrum for DMA after reaction with both oxidants. Some of the major ion peaks observed included \(m/z\) 30.034 (\(\text{CH}_4\text{N}^+\)), \(m/z\) 44.050 (\(\text{C}_2\text{H}_6\text{N}^+\)), \(m/z\) 58.066 (\(\text{C}_3\text{H}_8\text{N}^+\)), \(m/z\) 86.099 (\(\text{C}_5\text{H}_{12}\text{N}^+\)), and \(m/z\) 101.114 (\(\text{C}_6\text{H}_{15}\text{N}^+\)), which represent the backbone amine fragments. Fragments of large hydrocarbons including \(m/z\) 72.094 (\(\text{C}_5\text{H}_{12}^+\)), \(m/z\) 86.11 (\(\text{C}_6\text{H}_{14}^+\)), and \(m/z\) 94.078 (\(\text{C}_7\text{H}_{10}^+\)) were detected, with evidence of oxidation in \(m/z\) 72.058 (\(\text{C}_4\text{H}_8\text{O}^+\)) and \(m/z\) 97.065 (\(\text{C}_6\text{H}_9\text{O}^+\)). Table 3.4 lists a summary of major ion fragments detected during each amine experiment.

![Figure 3.5](image)

**Figure 3.5** Aerosol mass spectrum of the reaction of dimethylamine with ozone and NOₓ.
Table 3.3 The major PTR-MS ions and the proposed chemical species.

<table>
<thead>
<tr>
<th>DMA</th>
<th>DEA</th>
<th>DPA</th>
<th>DBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>CH$_3$NCH$_2$</td>
<td>Methylmethyleneimine</td>
<td>31</td>
</tr>
<tr>
<td>45</td>
<td>CH$_3$CHO</td>
<td>Acetaldehyde</td>
<td>45</td>
</tr>
<tr>
<td>46</td>
<td>(CH$_3$)$_2$NH</td>
<td>Dimethylamine</td>
<td>47</td>
</tr>
<tr>
<td>58</td>
<td>CH$_3$NCH$_2$CH$_3$</td>
<td>Methylethyleneimine</td>
<td>58</td>
</tr>
<tr>
<td>59</td>
<td>(CH$_3$)$_2$CO CH$_2$CH$_2$CHO</td>
<td>Acetone Propanal</td>
<td>60</td>
</tr>
<tr>
<td>60</td>
<td>(CH$_3$)$_2$N CH$_3$CH$_2$NO</td>
<td>Trimethylamine Nitrosoethane</td>
<td>61</td>
</tr>
<tr>
<td>62</td>
<td>CH$_3$NO$_2$</td>
<td>Nitromethane</td>
<td>72</td>
</tr>
<tr>
<td>91</td>
<td>(CH$_3$)$_2$NNO$_2$</td>
<td>Dimethylnitramine</td>
<td>74</td>
</tr>
<tr>
<td>88</td>
<td>CH$_3$CH$_2$NHCH$_2$ CHO</td>
<td>Ethyl-acetamide</td>
<td>88</td>
</tr>
<tr>
<td>119</td>
<td>(CH$_3$CH$_2$)$_2$N NO$_2$</td>
<td>Diethyl-nitramine</td>
<td>100</td>
</tr>
<tr>
<td>130</td>
<td>HN([(CH$_3$)$_2$CHO]$_2$</td>
<td>Dipropanamide</td>
<td>102</td>
</tr>
<tr>
<td>147</td>
<td>(CH$_3$(CH$_3$)$_2$N NO$_2$</td>
<td>Dipropyl nitramine</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.4 The major HR-TOF-AMS ions and empirical formula assignments.

<table>
<thead>
<tr>
<th>DMA</th>
<th>DEA</th>
<th>DPA</th>
<th>DBA</th>
<th>DPA*</th>
<th>DBA*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>m/z</strong></td>
<td><strong>Formula</strong></td>
<td><strong>m/z</strong></td>
<td><strong>Formula</strong></td>
<td><strong>m/z</strong></td>
<td><strong>Formula</strong></td>
</tr>
<tr>
<td>29.998</td>
<td>NO⁺</td>
<td>29.998</td>
<td>NO⁺</td>
<td>29.998</td>
<td>NO⁺</td>
</tr>
<tr>
<td>30.034</td>
<td>CH₃N⁺</td>
<td>30.034</td>
<td>CH₃N⁺</td>
<td>30.034</td>
<td>CH₃N⁺</td>
</tr>
<tr>
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<td>C₂H₅N⁺</td>
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<td>CH₂NO⁺</td>
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<td>CO₂⁺</td>
</tr>
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<td>45.993</td>
<td>NO₂⁺</td>
<td>44.05</td>
<td>C₂H₅N⁺</td>
<td>44.014</td>
<td>CH₂NO⁺</td>
</tr>
<tr>
<td>58.053</td>
<td>C₂H₅N⁺</td>
<td>45.993</td>
<td>NO₂⁺</td>
<td>44.05</td>
<td>C₂H₅N⁺</td>
</tr>
<tr>
<td>58.066</td>
<td>C₂H₅N⁺</td>
<td>58.066</td>
<td>C₂H₅N⁺</td>
<td>45.993</td>
<td>NO₂⁺</td>
</tr>
<tr>
<td>59.074</td>
<td>C₂H₅N⁺</td>
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<td>C₄H₈O⁺</td>
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<td>CH₂NO⁺</td>
</tr>
<tr>
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<td>C₄H₈O⁺</td>
<td>72.094</td>
<td>C₂H₁₂⁺</td>
<td>58.042</td>
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<tr>
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<td>86.099</td>
<td>C₂H₇N⁺</td>
<td>58.066</td>
<td>C₂H₅N⁺</td>
</tr>
<tr>
<td>86.099</td>
<td>C₂H₁₀⁺</td>
<td>86.11</td>
<td>C₂H₁₂⁺</td>
<td>72.058</td>
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</tr>
<tr>
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<td>C₂H₁₂⁺</td>
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<tr>
<td>94.066</td>
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<td>C₂H₃N⁺</td>
<td>86.097</td>
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<td>96.058</td>
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</tr>
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<td>139.133</td>
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<td>100.076</td>
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<td>114.096</td>
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<td>86.097</td>
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</tr>
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</tr>
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<td>C₂H₆N⁺</td>
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<td>C₂H₅N⁺</td>
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<td>136.119</td>
<td>C₂H₆N⁺</td>
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<td>C₂H₅N⁺</td>
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<td>C₂H₆N⁺</td>
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<td>C₂H₆NO⁺</td>
<td>136.114</td>
<td>C₂H₅N⁺</td>
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<td>191.07</td>
<td>C₂H₅N₂O₂⁺</td>
<td>142.130</td>
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<tr>
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<td></td>
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<td>158.116</td>
<td>C₂H₆NO₂⁺</td>
</tr>
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<td></td>
<td></td>
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<td>174.117</td>
<td>C₂H₆NO₃⁺</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>191.071</td>
<td>C₂H₆N₂O₂⁺</td>
</tr>
</tbody>
</table>
**DEA Reaction.** For the DEA reaction, the aerosol concentration stabilized around 6 μg/m³ about three hours after ozone injection. After NO injection, a large burst of aerosols were formed that reduced quickly before leveling off at 40 μg/m³ (Fig. 3.6). The amount of aerosol produced by DEA was less than that produced by DMA, which is curious since DEA is the larger molecule. A similar pattern was seen among the tertiary amines.

As with most of the aliphatic secondary amines, the gas-phase products of the DEA reaction with ozone/NOx included aldehydes (m/z 31 formaldehyde; m/z 45 acetaldehyde), imines (m/z 58 ethyl-methyleneimine; m/z 72 ethyl-ethyleneimine), and nitro groups (m/z 119 diethyl-nitramine). Additionally, amides were observed, such as m/z 74 (ethyl-formamide) and m/z 88 (ethyl-acetamide).

The HR-TOF-AMS mass spectrum for the DEA reaction is shown in Fig. 3.7. The major ion fragments included the amine backbone m/z 30.034 (CH₄N⁺), m/z 44.050 (C₂H₆N⁺), m/z 58.066 (C₃H₈N⁺), m/z 86.099 (C₅H₁₂N⁺), and m/z 100.113 (C₆H₁₄N⁺). Higher mass oxidized fragments included m/z 191.084 (C₆H₁₁N₂O₅⁺).

**DPA Reaction.** There was a small burst of aerosol formation after the injection of DPA that quickly leveled off. The aerosol concentration then abruptly dropped at ozone injection before a smooth increase in particles was observed (Fig. 3.8). The most likely explanation for this pattern is that some of the injected amine may have partitioned to the particle phase. When ozone was injected, the gas-to-particle partitioning equilibrium was altered along with the simultaneous initiation of gas phase amine oxidation. An alternate explanation is that these aerosol bursts are due to acid-base chemistry from HNO₃ leftover from the previous experiment. Ozone injection led to particle formation that
Figure 3.6 Time trends of gas phase parent ion and aerosol mass concentration from the diethylamine reaction with ozone/NO\textsubscript{x} as measured by the PTR-MS and SMPS.

Figure 3.7 Aerosol mass spectrum of the reaction of diethylamine with ozone and NO\textsubscript{x}.
reached levels higher than with the ozone reactions of DMA and DEA (11 μg/m³).

This is not surprising, seeing as DPA is the larger molecule. What is interesting is that after NO injection, new particle formation did not exceed that of either DEA or DMA, reaching only about 32 μg/m³.

Examples of gas-phase species detected by the PTR-MS for the DPA reaction include \( m/z \) 45 (acetaldehyde), \( m/z \) 58 (propyleneimine), \( m/z \) 130 (dipropanamide), and \( m/z \) 147 (dipropylnitramine). The concentration of the gas phase parent ion of DPA (\( m/z \) 102) was quite low, as can be seen in Fig. 3.9. However, \( m/z \) 100 was appended to show that some gas phase products of ozone oxidation decrease after NO injection. This indicates that NO₃ reacts with the oxidized products of the amine/ozone reaction as well as the parent amine.

The major ion fragment peaks formed during the DPA reaction can be seen in the HR-TOF-AMS spectrum (Fig. 3.9). As with the previous reactions, the amine backbone fragments (\( m/z \) 30.034, \( m/z \) 44.050, \( m/z \) 58.066, \( m/z \) 86.099, and \( m/z \) 100.113) were detected. Higher mass fragment ions include \( m/z \) 114.096 (\( C₆H₁₂NO⁺ \)), \( m/z \) 130.091 (\( C₆H₁₂NO₂⁻ \)), and 146.082 (\( C₆H₁₂NO₃⁻ \)). These represent fragments that have been oxidized by one, two, or three oxygen atoms. These fragment patterns were observed in the tertiary amine experiments. They are most likely formed by the isomerization of an amino-alkoxy radical to form hydroxyl-substituted amides. These amides were not seen in the PTR-MS as they have very low vapor pressures. Also observed was a higher mass oxidized fragment at \( m/z \) 191.07 (\( C₆H₁₁N₂O₅⁺ \)).

**DBA Reaction.** As with DPA, a small burst of aerosol accompanied the injection of DBA (Fig. 3.10). The gas phase parent ion of DBA (\( m/z \) 130) was not observed by the
Figure 3.8 Time trends of gas phase parent ion and aerosol mass concentration from the dipropylamine reaction with ozone/NO\textsubscript{x} as measured by the PTR-MS and SMPS.

Figure 3.9 Aerosol mass spectrum of the reaction of dipropylamine with ozone and NO\textsubscript{x}. 
PTR-MS. Partitioning of the parent amine to particle phase is not surprising considering the size and relatively low vapor pressures of DPA and DBA (Table 3.1). Particle formation after ozone injection stabilized around 43 μg/m³, just over the total aerosol generated in the DEA experiment. This is expected since DBA is almost twice the size of DEA. Total aerosol formation from DBA after NO injection (120μg/m³), however, did not exceed the maximum reached by DMA. This was also observed in the tertiary amine experiments.

Continuing the pattern of the other aliphatic amines, the DBA reaction with ozone/NOₓ formed gas phase aldehydes, like acetaldehyde (m/z 45), and amides, like butyl-formamide (m/z 102). Though there were no imines observed in this reaction, other alkenes such as m/z 55 (dibutene) were detected. Unlike the other aliphatic amines, there were no gas phase nitro compounds detected in the DBA reaction.

The major ion fragments formed in the DBA reaction can be seen in the HR-TOF-AMS mass spectrum (Fig. 3.11). Along with the amine backbone fragments and the oxidized aerosol observed in the previous aliphatic amine reactions, there was also detection of the hydroxyl-substituted amides, including m/z 158.116 (C₈H₁₆NO₂⁺) and m/z 174.117 (C₈H₁₆NO₃⁺), as well as the oxidized fragment at m/z 191.071 (C₆H₁₁N₂O₅⁺).

**DPA* Reaction.** To determine if the hydrogen attached directly to the nitrogen (R₂N-H) could be attacked by radical chemistry, two aromatic amines were investigated. One of the aromatic amines, Diphenylamine (DPA*), has only sp² hybridized carbons, while the other aromatic amine, Dibenzylation (DBA*), has two sp³ hybridized carbons. Although the DBA* experiment was conducted first, the results from that experiment will be discussed later.
Figure 3.10 Time trends of gas phase parent ion and aerosol mass concentration from the dibutylamine reaction with ozone/NO\textsubscript{x} as measured by the PTR-MS and SMPS.

Figure 3.11 Aerosol mass spectrum of the reaction of dibutylamine with ozone and NO\textsubscript{x}. 
The aromatic secondary amines had a tendency to crystallize out of solution before injection. DPA* had difficulty dissolving in water, therefore, pyridine was used as the solvent. Pyridine was chosen for its relative inactivity in previous smog chamber experiments. After ozone injection, a small amount of aerosols were formed (Fig. 3.12). After three hours, the concentration had stabilized at 3 μg/m³. After NO injection, that concentration increased to 8 μg/m³. The only gas phase species observed in the DPA* experiment was m/z 80 which corresponds to pyridine. As can be seen in Fig 3.13, pyridine is unchanged after injection of both ozone and NO.

Fig. 3.13 shows the HR-TOF-AMS mass spectrum for the DPA* reaction with ozone/NOx. The typical amine backbone fragmentation pattern is observed at lower mass (m/z 30.034 and m/z 58.066). Surprisingly, as with the larger aliphatic amines, the higher mass hydroxyl-substituted amides were detected. Additional higher mass fragments were seen that do not fit the fragmentation pattern of the aliphatic amines. These include m/z 170.07 (C₈H₁₂NO₃⁺) and m/z 196.089 (C₁₀H₁₄NO₃⁺) which relate to highly unsaturated hydroxyl-substituted amides. Also, m/z 206.111 (C₇H₁₄N₂O₅⁺) and m/z 220.101 (C₈H₁₆N₂O₅⁺) were observed and correspond to the combination of two oxidized amines. These oxidized amine combinations were seen in the larger secondary aliphatic amine reactions, as well as in the tertiary amine reactions.

**DBA* Reaction.** It was discovered, after performing the DBA* experiment, that aromatic amines tend to crystallize out of solution before injection into the chamber. An alternative solvent, pyridine, was therefore chosen for use in the DPA* experiment. Despite the low water solubility issue, it appeared that some DBA* had made it into the chamber. Though the reaction products with ozone by itself were negligible, an increase
Figure 3.12 Time trends of $m/z$ 80 (PTR-MS) and aerosol concentration (SMPS) for the reaction of diphenylamine with ozone/NO$_x$.

Figure 3.13 Aerosol mass spectrum of the reaction of diphenylamine with ozone and NO$_x$. 
in aerosol can be seen after the injection of NO (~0.5 μg/m³) (Fig. 3.14). There were 
no gas phase products observed by the PTR-MS for the DBA*/ozone/NOx reaction. It 
appears that DPA* produces more particles than DBA*, even though DBA* is the larger 
molecule and has two sp³ hybridized carbon reaction sites. This could, however, be due 
to the difference in solvents. Due to the amount of time needed for the oxidation 
reactions to stabilize, only one amine reaction experiment can be conducted a day. 
Additionally, as use of the UCR smog chamber facility is in high demand, it may not be 
possible to repeat an experiment right away. Had time permitted, the DBA* experiment 
would have been duplicated with pyridine as the solvent.

Though the amount of aerosol formed was low, there was enough to see a 
fragmentation pattern in the HR-TOF-AMS spectrum (Fig. 3.15). The typical amine 
backbone and hydrocarbon-like oxygenated aerosol fragments were observed.

Reaction Pathways. Similar gas phase products found in the aliphatic amine 
reactions were aldehydes, amides, imines, and nitro compounds. Fig. 3.16 shows the 
time trend data for some of these compounds observed in the amine/ozone/NOx reactions 
as measured by the PTR-MS. Previous studies have attributed aerosol formation to acid-
base salts (9, 14). Although the formation of aminium salts with nitric acid could be a 
plausible explanation, previous work with tertiary amines has shown that salt formation 
in these reactions is minimal (10). Nitrate salts give strong signals in the HR-TOF-AMS 
due to NO⁺ and NO₂⁺ fragments (Fig. 3.17). It was found, however, that these ions were 
not present in significant amounts in the secondary amine reactions. The contribution of 
the NO⁺ and NO₂⁺ fragments to the total intensity of the spectrum for each of the 
aliphatic secondary amines is shown in Fig. 3.18. In the case of DMA, the nitrate
Figure 3.14 Time trends of aerosol mass concentration from the dibenzylamine reaction with ozone/NO$_x$ as measured by the SMPS.

Figure 3.15 Aerosol mass spectrum of the reaction of dibenzylamine with ozone and NO$_x$. 
Figure 3.16  Time trends of mass-to-charge ions corresponding to certain gas phase species measured by the PTR-MS during the amine/ozone/NOx experiments. A) m/z 30, formaldehyde (from DPA reaction); B) m/z 45, acetaldehyde (from DPA reaction); C) m/z 72, ethyl-ethyleneimine (from DEA reaction); D) m/z 88, propyl-formamide (from DPA reaction); E) m/z 91, dimethyl-nitramine (from DMA reaction).
Figure 3.17 High-resolution mass spectral peaks ($m/z$ 30) measured by the HR-TOF-AMS.
Figure 3.18 Contribution of NO$^+$ and NO$_2^+$ ions associated with nitrate to the total aerosol mass spectrum for the four aliphatic secondary amines studied.
fragments account for, at most, ~15% of the total signal. Taking into account the mass of DMA (45 Da) compared to nitrate (62 Da), an acid-base salt can only account for ~26% of the total signal. The possible salt contribution is much less for the other aliphatic amines.

Homologous high mass aerosol fragments detected by the HR-TOF-AMS include $\text{C}_6\text{H}_{12}\text{NO}_3^+$ ($m/z$ 146) and $\text{C}_8\text{H}_{16}\text{NO}_3^+$ ($m/z$ 174) from the DPA and DBA reactions. These high mass fragments show that DPA and DBA gain three oxygen atoms while losing three hydrogen atoms. This pattern is consistent with tertiary amine observations. It appears that these molecular formulas are based on a building block structure of a dihydroxylated amide. The high mass fragments for DMA including $\text{C}_8\text{H}_{15}\text{N}^+$ ($m/z$ 125), $\text{C}_9\text{H}_{17}\text{N}^+$ ($m/z$ 139), and $\text{C}_{10}\text{H}_{19}\text{N}^+$ ($m/z$ 153) indicate chains of unsaturated amines, possibly imines. Similar peaks were observed in each of the aliphatic secondary amine reactions.

Determining, with absolute certainty, the products and reaction pathways of these experiments with the spectrometric methods employed is difficult. This is due to the possibility of molecules with different chemical composition having the same $m/z$ ratio (isobaric compounds). Even with the HR-TOF-AMS, we can only determine the molecular formula, which could have multiple structural isomers associated with it. However, knowing that our initial reactants contain only C, H, N and O, and understanding the preferred chemistry of the reactant species, we can develop proposed pathways for the secondary amine reactions. A few of the proposed pathways for the reaction of NO$_3$ with dipropylamine are shown in Fig. 3.19. The proposed products
Figure 3.19 Proposed amine/ozone/NO\textsubscript{x} reaction pathways with DPA as the initial amine. G = gas phase, A = Aerosol phase.
detected are shown with bold numbers 1-9 and letters G and A, which stands for gas and aerosol species respectively.

For secondary aliphatic amines, the N-H bond strength is greater than the C-H bond strength. This would suggest that the C-H hydrogen would be the preferred abstraction site. Work by Lindley et al. (27) has shown that 63% of the reactions of dimethylamine with OH produce an amine alkyl radical, ·CH₂NHCH₃, while the remainder produces an amino radical, (CH₃)₂N·. In our experiments, the reaction is initiated with an abstraction of hydrogen from the amine by NO₃. If the N-H hydrogen is abstracted, then the resulting amino radical can either lose a hydrogen to O₂ to form N-propyl-propyleneimine (1G) or react with NO₂ to form N,N-dipropylnitramine (2G). Lindley et al. also found that amino radical reactions with NO₂ were about 10⁷ times faster than the amino radical reactions with O₂. This could help explain the abundance of nitramines observed in this work.

If one of the alkyl hydrogens is abstracted, an amine alkyl radical is produced. The amine alkyl radical reacts with O₂ to form an aminyl alkylperoxy radical that can then react with ozone or another aminyl alkylperoxy radical to form an aminyl alkoxy radical. The resulting aminyl alkoxy radical can react several ways. It can react with O₂ to form N-propyl-N-propanal amine (3G). Repeating this process yields N,N-dipropanal-amine (4G). The aminyl alkoxy radical can also decompose into either propanal (5G) and an amino radical or acetaldehyde (6G) and an amine alkyl radical. If the propanal path is taken, the resulting amino radical can lose a hydrogen atom to form propyleneimine (7G). If the acetaldehyde path is taken, the amine alkyl radical can
repeat the previously outlined steps to form N-propyl-formamide (8G) and eventually N,N-diformamide (9G).

A possible route to aerosol formation for the larger secondary amines is by rearrangement of the aminyl alkoxy radical through a hydrogen shift to form a hydroxyaminyl alkyl radical. An explanation for the observation of this isomerization in the DPA and DBA reactions is that there are 1,4 and 1,5 hydrogen shifts available in these larger amines. The 1,4 and 1,5 hydrogen shifts are important due to the relative stability of a five or six member transition state (28). The isomerization restarts the alkyl radical chain reactions, thus leading to rapidly oxidized aerosol products, such as alcohols. Though there are several deviation points throughout the radical chain that allow for the formation of various amides and/or amine alcohols, the path displayed in the reaction scheme shows the formation of N-(3-hydroxypropyl)propanamide (1A).

The smog chamber experiments discussed in this chapter show that secondary amines, which are a common agricultural emission, could be a significant contributor to both gas phase and aerosol product formation. Amines react with ozone to form both gas phase and aerosol phase products. The possible gas phase products observed in each experiment included: aldehydes, imines, amides and nitro compounds. The subsequent addition of NO quickly produces nitrate radical (NO₃) through reactions with ozone. NO₃ then reacts with both the amine and oxidized amine products to form significantly more aerosol than ozone alone (~13 times more aerosol for DMA, ~6 times more for DEA, and ~3 times more for DPA and DBA). High-resolution aerosol mass spectra and gas phase species detected by the PTR-MS were used to propose likely pathways for the reaction of NO₃ with the secondary amines. Evidence of hydroxyl-substituted amide
aerosol is seen with the larger aliphatic amines. These amides, along with possible oxidized amine combinations, were also observed in the diphenylamine reaction.

Since the spectrometric methods employed in this study do not allow for absolute determination of the reaction pathways and products, further experiments will need to be performed. Future work could include repeating the amine/O$_3$/NO$_x$ reactions with isotopically labeled reactants to elucidate the chemical pathways occurring in the experiments. Additionally, filter collection of the aerosol products followed by spectroscopic analysis could provide confirmation for the proposed products in the reaction scheme. Furthermore, difficulties with water solubility in the case of the two aromatic amines resulted in a different solvent being used for each reaction. A repeat of the dibenzylamine experiment, with pyridine as the solvent, will need to be conducted in the future to verify the results of this experiment.

References


CHAPTER 4

SUMMARY

The objective of this thesis was to better understand the underlying reactions that lead to aerosol formation in Cache Valley. Studies were focused on exploring the role that organic amines play in local aerosol formation. Both field and laboratory (smog chamber) experiments were conducted on the reactivity and production of amine based aerosol.

Chapter 2 presented results from two field studies performed near agricultural facilities in California. These studies demonstrated that comparable ambient aerosol chemistry is observed in both California and Utah. Both locations are similar in that they are rural agricultural areas with a limited urban influence. The detection of a small amount of amine aerosol during the California field sampling is important in demonstrating that amine aerosol generation is not unique to Utah. The overall results of these field studies add to the overall knowledge base of ambient chemistry in California.

The smog chamber experiments discussed in chapter 3 show that secondary amines, which are a common agricultural emission, could be a significant contributor to both gas phase and aerosol product formation. Amines react with ozone to form both gas phase and aerosol phase products. The possible gas phase products observed in each experiment included: aldehydes, imines, amides and nitro compounds. The subsequent addition of NO quickly produces nitrate radical (NO₃) through reactions with ozone. NO₃ then reacts with both the amine and oxidized amine products to form significantly more aerosol than ozone alone (~13 times more aerosol for DMA, ~6 times more for...
DEA, and ~3 times more for DPA and DBA). High-resolution aerosol mass spectra and gas phase species detected by the PTR-MS were used to propose likely pathways for the reaction of NO₃ with the secondary amines. Evidence of hydroxyl-substituted amide aerosol is seen with the larger aliphatic amines. These amides, along with possible oxidized amine combinations, were also observed in the diphenylamine reaction.

Since the spectrometric methods employed in the smog chamber studies do not allow for absolute determination of the reaction pathways and products, further experiments will need to be performed. Future work could include repeating the amine/O₃/NOₓ reactions with isotopically labeled reactants to elucidate the chemical pathways occurring in the experiments. Additionally, filter collection of the aerosol products followed by spectroscopic analysis could provide confirmation for the proposed products in the reaction scheme. Furthermore, difficulties with water solubility in the case of the two aromatic amines resulted in a different solvent being used for each reaction. A repeat of the dibenzylamine experiment, with pyridine as the solvent, will need to be conducted in the future to verify the results of this experiment.

The information gained in the present agricultural field studies should help researchers in the future in performing similar studies in California and other locations. It is hoped that the amine smog chamber studies will provide researchers better insight into alternative reaction pathways that may be contributing to the atmospheric pollution both here in Cache Valley and at other locations.