

This discussion paper is/has been under review for the journal *Atmospheric Chemistry and Physics (ACP)*. Please refer to the corresponding final paper in *ACP* if available.

**SOA formation from  
tertiary amines**

M. E. Erupe et al.

# Secondary organic aerosol formation from reaction of tertiary amines with nitrate radical

M. E. Erupe<sup>1</sup>, D. J. Price<sup>1</sup>, P. J. Silva<sup>1</sup>, Q. G. J. Malloy<sup>2</sup>, L. Qi<sup>2</sup>, B. Warren<sup>2</sup>, and  
D. R. Cocker III<sup>2</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, Utah State University, Logan, UT, USA

<sup>2</sup>Department of Chemical and Environmental Engineering and College of Engineering,  
Center for Environmental Research and Technology (CE-CERT), University of California,  
Riverside, CA, USA

Received: 1 July 2008 – Accepted: 6 August 2008 – Published: 1 September 2008

Correspondence to: P. J. Silva (phil.silva@usu.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

Secondary organic aerosol formation from the reaction of tertiary amines with nitrate radical was investigated in an indoor environmental chamber. Particle chemistry was monitored using a high resolution aerosol mass spectrometer while gas-phase species were detected using a proton transfer reaction mass spectrometer. Trimethylamine, triethylamine and tributylamine were studied. Results indicate that tributylamine forms the most aerosol mass followed by trimethylamine and triethylamine respectively. Spectra from the aerosol mass spectrometer indicate the formation of complex non-salt aerosol products. We propose a reaction mechanism that proceeds via abstraction of a proton by nitrate radical followed by  $RO_2$  chemistry. Rearrangement of the aminyl alkoxy radical through hydrogen shift leads to the formation of hydroxylated amides, which explain most of the higher mass ions in the mass spectra. These experiments show that oxidation of tertiary amines by nitrate radical may be an important night-time source of secondary organic aerosol.

## 1 Introduction

Aliphatic amines constitute an important class of volatile organic compounds due to their malodorous properties (Chang et al., 2005; Filipy et al., 2006; Rappert et al., 2005). Amines have also shown a propensity to form aerosols (Murphy et al., 2007; Silva et al., 2008) which could have implications on health, visibility and climate change (Dockery et al., 1993; Seinfeld et al., 2003; Watson et al., 2002; IPCC, 2007). Amines are emitted from a variety of anthropogenic sources that include feedlots, car exhaust, biomass burning, sewage treatment plants and industries (Cadle et al., 1980; Westerholm et al., 1993; Mosier et al., 1973; Kataoka et al., 1996; You et al., 2002). In the biosphere, they result from bacterial degradation of nitrogen containing organic matter such as proteins and amino acids (Wright, et al., 1976). There is limited data on emissions of amines from the various sources, but they are generally associated

## SOA formation from tertiary amines

M. E. Erupe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



with animal husbandry practices. Schade and Crutzen (1995) estimated the global emission of methylamines to be 150 Gg N/year, most of which was trimethylamine.

The lifetime of alkylamines in the atmosphere range from a few hours to tens of hours. Since they do not undergo photolysis in the atmosphere, their main removal processes are reactions with atmospheric reactants such as hydroxyl radical, ozone, atmospheric acids and nitrate radical (Tuazon et al., 1994; Pitts et al., 1978; Angelino et al., 2001; Murphy et al., 2007). Some of the products resulting from these reactions may be highly volatile in which case they remain in the gas phase. Others may have sufficiently low vapor pressure to exist in particulate phase. A number of studies have reported detecting particulate and aqueous phase amines in the atmosphere (Tan et al., 2002; Murphy et al., 1997; Zhang et al., 2003). Recent field measurements and lab experiments have shown that amine compounds can be a significant portion of aerosol mass especially during the night-time (Silva et al., 2008). However, the chemistry that leads to particulate amines is not well understood.

Few smog chamber experiments have been conducted to probe the chemistry of amines. These experiments have shown that amine reactions result in the formation of both volatile and condensed products. For example, photo-oxidation experiments by Pitts et al. (1978) of ethylamine and triethylamine in an outdoor chamber resulted in aerosol formation. Triethylamine yielded more aerosol than ethylamine. Amine aerosol chemistry did not get much attention during this time as the focus was on formation of carcinogenic nitrosamines. Years later, studies have shown that the chemistry that leads to the formation of aerosol is more complex and is dependent on the class of amine reacted (Angelino et al., 2001; Murphy et al., 2007). Tertiary amines in particular react to form more aerosol mass than secondary and primary amines (Murphy et al., 2007). None of these studies looked at the chemistry of amines with the nitrate radical.

In our recent work, we reported results from a series of experiments in which trimethylamine was reacted with ozone, nitrate radical and nitric acid (Silva et al., 2008). These results showed that the reaction of trimethylamine with nitrate radical produced mostly secondary organic aerosol. Formation of aminium salts was minimal. The re-

**SOA formation from  
tertiary amines**

M. E. Erupe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



action also exhibited relatively fast kinetics and high aerosol yields. This paper builds on that work in order to achieve a three-fold objective:

- i) to extend the study of trimethylamine to other tertiary amines,
- ii) to examine the products formed and
- 5 iii) to devise a reaction mechanism that is consistent with the observations.

The amines under investigation here are trimethylamine (TMA), triethylamine (TEA) and tributylamine (TBA).

## 2 Experimental

A series of experiments were conducted in the UC Riverside/CE-CERT environmental chamber. The chamber facility has been previously described by Carter et al. (2005). Briefly, the environmental chamber consists of a temperature controlled enclosure that is continually flushed with purified air. Two 90 m<sup>3</sup> Teflon (2 mil FEP Teflon) film reactors are hung on a rigid frame that descends during the experiment to maintain a slight positive differential pressure between the bags and the enclosure. All experiments were  
10 conducted under dry (RH<0.1%) conditions. A Dasibi Environmental Corp. 1003-AH Ozone analyzer monitored ozone concentration. Thermal Environmental Instruments model 42C chemiluminescent NO<sub>x</sub> analyzer monitored NO, NO<sub>2</sub> and NO<sub>x</sub>, for all experiments. Particle size and concentration was measured throughout the experiment  
15 using an in-house built scanning mobility particle spectrometer (SMPS) located inside the chamber enclosure. The SMPS consists of a TSI model 3077 <sup>85</sup>Kr neutralizer, a TSI model 3081 long column cylindrical differential mobility analyzer, and a TSI model 3760A condensation particle counter. A voltage scan from 40 V to 7000 V provided particle size distribution from 28 nm to 730 nm. Aerosol volumes were wall-loss corrected using a first order decay rate based on number concentrations (Bowman et al., 1997).  
20

### SOA formation from tertiary amines

M. E. Erupe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**SOA formation from  
tertiary amines**

M. E. Erupe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



A proton transfer reaction mass spectrometer (PTR-MS, Iconicon Analytik) was used to detect and analyze volatile organic compounds in real time and with high sensitivity. A detailed description of PTR-MS has been given by Lindinger et al. (1997) and only a summary of the key features will be given here. The instrument consists of four main components: an ion source, a drift tube, a mass analyzer (quadrupole), and an ion detector/amplifier.  $\text{H}_3\text{O}^+$  ions are produced at high concentrations from pure water vapor within a hollow cathode ion source and pass via a Venturi-type inlet into the drift tube. The air sample to be analyzed is introduced into the drift tube and because of their low proton affinities, the major components of air undergo non-reactive collisions with  $\text{H}_3\text{O}^+$  ions and therefore act as buffer gas. However, any collisions of  $\text{H}_3\text{O}^+$  ions with the volatile organic compounds (VOCs) present in the gas flow possessing a greater proton affinity than water will result in a proton transfer reaction (Eq. R1).



The resultant ions are mass-selected using a quadrupole mass analyzer and measured as count rates by an electron multiplier detector. The online PTR-MS was used in scan mode to monitor the ion traces from  $m/z$  21 to  $m/z$  200 with a dwell time of 0.2 s per mass.

5 The aerosol mass spectrometer (AMS, Aerodyne Inc.) has previously been discussed (Jayne et al., 2000; Jimenez et al., 2003; Canagaratna et al., 2007). For the experiments described here, the high resolution time of flight mass spectrometer (HR-ToF-AMS) was used and its details can be found in a paper by DeCarlo et al. (2006). Briefly, it is made up of three differentially pumped chambers; the sampling chamber,  
10 the particle time-of-flight chamber and the analysis chamber. Pressure differential between the smog chamber air and the AMS sampling chamber continuously draws air sample into the instrument at a nominal flow rate of about  $1.2 \text{ cm s}^{-1}$  where it passes through an aerodynamic lens that collimates the sample into a tight beam while removing as much gas phase species as possible. After the particles exit the lens, they  
15 enter into the particle ToF region then accelerated until they impact the oven. The non-refractory components are flash vaporized at about  $600^\circ\text{C}$  and then subjected to a

beam of electrons at 70eV that ionizes them before being sorted by a time of flight mass analyzer and detected using an MCP detector. Ion measurements were alternated between a shorter flight path (V-Mode) that gives higher ion throughput and therefore better sensitivity and the longer flight path (W-mode) that offers better separation but lower sensitivity. The strength of HR-ToF-AMS lies in its ability to offer a high resolving power of up to 4300 times for W-mode and about 2100 times for V-mode (at  $m/z$  200) better than that of the quadrupole AMS (Q-AMS). This ability was useful in definitive identification of the product peaks. The AMS was operated in the scanning mode in the mass range between  $m/z$  10 to  $m/z$  500.

## 2.1 Experimental protocol

Each experiment started with thorough cleaning of the bags as outlined in Carter et al. (2005). Background concentrations of  $\text{NO}_x$  and ozone were also determined to be at an acceptable low level (<2 ppb for ozone and  $\text{NO}_x$ ). The amines were introduced into the chamber by injecting a known volume of liquid amine into a small glass injection manifold or by introducing a known volume of the gas phase amine into a calibrated bulb based on calculated partial pressures. Pure nitrogen was then passed over the liquid or through the bulb, flushing the amine into the reactors. Injections of amines were verified using PTR-MS. Table 1 lists the initial conditions of all experiments in this paper. After amine injection, ozone was introduced by passing 20 psig of pure air through two UV ozone generators and the reaction was left to proceed until the amount of wall-loss corrected aerosol formed stabilized (usually 1–2 h). Then  $\text{NO}_x$  was added to the reactors as NO using a calibrated bulb (usually ~1–2 h after ozone addition). The reaction was left to proceed until the amount of wall-loss corrected aerosol formed leveled off (usually 2–3 h after injection of  $\text{NO}_x$ ). The ozone and  $\text{NO}_2$  in the chamber react to form nitrate radical as shown in Eq. (R2). All the experiments were conducted in the dark to simulate night-time  $\text{NO}_3$  radical chemistry.



## SOA formation from tertiary amines

M. E. Erupe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



### 3 Results

#### 3.1 TMA reaction

Smog chamber reactions of TMA with nitrate radical have been reported by Silva et al. (2008). The discussion here will only dwell on details pertinent to the objectives of this paper. Figure 1a shows a typical TMA reaction profile. In this experiment, some aerosol formed after injection of ozone. The aerosol concentration leveled off at about  $30 \mu\text{g m}^{-3}$  (This was obtained from wall-loss corrected SMPS volume concentration using density of  $1 \text{ g cm}^{-3}$ ). Four hours after ozone injection, NO was introduced leading to more aerosol formation leveling off at about  $90 \mu\text{g m}^{-3}$ . TMA quasi parent ion peak ( $m/z$  60) was monitored by the PTR-MS. This peak started decaying immediately ozone was injected. The decay continued as more TMA was converted into aerosol phase.

Table 2 displays the high intensity peaks that were detected with the PTR-MS and the assigned VOCs. Peaks at  $m/z$  31 (formaldehyde),  $m/z$  45 (acetaldehyde),  $m/z$  47 (formic acid),  $m/z$  59 (acetone/propanal) and  $m/z$  61 (acetic acid/propanol) were present in all the three tertiary amines reacted. During the TMA reaction, the PTR-MS also detected  $m/z$  74 (dimethyl formamide),  $m/z$  88 (methyldiformamide),  $m/z$  102 (triformamide),  $m/z$  91 (dimethylnitramine) and  $m/z$  75 (dimethylnitrosamine). As expected, dimethylnitramine and dimethylnitrosamine were detected only after injection of  $\text{NO}_x$ . The ion peak detected at  $m/z$  44 was specific to TMA reaction and it likely represents methyl-methyleneimine ( $\text{CH}_2=\text{NCH}_3$ ). Since imines have double bonds, they can potentially be attacked by ozone to form other products, but at least one study has indicated that this reaction is too slow to be of any significance (Mori et al., 1988).

An average mass spectrum of the particulate products from the TMA reaction with the ozone/ $\text{NO}_x$  system is shown in Fig. 1b. The ion peaks at  $m/z$  44.052 ( $\text{C}_2\text{H}_6\text{N}^+$ ) and  $m/z$  58.066 ( $\text{C}_3\text{H}_8\text{N}^+$ ) represent amine backbone fragments while  $m/z$  58.030 ( $\text{C}_2\text{H}_4\text{NO}^+$ ), 76.040 ( $\text{C}_2\text{H}_6\text{NO}_2^+$ ),  $m/z$  88.037 ( $\text{C}_3\text{H}_6\text{NO}_2^+$ ) and  $m/z$  104.040 ( $\text{C}_3\text{H}_6\text{NO}_3^+$ ) represent fragments of amines that have been oxidized. Table 3 summa-

## SOA formation from tertiary amines

M. E. Erupe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



rizes other major ion fragments detected. We examined spectra for evidence of amine-N-oxide, a possible product according to Angelino et al. (2001). Trimethylamine-N-oxide (TMAO) parent-ion peak is  $m/z$  75. The ion peak at  $m/z$  75 was detected albeit at low intensity. The HR-ToF-AMS spectrum (Fig. 2a) indicates it consists of two peaks,  $m/z$  75.029 ( $C_2H_5NO_2^+$ ) and  $m/z$  75.065 ( $C_3H_9NO^+$ ). As shown in Fig. 2b, after injection of  $NO_x$  only  $m/z$  75.029 was detected. This indicates that TMAO was present after the reaction with ozone, but was reduced after  $NO_x$  injection. There was no protonated TMAO ( $m/z$  76.073) detected in the mass spectra during either injection. The plausible explanation for this observation is that ozone indeed reacts with TMA to form TMAO, but it may be vulnerable to radical chemistry itself to form other products.

### 3.2 TEA reaction

The reaction of TEA with ozone/ $NO_x$  followed a pattern similar to that of TMA. After ozone injection, some aerosol was formed leveling off at about  $20 \mu\text{g m}^{-3}$ . Two hours later,  $NO$  was injected resulting in formation of more aerosol that leveled off at about  $40 \mu\text{g m}^{-3}$  (Fig. 3a). The amount of aerosol from TEA reaction was less than that of TMA even though TEA has higher molecular weight and should theoretically form more aerosol. Immediately after  $NO$  injection, there was sudden buildup of aerosol that quickly dropped before leveling off.

Injection of TEA was confirmed with PTR-MS by monitoring the quasi parent ion peak ( $m/z$  102) that gradually decayed during the course of the experiment as more aerosol was being formed. Other volatile products detected specific to the TEA reaction include amides: diethylacetamide ( $m/z$  119) and ethylformamide ( $m/z$  74); nitro/nitroso species: diethylnitramine ( $m/z$  116) and diethylnitrosamine ( $m/z$  103) and an imine: ethyl-ethyleneimine ( $m/z$  72).

The AMS spectrum for TEA reaction is shown in Fig. 3b. The low mass peaks for these reactions include  $m/z$  44.052 ( $C_2H_6N^+$ ),  $m/z$  58.065 ( $C_3H_8N^+$ ),  $m/z$  72.082 ( $C_4H_{10}N^+$ ) and  $m/z$  86.095 ( $C_5H_{12}N^+$ ) that represent fragments from the amine backbone. Other ions detected are  $m/z$  72.046 ( $C_3H_6NO^+$ ),  $m/z$  86.068 ( $C_4H_8NO^+$ ),  $m/z$

## SOA formation from tertiary amines

M. E. Erupe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





**SOA formation from  
tertiary amines**

M. E. Erupe et al.

102.05 ( $C_4H_8NO_2^+$ ) and  $m/z$  146.07. ( $C_6H_{12}NO_3^+$ ) In each of these cases, one, two, or three oxygen atoms have been added representing oxidized amine fragments. There were fewer high mass peaks in the TEA reaction compared to that of TMA. Shortly after the NO injection, the nitrate fragments ( $NO^+/NO_2^+$ ) were detected as shown in Fig. 4a–d. The salt burst was short-lived and did not appear in the other two amines investigated. It is likely that this observation was as a result of sudden build up in nitric acid in the chamber near the injection/sampling port. Apart from this instantaneous period, nitrate salt formation was generally minimal as depicted by the low intensity of  $NO^+$  and  $NO_2^+$  peaks at  $m/z$  30 and  $m/z$  46 respectively.

### 3.3 TBA reaction

Figure 5a presents results of the TBA reaction with ozone/ $NO_x$ . The amount of aerosol formed after ozone injection (at  $\sim 60 \mu g m^{-3}$ ) was more than the total amount of aerosol formed during the TEA-ozone/ $NO_x$  reaction. This was expected because TBA is a twelve-carbon compound and the oxidation products are expected to have lower vapor pressure. The maximum aerosol recorded for the TBA reaction was  $\approx 160 \mu g m^{-3}$  after injection of NO approximately 3 h after ozone injection.

PTR-MS quasi parent peaks of  $m/z$  60 (TMA) and  $m/z$  102 (TEA) showed clear decay in the course of the experiment. This was not the case with TBA quasi parent peak ( $m/z$  186) which was not detected even though TBA has the highest proton affinity of the three tertiary amines (Green-Church et al., 2000). A possible explanation could be that the ion transmission efficiency was lower for TBA parent ion than the other two amines. Volatile products detected by the PTR-MS for the TBA reaction were similar to those formed by TMA and TEA (Table 2) and include an amide (dibutylbutanamide;  $m/z$  200), a nitro-compound (dibutylnitramine;  $m/z$  175), a nitroso-compound (dibutyl-nitrosamine;  $m/z$  159) and an imine (butyl-butyleneimine;  $m/z$  128).

Figure 5b shows the AMS mass spectrum for the TBA reaction where high intensity ion peaks were detected at  $m/z$  44.052 ( $C_2H_6N^+$ ),  $m/z$  58.065 ( $C_3H_8N^+$ ),  $m/z$

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

72.082 ( $C_4H_{10}N^+$ ),  $m/z$  86.095 ( $C_5H_{12}N^+$ ) and  $m/z$  126 ( $C_8H_{16}N^+$ ). The oxygenated fragments from TBA reaction were  $m/z$  100 ( $C_5H_{10}NO^+$ ),  $m/z$  142 ( $C_8H_{16}NO^+$ ),  $m/z$  174 ( $C_8H_{16}NO_3^+$ ) and  $m/z$  230 ( $C_{12}H_{24}NO_3^+$ ). Others ions are listed in Table 3.

### 3.4 Reaction mechanism

Patterns in both gas phase and aerosol phase products emerged from all three tertiary amines reacted. Homologous volatile products include amides, nitro/nitroso compounds and imines. Formation of aminium salt with nitric acid was minimal, based on the low intensities of nitrate ions ( $m/z$  30 and 46). The high mass fragments  $C_3H_6NO_3^+$  ( $m/z$  104),  $C_6H_{12}NO_3^+$  ( $m/z$  146) and  $C_{12}H_{24}NO_3^+$  ( $m/z$  230) from TMA, TEA and TBA reactions are similar. These high mass fragments indicate that each tertiary amine gains three oxygen atoms during the reaction while losing three hydrogen atoms. Because molecules containing one nitrogen atom in the structure must have an odd molecular mass, the ion peak at  $m/z$  104 for TMA ( $C_3H_6NO_3^+$ ) is a fragment ion of a larger molecule. Further, the degree of unsaturation suggests the structure contains only one double bond. This ion is replicated for TEA at  $m/z$  146 ( $C_6H_{12}NO_3^+$ ) and for TBA at  $m/z$  230 ( $C_{12}H_{24}NO_3^+$ ). The structure for all three tertiary amines is consistent with the formation of a di-hydroxylated amides. This structure can account for all high mass fragments present in the spectra for all three compounds with the exception of the TMA reaction where it appeared to be forming dimers, possibly oligomers (Silva et al., 2008).

With the high resolution aerosol mass spectra and gas phase species detected by PTR-MS, we propose a reaction mechanism for the ozone/ $NO_x$  interaction with tertiary amines as shown in Fig. 6. Some of the products detected are shown with bold numbers (1–11) in Fig. 6 and the text below.

The reaction with the nitrate radical starts with an initial abstraction step of the hydrogen atom from one of the alkyl groups in the amine. The resulting amine alkyl radical then reacts solely with  $O_2$  to form an aminyl alkylperoxy radical, which reacts with NO to form an aminyl alkoxy radical. The aminyl alkoxy radical then either reacts

## SOA formation from tertiary amines

M. E. Erupe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**SOA formation from tertiary amines**

M. E. Erupe et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

with O<sub>2</sub> to form dimethylformamide (1) or decomposes to form formaldehyde (2) and an aminyl alkyl radical. The resulting aminyl alkyl radical can react with NO or NO<sub>2</sub> to form dimethylnitrosamine (3) and dimethylnitramine (4) respectively or it can lose a proton to form methyl-methyleneimine (5). This procedure, starting with the initial abstraction of proton from the alkyl group can repeat itself until methyl-diformamide (6) and triformamide (7) are formed.

For aerosol formation, we propose that the reaction proceeds via rearrangement of the aminyl alkoxy radical through 1,4 H-shift to form a hydroxyaminyl alkyl radical that then reacts with oxygen, NO and oxygen again to form hydroxymethyl-methylformamide (8). This procedure can be repeated until formyl-hydroxymethyl-formamide (9) and N, N-bis(hydroxymethyl) formamide (10) are formed. The vapor pressures of the hydroxylated products are calculated to be much lower than the corresponding aldehydes. For example, the theoretical estimation of the vapor pressure of dihydroxymethyl-formamide is  $\sim 6.38 \times 10^{-8}$  Torr, at 25°C, and would therefore be consistent with a condensed phase species (Scifinder Scholar, 2008). The major high mass AMS peaks for TMA reaction such as C<sub>3</sub>H<sub>6</sub>NO<sub>3</sub><sup>+</sup> (*m/z* 104) and C<sub>3</sub>H<sub>6</sub>NO<sub>2</sub><sup>+</sup> (*m/z* 88) can well be explained from loss of proton and OH respectively from N, N-bis(hydroxymethyl) formamide. Formation of aerosol via the ozone only route has been previously reported by Tuazon et al. (1994). In this mechanism for example, TMA is oxidized to TMAO (11) as hypothesized by Angelino et al. (2001).

Since TMA products exhibit oligomeric properties, this is possible through fusing together of two or more C<sub>3</sub>H<sub>6</sub>NO<sub>3</sub><sup>+</sup> at the OH end with loss of one proton resulting in a repeating unit of *m/z* 103. This explains AMS peaks such as *m/z* 207 (two C<sub>3</sub>H<sub>6</sub>NO<sub>3</sub><sup>+</sup> with a loss of proton) and *m/z* 191 (two C<sub>3</sub>H<sub>6</sub>NO<sub>3</sub><sup>+</sup> with a loss of OH). Since this repeating behavior was not seen in TEA and TBA (perhaps due to steric hindrance), it also explains why TMA, a three-carbon compound formed more aerosol than TEA which is a six-carbon compound.

## 4 Implication

This study shows that tertiary amines, major constituents of animal husbandry practices do react with nitrate radical, an important night-time oxidant. The products include both gas phase species and secondary organic aerosol formation (SOA).

5

*Acknowledgements.* This research was supported by the National Science Foundation under grants ATM-0735396 and ATM-0449778 and the W. M. Keck Foundation.

## References

- Angelino, S., Suess, D. T., and Prather, K. A.: Formation of aerosol particles from reactions of secondary and tertiary alkylamines: Characterization by aerosol time-of-flight mass spectrometry, *Environ. Sci. Technol.*, **35**, 3130–3138, 2001.
- Bowman, F. M., Odum, J. R., Seinfeld, J. H., and Pandis, S. N.: Mathematical model for gas-particle partitioning of secondary organic aerosols, *Atmos. Environ.*, **31**, 3921–3931, 1997.
- Cadle, S. H. and Mulawa, P. A.: Low molecular weight aliphatic amines in exhaust from catalyst-equipped cars, *Environ. Sci. Technol.*, **14**, 718–723, 1980.
- Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Chemical and microphysical characterization of ambient aerosols with the Aerodyne aerosol mass spectrometer, *Mass Spectrom. Rev.*, **26**, 185–222, 2007.
- Carter, W. P. L., Cocker, D. R., Fitz, D. R., Malkina, I. L., Bumiller, K., Sauer, C. G., Pisano, J. T., Bufalino, C., and Song C.: A new environmental chamber for evaluation of gas-phase chemical mechanisms and secondary aerosol formation, *Atmos. Environ.*, **39**, 7768–7788, 2005.
- Chang, J. S., Abu-Orf, M., and Dentel, S. K.: Alkylamine odors from degradation of flocculant polymers in sludges, *Water Res.*, **39**, 3369–3375, 2005.
- DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K., Worsnop, D. R., and Jimenez, J. L.: Field-deployable,

ACPD

8, 16585–16608, 2008

## SOA formation from tertiary amines

M. E. Erupe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



high-resolution, time-of-flight aerosol mass spectrometer, *Anal. Chem.*, 78, 8281–8289, 2006.

Dockery, D. W. and Pope, C. A.: Mortality risks of air pollution: A prospective cohort study, *New Engl. J. Med.*, 329, 1753–1759, 1993.

Filipy, J., Rumburg, B., Mount, G., Westberg, H., and Lamb, B.: Identification and quantification of volatile organic compounds from a dairy, *Atmos. Environ.*, 40, 1480–1494, 2006.

Finlayson-Pitts, B. J. and Pitts Jr., J. N.: *Chemistry of the upper and lower atmosphere*, Academic Press, NYC, USA, 2000.

Green-Church, K. B. and Limbach, P. A.: Mononucleotide gas-phase proton affinities as determined by the kinetic method, *J. Am. Soc. Mass Spectr.*, 11, 24–32, 2000.

IPCC: Summary for Policymakers, in: *Climate Change 2007: the Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, UK and New York, NY, USA, 2007.

Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R.: Development of an aerosol mass spectrometer for size and composition analysis of submicron particles, *Aerosol Sci. Tech.*, 33, 49–70, 2000.

Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X., Smith, K. A., Morris, J., and Davidovits, P.: Ambient aerosol sampling with an aerosol mass spectrometer, *J. Geophys. Res.-Atmos.*, 108(D7), 8425, doi:10.1029/2001JD001213, 2003.

Kataoka, H.: Derivatization reactions for the determination of amines by gas chromatography and their applications in environmental analysis, *J. Chromatogr. A*, 733, 19–34, 1996.

Lindinger, W. and Hansel, A.: Analysis of trace gases at ppb levels by proton transfer reaction mass spectrometry (PTR-MS), *Plasma Sources Sci. T.*, 6, 111–117, 1997.

Mori, M., Nojima, M., Kubayashi, S., and Mccullough, K. J.: Synthesis of 1,2,4-diazolidines by the ozonolysis of vinyl ethers in the presence of imines: the first [3+2] cycloaddition of carbonyl oxide to the carbon-nitrogen bond, *J. Chem. Soc. Chem. Comm.*, 1150–1552, 1988.

Mosier, A. R., Andre, C. E., and Viets Jr., F. G.: Identification of aliphatic amines volatilized from cattle feedyard, *Environ. Sci. Technol.*, 7, 642–644, 1973.

Murphy, D. M. and Thomson, D. S.: Chemical composition of single aerosol particles at Idaho

**SOA formation from tertiary amines**

M. E. Erupe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**SOA formation from  
tertiary amines**

M. E. Erupe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Hill: Positive ion measurements, *J. Geophys. Res.*, 102, 6341–6352, 1997.

Murphy, S. M., Sorooshian, A., Kroll, J. H., Ng, N. L., Chhabra, P., Tong, C., Surratt, J. D., Knipping, E., Flagan, R. C., and Seinfeld, J. H.: Secondary aerosol formation from the atmospheric reactions of aliphatic amines, *Atmos. Chem. Phys.*, 7, 2313–2337, 2007,  
5 <http://www.atmos-chem-phys.net/7/2313/2007/>.

Pitts, J. N., Grosjean, D., Vancauwenberghe, K., Schmid, J. P., and Fitz, D. R.: Photo oxidation of aliphatic-amines under simulated atmospheric conditions – formation of nitrosamines, nitramines, amides, and photo-chemical oxidant, *Environ. Sci. Technol.*, 12, 946–953, 1978.

Rabaud, N. E., Ebelerb, S. E., Ashbaugh, L. L., and Flocchini, R. G.: Characterization and  
10 quantification of odorous and non-odorous volatile organic compounds near a commercial dairy in California, *Atmos. Environ.*, 37, 933–940, 2003.

Rappert, S. and Muller R.: Microbial degradation of selected odorous substances, *Waste Manage.*, 25, 940–954, 2005.

Schade, G. W. and Crutzen, P. J. J.: Emissions of aliphatic amines from animal husbandry and their reactions: Potential source of N<sub>2</sub>O and HCN, *J. Atmos. Chem.*, 22, 319–346, 1995.

Scifinder Scholar: Calculated using Advanced Chemistry Development (ACD/Labs) Software V8.14 for Solaris (© 1994–2008 ACD/Labs), 2008.

Seinfeld, J. H. and Pankow, J. F.: Organic atmospheric particulate material, *Annu. Rev. Phys. Chem.*, 54, 121–140, 2003.

20 Silva, P. J., Erupe, M. E., Derek, P., Elias, J., Malloy, Q. G. J., Qi, L., Warren, B., and Cocker III, D. R.: Trimethylamine as precursor to secondary organic aerosol formation via nitrate radical reaction in the atmosphere, *Environ. Sci. Technol.*, 42, 4689–4696, 2008.

Tan, P. V., Evans, G. J., Tsai, J., Owega, S., Fila, M. S., Malpica, O., and Brook, J. R.: On-line analysis of urban particulate matter focusing on elevated wintertime aerosol concentrations, *Environ. Sci. Technol.*, 36, 3512–3518, 2002.

25 Tuazon, E. C., Atkinson, R., Aschmann, S. M., and Arey, J.: Kinetics and products of the gas-phase reactions of O<sub>3</sub> with amines and related-compounds, *Res. Chem. Intermediat.*, 20, 303–320, 1994.

Watson, J. G.: Visibility: science and regulation, *J. Air Waste Manage.*, 52, 628–713, 2002.

30 Westerholm, R., Li, H., and Almen, J.: Estimation of 5 aliphatic amine emissions in automobile exhausts, *Chemosphere*, 27, 1381–1384, 1993.

Wright, J. L. C. and Vining, L. C.: Secondary metabolites derived from non-aromatic amino acids, *Filamentous Fungi*, 2, 475–502, 1976.

- You, J., Zhang, W., Zhang, Q., Zhang, L., Yan, C., and Zhang, Y.: Development of a precolumn derivatization method for the determination of free amines in wastewater by high-performance liquid chromatography via fluorescent detection with 9-(2-hydroxyethyl)acridone, *Anal. Chem.*, 74, 261–269, 2002.
- 5 Zhang, Q. and Anastasio, C.: Conversion of fogwater and aerosol organic nitrogen to ammonium, nitrate, and  $\text{NO}_x$  during exposure to simulated sunlight and ozone, *Environ. Sci. Technol.*, 37, 3522–3530, 2003.

ACPD

8, 16585–16608, 2008

---

**SOA formation from  
tertiary amines**

M. E. Erupe et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**SOA formation from  
tertiary amines**

M. E. Erupe et al.

**Table 1.** Initial conditions and results obtained from reaction of tertiary amines with ozone/NO<sub>x</sub>.

Amine	[Amine] (ppb)	[NO <sub>x</sub> ] (ppb)	[Ozone] (ppb)	[Aerosol] <sub>max</sub> (μm <sup>3</sup> cm <sup>-3</sup> )
Trimethylamine	100	50	300	90
Triethylamine	100	40	245	40
Tributylamine	100	35	255	110

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



SOA formation from  
tertiary amines

M. E. Erupe et al.

**Table 2.** Major PTR-MS peaks and assigned VOCs.

TMA <i>m/z</i>	Formula	VOC	TEA <i>m/z</i>	Formula	VOC	TBA <i>m/z</i>	Formula	VOC
31	HCHO	Formaldehyde	31	HCHO	Formaldehyde	31	HCHO	Formaldehyde
33	CH <sub>3</sub> OH	Methanol	45	CH <sub>3</sub> CHO	Acetaldehyde	45	CH <sub>3</sub> CHO	Acetaldehyde
44	CH <sub>3</sub> NCH <sub>2</sub>	Methylmethyleimine	47	HCOOH/CH <sub>3</sub> CH <sub>2</sub> OH	Formic Acid/Ethanol	47	HCOOH CH <sub>3</sub> CH <sub>2</sub> OH	Formic Acid Ethanol
45	CH <sub>2</sub> CHO	Acetaldehyde	59	(CH <sub>3</sub> ) <sub>2</sub> CO CH <sub>3</sub> CH <sub>2</sub> CHO	Acetone Propanal	59	(CH <sub>3</sub> ) <sub>2</sub> CHO CH <sub>3</sub> CH <sub>2</sub> CHO	Acetone Propanal
47	HCOOH CH <sub>3</sub> OH	Formic Acid Ethanol	60	CH <sub>3</sub> CH <sub>2</sub> NO	Nitrosoethane	61	CH <sub>3</sub> COOH CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> OH	Acetic acid Propanol
59	(CH <sub>3</sub> ) <sub>2</sub> CO/CH <sub>3</sub> CH <sub>2</sub> CHO	Acetone/Propanal	61	(CH <sub>3</sub> ) <sub>2</sub> CO/CH <sub>3</sub> CH <sub>2</sub> CHO	Acetic Acid/Propanol	73	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO	Butanal
60	(CH <sub>3</sub> ) <sub>3</sub> N	Trimethylamine	72	CH <sub>3</sub> CH <sub>2</sub> NCH <sub>3</sub>	Ethylidene-Ethanamine	75	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> OH	Butanol
61	CH <sub>3</sub> COOH CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> OH	Acetic Acid Propanol	74	CH <sub>3</sub> CH <sub>2</sub> NCHO	EthylFormamide	100	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> NO <sub>2</sub>	Nitrobutane
62	CH <sub>3</sub> NO <sub>2</sub>	Nitromethane	76	CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub>	Nitroethane	128	C <sub>4</sub> H <sub>9</sub> NCH(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	Butylimine
74	(CH <sub>3</sub> ) <sub>2</sub> NCHO	Dimethylformamide	102	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> N	Triethylamine	159	[CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> NNO	Dibutylnitrosamine
75	(CH <sub>3</sub> ) <sub>2</sub> NNO	Dimethylnitrosamine	103	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NNO	Diethylnitrosamine	175	[CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> NNO <sub>2</sub>	Dibutylnitramine
88	CH <sub>3</sub> N(CHO) <sub>2</sub>	Methylidformamide	116	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> CHO	Diethylacetamide	186	[CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> N	Tributylamine
90	CH <sub>2</sub> OHCH <sub>2</sub> NCHO	Hydoxymethylmethylformamide	119	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NNO <sub>2</sub>	Diethylnitramine	200	[C <sub>4</sub> H <sub>9</sub> ] <sub>2</sub> N(CH <sub>2</sub> ) <sub>3</sub> CHO	Dibutylbutanamide
91	(CH <sub>3</sub> ) <sub>2</sub> NNO <sub>2</sub>	Dimethylnitramine						
102	(CHO) <sub>3</sub> N	Triformamide						

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



SOA formation from  
tertiary amines

M. E. Erupe et al.

**Table 3.** Major AMS ion peaks and assignments.

<i>m/z</i>	TMA Formula	<i>m/z</i>	TEA Formula	<i>m/z</i>	TBA Formula
30.010	CH <sub>2</sub> O <sup>+</sup>	30.000	NO <sup>+</sup>	44.027	C <sub>2</sub> H <sub>4</sub> O <sup>+</sup>
30.036	CH <sub>4</sub> N <sup>+</sup>	30.036	CH <sub>4</sub> N <sup>+</sup>	44.051	C <sub>2</sub> H <sub>6</sub> N <sup>+</sup>
43.982	CO <sub>2</sub> <sup>+</sup>	44.024	C <sub>2</sub> H <sub>4</sub> O <sup>+</sup>	58.065	C <sub>3</sub> H <sub>8</sub> N <sup>+</sup>
44.052	C <sub>2</sub> H <sub>6</sub> N <sup>+</sup>	44.052	C <sub>2</sub> H <sub>6</sub> N <sup>+</sup>	72.080	C <sub>4</sub> H <sub>10</sub> N <sup>+</sup>
45.993	NO <sub>2</sub> <sup>+</sup>	58.066	C <sub>3</sub> H <sub>8</sub> N <sup>+</sup>	86.092	C <sub>5</sub> H <sub>12</sub> N <sup>+</sup>
46.03	CH <sub>4</sub> NO <sup>+</sup>	72.046	C <sub>3</sub> H <sub>6</sub> NO <sup>+</sup>	100.080	C <sub>5</sub> H <sub>10</sub> NO <sup>+</sup>
58.066	C <sub>3</sub> H <sub>8</sub> N <sup>+</sup>	72.082	C <sub>4</sub> H <sub>10</sub> N <sup>+</sup>	114.090	C <sub>6</sub> H <sub>12</sub> NO <sup>+</sup>
76.040	C <sub>2</sub> H <sub>6</sub> NO <sub>2</sub> <sup>+</sup>	86.068	C <sub>4</sub> H <sub>8</sub> NO <sup>+</sup>	126.130	C <sub>8</sub> H <sub>16</sub> N <sup>+</sup>
88.040	C <sub>3</sub> H <sub>6</sub> NO <sub>2</sub> <sup>+</sup>	86.095	C <sub>5</sub> H <sub>12</sub> N <sup>+</sup>	142.120	C <sub>8</sub> H <sub>16</sub> NO <sup>+</sup>
104.040	C <sub>3</sub> H <sub>6</sub> NO <sub>3</sub> <sup>+</sup>	102.050	C <sub>4</sub> H <sub>8</sub> NO <sub>2</sub> <sup>+</sup>	158.120	C <sub>8</sub> H <sub>16</sub> NO <sub>2</sub> <sup>+</sup>
191.070	C <sub>6</sub> H <sub>11</sub> N <sub>2</sub> O <sub>5</sub> <sup>+</sup>	130.080	C <sub>6</sub> H <sub>12</sub> NO <sub>2</sub> <sup>+</sup>	174.110	C <sub>8</sub> H <sub>16</sub> NO <sub>3</sub> <sup>+</sup>
207.060	C <sub>6</sub> H <sub>11</sub> N <sub>2</sub> O <sub>6</sub> <sup>+</sup>	146.070	C <sub>6</sub> H <sub>12</sub> NO <sub>3</sub> <sup>+</sup>	214.180	C <sub>12</sub> H <sub>24</sub> NO <sub>2</sub> <sup>+</sup>
				230.170	C <sub>12</sub> H <sub>24</sub> NO <sub>3</sub> <sup>+</sup>

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

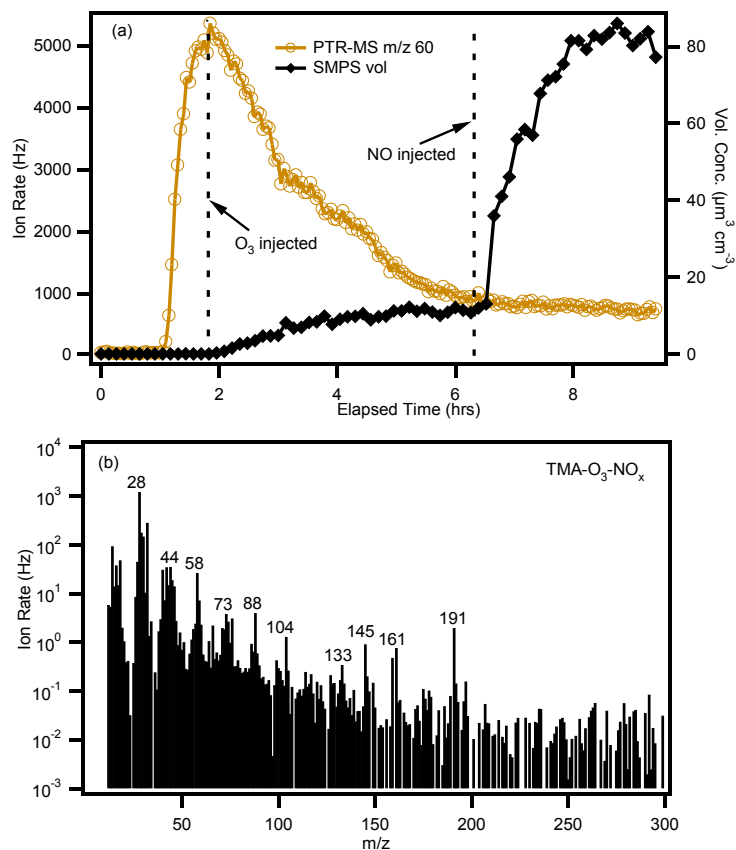
Printer-friendly Version

Interactive Discussion



SOA formation from  
tertiary amines

M. E. Erupe et al.

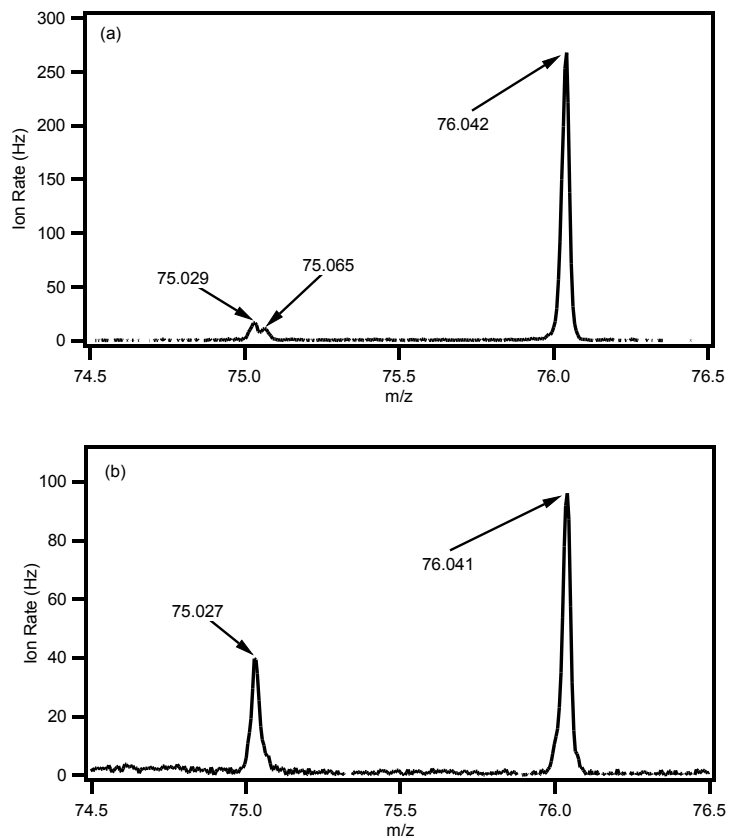


**Fig. 1.** Panel (a) Temporal profiles of  $m/z$  60 (from PTR-MS) and aerosol volume concentration (from SMPS) for the reaction of TMA with ozone/ $\text{NO}_x$ . Panel (b) Aerosol mass spectrum taken at the end of the experiment after the SMPS volume concentration leveled off.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

SOA formation from  
tertiary amines

M. E. Erupe et al.

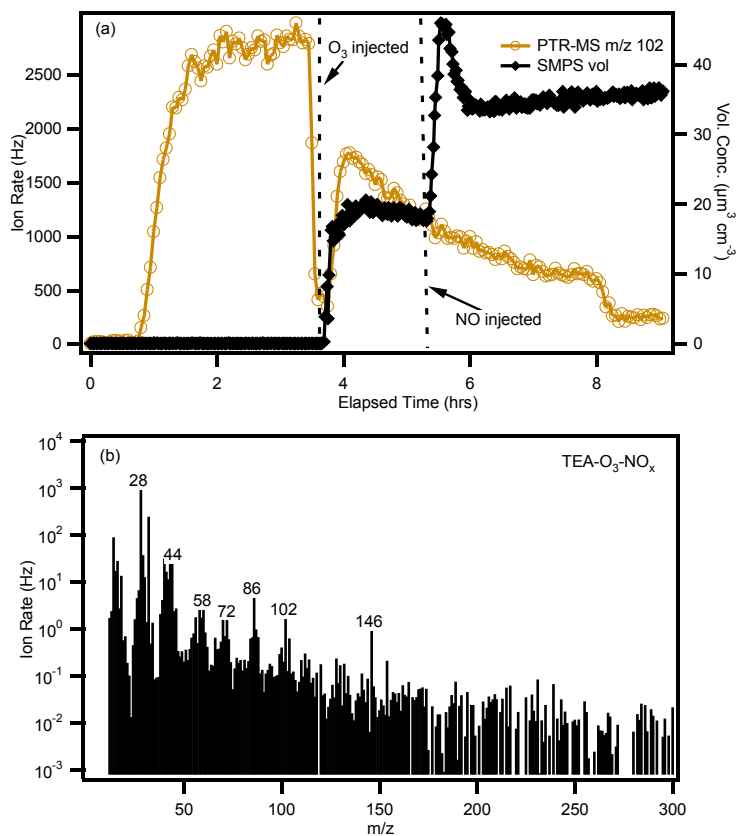


**Fig. 2.** Expanded  $m/z$  75 and  $m/z$  76 peaks from the HR-ToF-AMS. Panel (a) TMA- $O_3$  reaction system. Panel (b) TMA- $O_3$ - $NO_x$  reaction system.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

SOA formation from  
tertiary amines

M. E. Erupe et al.

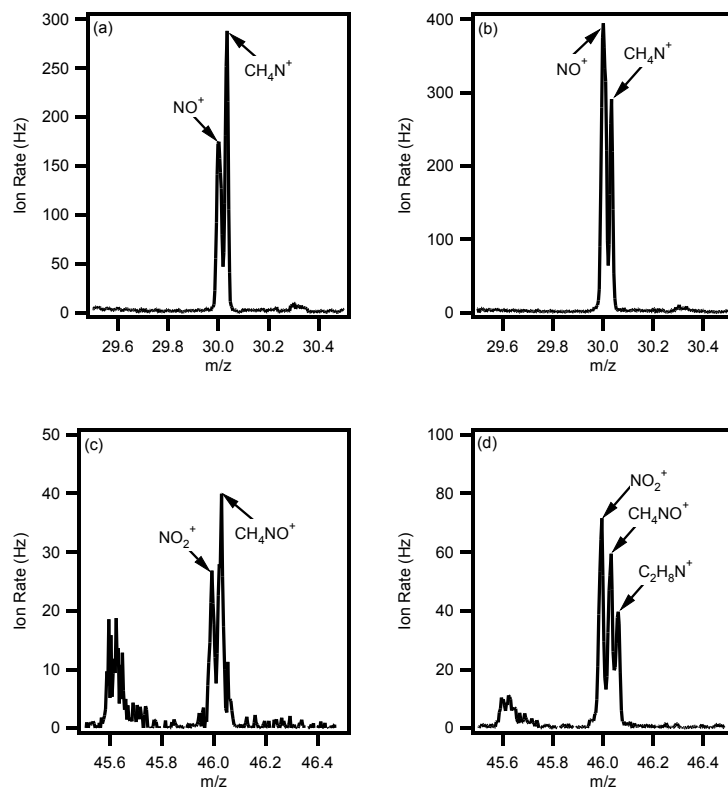


**Fig. 3.** Panel (a) Temporal profiles of  $m/z$  102 (from PTR-MS) and aerosol volume concentration (from SMPS) for the reaction of TEA with ozone/ $\text{NO}_x$ . Panel (b) Aerosol mass spectrum taken at the end of the experiment after the SMPS volume concentration leveled off.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

SOA formation from  
tertiary amines

M. E. Erupe et al.

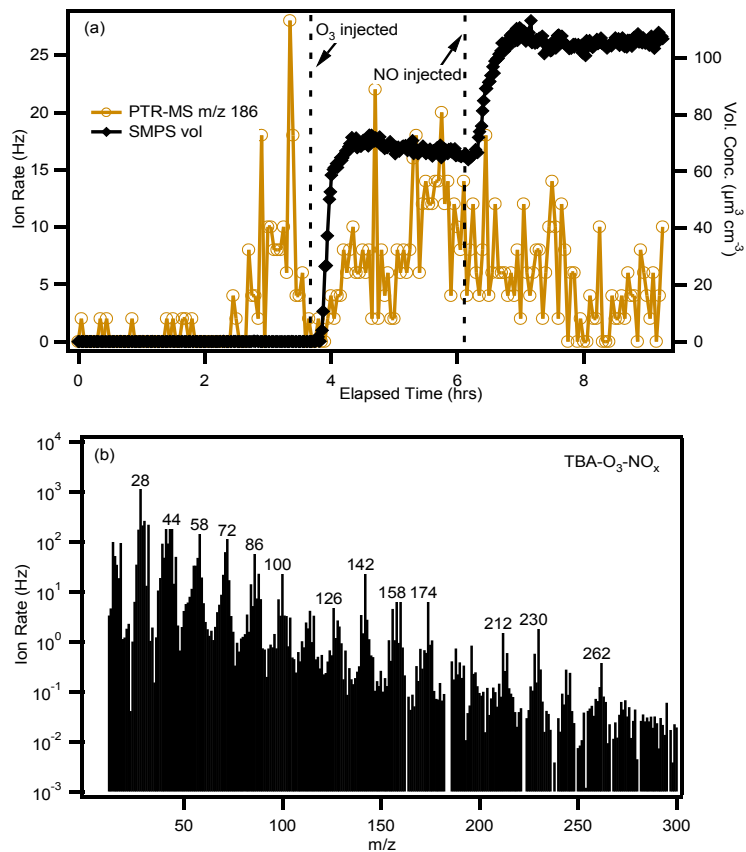


**Fig. 4.** Expanded product peaks for the TEA reaction (from HR-ToF-AMS): **(a)**  $m/z$  30 after ozone injection, **(b)**  $m/z$  30 shortly after  $\text{NO}_x$  injection, **(c)**  $m/z$  46 after ozone injection, **(d)**  $m/z$  46 shortly after  $\text{NO}_x$  injection.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

SOA formation from  
tertiary amines

M. E. Erupe et al.

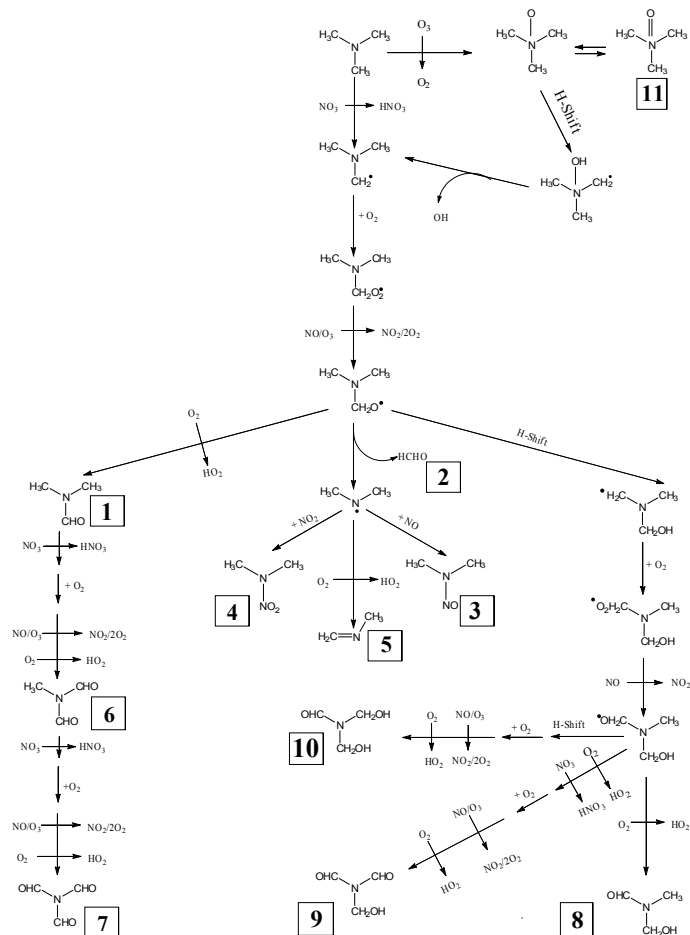


**Fig. 5.** Panel (a) Temporal profiles of  $m/z$  186 (from PTR-MS) and aerosol volume concentration (from SMPS) for the reaction of TBA with ozone/ $\text{NO}_x$ . Panel (b) Aerosol mass spectrum taken at the end of the experiment after the SMPS volume concentration leveled off.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

SOA formation from  
tertiary amines

M. E. Erupe et al.



**Fig. 6.** Proposed mechanism for the reaction of TMA with nitrate radical. TMA oxidation by ozone (Tuazon et al., 1994) is also shown.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

