



New Insights Into the Atmospheric Role and Fate of Reactive Intermediates from Chemical Ionization Mass Spectrometry

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New insights into the atmospheric role and fate of reactive intermediates from chemical ionization mass spectrometry

A DISSERTATION PRESENTED

BY

ALEXANDER ZAYTSEV

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New insights into the atmospheric role and fate of reactive intermediates from chemical ionization mass spectrometry

ABSTRACT

Atmospheric radical and reactive intermediate species control the oxidative removal of many natural trace gases and anthropogenic compounds in the troposphere. This process results in formation of secondary pollutants, such as ozone and particulate matter, which have large impacts on climate and human health. High reactivity and rapid cycling of radicals and reactive intermediates determine their key importance in the atmosphere but also make quantification of these components challenging. Extremely sensitive detection systems are required to measure minute mixing ratio, typically a few parts per trillion or less, of these short-lived species. In this work, a new chemical ionization mass spectrometer (CIMS) was developed and built. This instrument can be operated in two ionization modes: hydronium reagent ions (H_3O^+ CIMS) are used to detect the broadest range of organic species, while the use of ammonia reagent ions (NH_4^+ CIMS) allows for quantification of a plethora of oxidized organic compounds without the need of their direct calibration. CIMS instrumentation was further implemented to study photooxidation chemistry of several aromatic compounds and the fate of produced bicyclic peroxy radicals (RO_2). It was shown that under relevant urban conditions these radicals can undergo unimolecular reactions leading to the formation of highly oxygenated organic

molecules that contribute significantly to secondary organic aerosol formation. In addition, CIMS was coupled with spin trapping and chemical derivatization techniques to detect peroxy radicals and Criegee intermediates (CIs) produced via ozonolysis of several alkenes. Effective stabilization and scavenging of CIs and RO₂ species using spin traps and chemical derivatization agents allow for suppression of the radical secondary chemistry, which eliminates potential interferences. This analytical method was used for integrated production measurements of CIs and RO₂ in laboratory experiments and can be implemented for detecting these components in the ambient atmosphere in the future.

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TO MY FAMILY.

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*Alice laughed. 'There's no use trying,' she said. 'One can't
believe impossible things.'*

'I daresay you haven't had much practice,' said the Queen.

*'When I was your age, I always did it for half-an-hour a
day. Why, sometimes I've believed as many as six impossible
things before breakfast.'*

Lewis Carroll

1

Introduction

1.1 ATMOSPHERIC OXIDATION BY OH AND O₃

THE TROPOSPHERE CAN BE THOUGHT as behaving like a low-temperature combustion system, with hydrocarbons, also known as volatile organic compounds (VOCs), acting as 'fuel' and atmospheric radicals serving as catalysts in the oxidative process¹. VOCs are

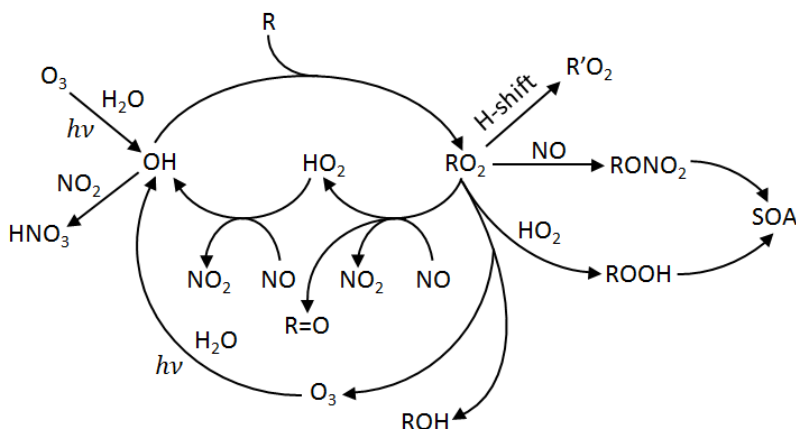


Figure 1.1.1: Simplified scheme of atmospheric oxidation of a generic volatile compound, R . The scheme shows radical cycling of OH , HO_2 and RO_2 . The conversion of NO to NO_2 leads to formation of tropospheric ozone. The oxidation products $ROOH$ and $RONO_2$ may be less volatile than the original compound R and therefore contribute to formation of secondary organic aerosol.

emitted into the atmosphere mainly from biogenic sources as well as anthropogenic activity. While the details of the atmospheric oxidation of these compounds are complex, the overall oxidation process follows a general pattern. The initial step of this process involves reaction of the parent VOC with an atmospheric radical, such as hydroxy radical (OH), ozone (O_3), NO_3 , or Cl - and Br -atoms. A simplified overview of the OH -initiated oxidation scheme of a generic VOC, R , is shown in Fig. 1.1.1.

The primary source of OH in the atmosphere is photolysis of ozone in the presence of water. The reaction of OH with a generic VOC, R , leads to the production of an organic peroxy radical, RO_2 . The fate of organic peroxy radicals depends on the atmospheric

conditions. Under urban high-NO conditions, the dominant fate of RO_2 is reaction with NO resulting in the formation of organonitrates RONO_2 or alkoxy radicals RO that can further decompose. Under more pristine low-NO conditions, RO_2 predominantly react with HO_2 or other RO_2 and form hydroperoxides ROOH and carbonyls R=O . In addition, peroxy radicals can undergo unimolecular H migration followed by O_2 addition (so-called “autooxidation”), leading to the formation of highly oxygenated organic molecules² (HOMs). Ultimately, gas-phase organic compounds, if they remain in the atmosphere, are oxidized to carbon dioxide³. Detailed understanding of oxidative processes requires speciated measurements of oxidizing compounds that are present in the atmosphere.

Ozone is another important atmospheric oxidant. Ozonolysis of alkenes results in the formation of primary ozonides that rapidly decompose to a stable carbonyl and a vibrationally excited carbonyl oxide, also known as a Criegee intermediate (CI) (Fig 1.1.2). An excited Criegee intermediate can further decompose or form a stabilized Criegee intermediate (sCI) via collisional relaxation. Decomposition of sCI can be a significant source of OH and HO_2 radicals, accounting for up to 12% of the overall OH production in certain regions of the world⁴. In addition, sCIs have been shown to be highly reactive towards sulfur dioxide (SO_2), resulting in formation of sulfuric acid⁵.

Comprehensive and precise speciated measurements of VOCs, their oxidation products as well as radicals and reactive intermediates are necessary to understand atmo-

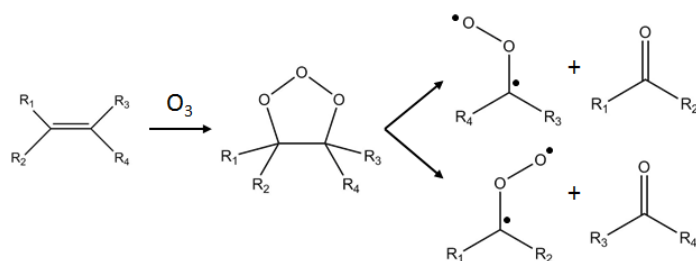


Figure 1.1.2: Ozonolysis of alkenes occurs via formation of a primary ozonide followed by a decomposition to a carbonyl and a Criegee intermediate.

spheric chemistry leading to the production of tropospheric ozone and particulate matter, which is in turn required to inform policy decisions aimed at improving air quality around the world. However, these measurements are challenging: it is estimated that there are 10^4 to 10^5 individual organic species both in the gas- and particle-phases in a typical air sample⁶. The chemical composition and the individual mixing ratios of these organic species vary significantly, both spatially and temporally. While the measurements of organic species are already challenging, atmospheric radicals and reactive intermediates are even more difficult to detect due to their high reactivity and fast cycling. Extremely sensitive detection systems with specialized sampling lines, which eliminate wall losses and secondary reactions, are required to measure the minute radical concentrations, typically less than a few parts per trillion⁷. Classical monitoring techniques, such as UV absorption and electron spin resonance, cannot speciate among those components. Improvements to the current state-of-the-art measurements of organic compounds are still possible and would help the community better understand oxidative

chemistry in the atmosphere.

1.2 MEASUREMENT OF GAS- AND PARTICLE-PHASE ORGANICS USING CHEMICAL IONIZATION MASS SPECTROMETRY

Several different methods have been developed to conduct in-situ online measurements of organic compounds in the atmosphere. Optical spectroscopy techniques are extensively used for speciated measurements of very small organic compounds (C_1 , C_2). Optical spectroscopies are the only analytical techniques applicable for remote sensing⁸. However, these techniques mainly provide information specific to chemical groups and bonds, rather than full structural information. Hence, optical spectroscopy is more often implemented for the quantification of known small organic compounds than for the identification of unknown atmospheric species⁹.

Another class of methods is based on gas chromatography (GC). GC techniques have very low detection limits if used with cryogenic or absorbed pre-concentration methods. They can also be used to unambiguously identify detected compounds and provide their molecular structure⁸. However, GC techniques usually have lower time resolution, with typical sample periods from dozens of minutes to several hours. Pre-treatment steps, including removal of water and ozone and various pre-concentration techniques, may result in loss of specific classes of organic compounds or lead to measurement interferences^{10,11}.

Chemical ionization mass spectrometry (CIMS) techniques provide a complimentary approach. A typical CIMS instrument consists of three parts: a reagent ion source, an ion-molecule reaction chamber and a mass spectrometer. Reagent ions are commonly generated by glow discharge¹² or a radioactive ion source¹³. These ions subsequently undergo ligand switching, reactive electron or proton transfer reactions with analyte molecules resulting in the formation of product ions which are detected by a mass spectrometer. Modern CIMS instruments routinely use time-of-flight mass spectrometers (ToF-MS) which allow for simultaneous detection of all individual product ions and obtaining their chemical composition. Some of the benefits of CIMS instruments include high sensitivity, fast time response, linearity, and reproducibility. Detection efficiency and sensitivity of CIMS depend critically on both the reagent ion and the measured sample molecule¹⁴. A variety of reagent ions of both polarities can be used to detect different classes of VOCs and their oxidation products. Nitrate ion CIMS has been used to detect highly oxidized organic molecules as well as sulfuric acid^{15,16}. Iodide adduct CIMS and acetate CIMS (both negative ion polarity) have played a key role in the measurement of carboxylic acids^{17,18}. CF_3O^- CIMS has been used to measure specific classes of VOCs such as hydroperoxides¹⁹. Protonated water clusters have been used to detect a broad range of chemical compounds containing oxygen, nitrogen, and sulfur^{20,21}. In this case ionization of analyte molecules primarily occurs via proton transfer from hydronium ions (H_3O^+) or exothermic ligand switching reactions with the hydronium water clusters $(\text{H}_2\text{O})_n \cdot \text{H}_3\text{O}^+$. Hence, this analytical method is called proton-transfer-reaction

mass spectrometry (PTR-MS). Although proton transfer reactions can be achieved with several different reagents, such as methane, isobutene, or ammonia, in atmospheric applications “PTR-MS” almost exclusively refers to proton transfer using hydronium ions and hydronium water clusters. Therefore, the terms “PTR-MS” and “ H_3O^+ CIMS” will be used interchangeably throughout this dissertation. Recently, two new proton-transfer-reaction time-of-flight mass spectrometers have been developed: the PTR₃²² and the Vocus 2R PTR-TOF²³. Both instruments show sensitivities exceeding 10 000 cps ppbv⁻¹ (counts per second per part per billion by volume) for select compounds.

CIMS instruments have also been used for analyzing sub-micrometer particulate organic matter. Hellen et al.²⁴ equipped the inlet of the PTR-MS instrument with a denuder to remove the gas-phase organics and a heater to vaporize the aerosol particles. Similarly, Eichler et al.²⁵ introduced the CHARON–PTR-ToF-MS setup that transmits particles with a 75%–90% efficiency. FIGAERO–HRTof-CIMS²⁶ uses a new filter inlet for thermal desorption of ambient submicron particles.

1.3 INSIGHTS INTO THE ROLE AND FATE OF ATMOSPHERIC RADICALS AND REACTIVE INTERMEDIATES ENABLED BY NEW ANALYTICAL METHODS

The measurement capabilities of CIMS instruments have significantly improved over the past two decades. In this dissertation, I describe further development of CIMS techniques, specifically NH_4^+ CIMS and H_3O^+ CIMS, and the application of those techniques to detection of VOCs and their oxidation products as well as atmospheric radicals and reactive intermediates.

Chapter 2 describes development of a new CIMS instrument to measure hundreds of oxidized molecules in the atmosphere. One of the advantages of this instrument is the possibility to use several reagent ions, including $(\text{H}_2\text{O})_n \cdot \text{H}_3\text{O}^+$ (as H_3O^+ CIMS) and $(\text{H}_2\text{O})_n \cdot \text{NH}_4^+$ (as NH_4^+ CIMS). We show how a mass spectrometric voltage scanning procedure based on collision-induced dissociation can be used to determine the stability of ammonium-organic ions detected by the instrument in the NH_4^+ mode. Using this procedure, instrument sensitivity to a plethora of observed compounds in both gas- and particle-phase can be effectively constrained.

In chapter 3, we demonstrate implementation of CIMS instrumentation in a series of toluene and 1,2,4-trimethylbenzene photooxidation experiments. We observe the formation of compounds with high oxygen content (an O:C ratio of up to 1.1) which

can be produced via phenolic, benzaldehyde or peroxide-bicyclic pathways. Additionally we find that under relevant polluted conditions peroxy radicals, formed via peroxide-bicyclic pathway, can undergo unimolecular reactions leading to production of highly oxygenated organic molecules (HOMs) that can contribute significantly to formation of particulate matter in the atmosphere.

In chapter 4, the focus turns to analytical challenges related to ambient measurements of atmospheric radicals and reactive intermediates, such as peroxy radicals and Criegee intermediates. We present a novel analytical method that combines spin trapping and chemical derivatization techniques with CIMS. Using this method, it is possible to detect and quantify a wide range of short-lived atmospheric radicals and intermediates under close to ambient conditions. Secondary reactions and cycling of these species are effectively suppressed, which reduces measurement interferences. Comparison between the CIMS data and results from numeric modelling shows that the method can be used for integrated production measurements of these species in laboratory experiments.

Finally, Chapter 5 summarizes the research presented in this dissertation and provides outlook for future work.

2

Development and characterization of ammonia chemical ionization mass spectrometer (NH_4^+ CIMS) to quantify oxygenated volatile organic compounds

2.1 ABSTRACT

CHEMICAL IONIZATION MASS SPECTROMETRY (CIMS) instruments routinely detect hundreds of oxidized organic compounds in the atmosphere. A major limitation of these instruments is the uncertainty in their sensitivity to many of the detected ions. We de-

This chapter originally published as A. Zaytsev et al. (2019). “Using collision-induced dissociation to constrain sensitivity of ammonia chemical ionization mass spectrometry (NH_4^+ CIMS) to oxygenated volatile organic compounds”. *Atmospheric Measurement Techniques* 12.3, pp. 1861-1870. This material is based upon work supported by the Harvard Global Institute and the NSF award AGS-1638672.

scribe the development of a new high resolution time-of-flight chemical ionization mass spectrometer that operates in one of two ionization modes: using either ammonium ion ligand-switching reactions such as for NH_4^+ CIMS or proton transfer reactions such as for proton transfer-reaction mass spectrometer (PTR-MS). Switching between the modes can be done within 2 minutes. The NH_4^+ CIMS mode of the new instrument has sensitivities of up to 67 000 dcps ppbv⁻¹ (duty-cycle-corrected ion counts per second per part per billion by volume) and detection limits between 1 and 60 pptv at 3σ for a 1 second integration time for numerous oxygenated volatile organic compounds. We present a mass spectrometric voltage scanning procedure based on collision-induced dissociation that allows us to determine the stability of ammonium-organic ions detected by the NH_4^+ CIMS instrument. Using this procedure, we can effectively constrain the sensitivity of the ammonia chemical ionization mass spectrometer to a wide range of detected oxidized volatile organic compounds for which no calibration standards exist. We demonstrate the application of this procedure by quantifying the composition of secondary organic aerosols in a series of laboratory experiments.

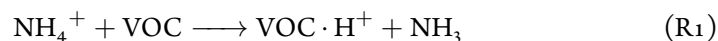
2.2 INTRODUCTION

Understanding the photochemical oxidation of volatile organic compounds (VOCs) in the atmosphere is crucial for estimating their contribution to the formation of secondary organic aerosol (SOA) and tropospheric ozone, key components of photochem-

ical smog^{28,29}. Identification and quantification of VOCs have remained an analytical challenge due to the complexity of multigenerational chemical systems and high variability in VOC concentrations in the atmosphere.

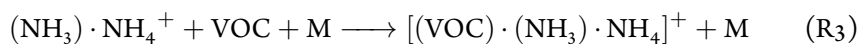
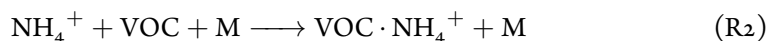
Chemical ionization mass spectrometry (CIMS) has become an important analytical tool for measurements of organic molecules in the atmosphere. Reagent ions are typically produced by glow discharge¹² or a radioactive ion source¹³. These ions subsequently react with analyte molecules by ligand switching, reactive electron transfer, or proton transfer and form product ions which are later detected by a mass spectrometer. Many modern CIMS instruments use time-of-flight mass spectrometers (ToF-MSs) which have high mass resolving power and allow for simultaneous detection of all ions. Some of the benefits of CIMS instruments include high sensitivity, fast time response, linearity, and reproducibility. A wide variety of reagent ions can be used to detect different classes of VOCs and their oxidation products.

In this work, we describe the use of protonated ammonia molecules (ammonium, NH_4^+) for soft ionization of analyte molecules. Ammonium has been previously used as a CIMS reagent ion. Lindinger et al.²⁰ showed that proton transfer reactions can be utilized to softly ionize VOCs, yielding product ions $\text{VOC} \cdot \text{H}^+$:



The proton transfer reaction R1 is exothermic for molecules that have proton affinities

higher than those of ammonia (854 kJ mol^{-1}) and is therefore more selective than the reaction with traditional hydronium ions as proton donors (proton affinity of water is 691 kJ mol^{-1}). Blake et al.³⁰ showed that numerous VOCs can be detected through an association reaction of analyte molecules with ammonium clusters (NH_4^+ and $\text{NH}_3 \cdot \text{NH}_4^+$):



where M is a third-body molecule. Shen et al.³¹ used these methods for online detection of the explosive triacetone triperoxide (TATP).

Most recently, Hansel et al.³² showed that ammonium–water clusters can be utilized for soft ionization of organic compounds via exothermic ligand-switching reaction:



Hansel et al.³² used a modified version of the PTR₃ instrument (called $\text{NH}_4^+ \text{-Cl}_3\text{-ToF}$) to detect first-generation peroxy radicals and closed-shell products from ozonolysis of cyclohexene and achieved sensitivities of up to $28\,000 \text{ cps ppbv}^{-1}$ for these compounds. However, the enhanced reaction time and increased pressure (4 ms and 80 mbar compared to 0.1 ms and 2 mbar for PTR-MS instruments operated under standard conditions, respectively) raise the probability of reverse ligand-switching reactions, which

make it difficult to estimate sensitivities of the NH_4^+ -CI₃-ToF to species that cannot be calibrated directly.

In this study, we present a new instrument that is equipped with three similar corona discharge ion sources and currently can be operated in two different modes: (1) ligand-switching reactions from adduct ions $\text{NH}_4^+ \cdot (\text{H}_2\text{O})_n$, ($n = 0, 1, 2$) (NH_4^+ CIMS) and (2) proton transfer reactions with $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$, ($n = 0, 1, 2$) ions (PTR-MS). The instrument is a modified version of the PTR₃ with a helical tripole reaction chamber and a long-time-of-flight mass spectrometer (Tofwerk AG, Switzerland), and it can be used for measurements of organic molecules in both gas and particle phases. Here we discuss the performance of the new instrument and compare the two detection modes. We demonstrate a mass spectrometric voltage scanning procedure which is based on collision-induced dissociation that allows for the determination of the stability of detected ammonium–organic clusters. With this technique, we can experimentally estimate sensitivities of the NH_4^+ CIMS to the vast array of oxygenated organic compounds without their direct calibration in a matter of minutes. Finally, we present how this procedure can be applied to the measurement of organic aerosol composition in laboratory experiments.

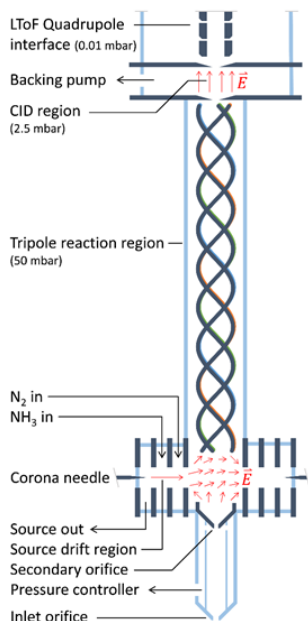


Figure 2.3.1: Schematic drawing of the NH_4^+ CIMS instrument.

2.3 NH_4^+ CIMS INSTRUMENT DESCRIPTION

The instrument developed in this work is based on the PTR₃, which is described in detail by Breitenlechner et al.²² Here, we summarize the basic operating principle and describe the two major design changes made to the original design. The schematic drawing of the NH_4^+ CIMS instrument is shown in Fig. 2.3.1.

Reagent ions are generated in a corona discharge region and are extracted using a source drift region as indicated by red arrows in Fig. 2.3.1. The reaction chamber uses a tripole electrode configuration and is operated at typical pressures between 50 and 70

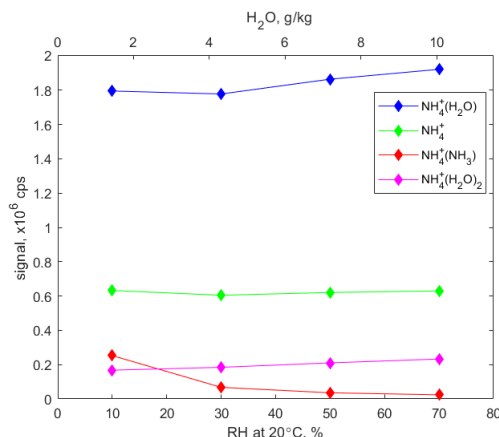


Figure 2.3.2: NH_4^+ CIMS reagent ion signals as a function of water vapor mixing ratios of the sampled air.

mbar. Unlike many other PTR instruments, there is no axial electric field accelerating ions towards the exit of the reaction chamber. Therefore, the reaction time is exclusively determined by the flow velocity of the sampled gas in the axial direction, leading to a typical reaction time of 3 ms. The long time-of-flight (LToF) mass spectrometer with a mass resolution $m/\Delta m$ of up to 8000 allows for the separation of the components with the same nominal mass.

The first major instrument design change consists of replacing the single ion source with three ion sources, one active at a time. Currently, we use two sources: one for producing $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ ($n = 0, 1$) reagent ions (as PTR-MS, called H_3O^+ mode) and another for producing $\text{NH}_4^+ \cdot (\text{H}_2\text{O})_n$ ($n = 0, 1, 2$) reagent ions (as NH_4^+ CIMS, called NH_4^+ mode). $\text{NH}_4^+ \cdot (\text{H}_2\text{O})_n$ ions are produced in the corona discharge ion source from

NH_3 and H_2O . A constant flow (20 sccm) of ammonia and water vapor is added to the ion source region from the headspace of a solution of ammonium hydroxide in water. For our setup, the concentration of the ammonium hydroxide aqueous solution of approximately 10% leads to an optimal $\text{NH}_4^+ \cdot (\text{H}_2\text{O})_n$ primary ion signal with moderate impurities (Fig. 2.3.2). At smaller concentrations, excessive $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ primary ions are produced, while at higher concentrations $\text{NH}_4^+ \cdot \text{NH}_3$ becomes more prominent. Figure 2.3.1 shows the instrument in the NH_4^+ mode with the active ion source on the left, while the two other ion sources (depicted as a single ion source on the right) are inactive. The innermost source drift plate of the active ion source and the innermost source drift plates of both inactive sources generate an electric field perpendicular to the tripole axis. In addition, another component of the electric field is generated parallel to the tripole axis by biasing the electric potential at the secondary orifice relative to the tripole offset potential. Figure 2.3.1 illustrates the resulting electric field in this transfer region. This geometry allows for effective ion guiding from the active ion source to the centre of the reaction tripole chamber. Compared to single-source designs, separate ion sources allow for faster switching between reagent ion species. As shown in Fig. 2.3.3, switching from the H_3O^+ mode to the NH_4^+ mode occurs within 1 minute, while the reverse switching from the NH_4^+ mode to the H_3O^+ mode can be done within 2 minutes.

The second major design change consists of replacing the straight tripole electrode rods with a helix. Simulations of ion trajectories in the original tripole showed that ions

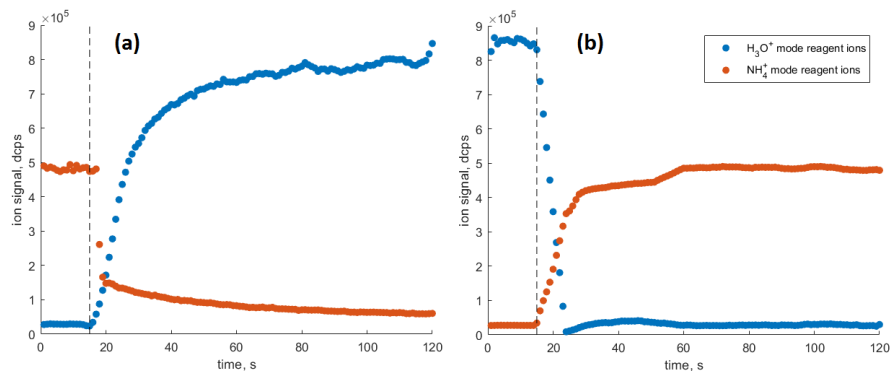


Figure 2.3.3: Reagent ion tracers during switching between the two ionization modes in the CIMS instrument. H_3O^+ mode reagent ions comprise $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$, ($n = 0, 1$); NH_4^+ mode reagent ions comprise $\text{NH}_4^+ \cdot (\text{H}_2\text{O})_n$, ($n = 0, 1, 2$). (a) Switching from the NH_4^+ mode to the H_3O^+ mode. Switching effectively occurs within two minutes. (b) Switching from the H_3O^+ mode to the NH_4^+ mode. Switching effectively occurs within one minute.

are lost mostly by exiting the device through spaces between the rods, rather than by collisions with the rods themselves, probably due to inhomogeneous effective potentials generated by the tripole radio frequency (RF) fields²². The helical structure effectively averages these inhomogeneities, increasing the ion transmission efficiency and therefore the overall instrument performance.

The instrument can be used for measurements of organic molecules in both the gas and particle phases. During particle-phase measurements, sampled air passes through a gas-phase denuder (IONICON Analytik GmbH, Austria) that removes the gas-phase organics and then through a thermal desorption region heated to 180 °C that vaporizes the aerosol particles.

2.4 NH_4^+ CIMS INSTRUMENT PERFORMANCE

Multiple reagent ions are observed in the mass spectrum of this instrument in the NH_4^+ mode, including ammonium–water clusters $\text{NH}_4^+ \cdot (\text{H}_2\text{O})_n$, ($n = 0, 1, 2$) and ammonium ammonia dimers $\text{NH}_4^+ \cdot \text{NH}_3$. Humidity of the sampled air only slightly affects the distribution of the reagent ions, as shown in Fig. 2.3.2. Most organic molecules are detected as ammonium–organic clusters $\text{NH}_4^+ \cdot \text{VOC}$ with a few exceptions for which protonated ions $\text{VOC} \cdot \text{H}^+$ are also observed. The protonated ions could be produced through proton switching reaction from either $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ or NH_4^+ . However, for all of these molecules the intensity of the ammonia–organic cluster is at least 1 order of magnitude higher than the intensity of the corresponding protonated ion.

A series of laboratory experiments were performed to obtain instrument sensitivities to various organic compounds as a function of relative humidity. Table 2.4.1 shows sensitivities to 16 compounds measured using a liquid calibration unit (LCU, IONICON Analytik GmbH, Austria) at 10% RH and 20°C. The LCU quantitatively evaporates aqueous standards into the gas stream. A total of 16 standards were prepared gravimetrically or volumetrically, depending on the compound, with aqueous volume mixing ratios of compounds ranging between 2 and 6 ppmv. An amount of 10 $\mu\text{L min}^{-1}$ flow of each of these solutions was then evaporated into a humidified gas stream of synthetic air (9 slpm), resulting in calibration standards containing 1–2 ppbv of each calibrated component. In Table 2.4.1 we present sensitivities calculated in duty-cycle-corrected counts per

second per part per billion by volume (dcps ppbv⁻¹, normalized to $m/z = 100$). The duty cycle correction compensates for the mass-dependent extraction efficiency into the time-of-flight mass spectrometer: $\text{dcps}(i) = \text{cps}(i) \cdot \sqrt{100/m_i}$. The extraction frequency of the ToF was set at 14 kHz. Limits of detection are calculated for a 1 second integration time as 3 standard deviations of measured background divided by derived sensitivity. Sensitivity to each compound was measured at 10%, 30%, 50%, and 70% RH at 20°C. There is no strong correlation between the sensitivity to the calibrated compounds and their molecular weight ($R^2 = 0.35$, Fig. 2.4.1).

Table 2.4.1: Sensitivities and detection limits of NH_4^+ CIMS for various VOC species, voltage (V_{50}), and corresponding kinetic energy ($\text{KE}_{\text{cm } 50}$) at which half of the ions have dissociated.

Species	Ion formula	m/z	Sensitivity (dcps/ppb)	3σ – LOD (pptv) (1s)	V_{50} (V)	$\text{KE}_{\text{cm } 50}$ (eV)
Methanol	$\text{CH}_4\text{ONH}_4^+$	50.06	83	93	27.8	0.091
Acetonitrile	$\text{C}_2\text{H}_3\text{NNH}_4^+$	59.0604	12,600	9	34.5	0.120
Acetone	$\text{C}_3\text{H}_6\text{ONH}_4^+$	76.0757	24,600	2.75	36.4	0.129
Acetic acid	$\text{C}_2\text{H}_4\text{O}_2\text{NH}_4^+$	78.055	2,140	99	31.4	0.105
Isopropanol	$\text{C}_3\text{H}_8\text{ONH}_4^+$	78.0913	1,240	23	36.5	0.131
MVK	$\text{C}_4\text{H}_6\text{ONH}_4^+$	88.0757	29,700	20	36.9	0.131
MEK	$\text{C}_4\text{H}_8\text{ONH}_4^+$	90.0913	41,400	8	37.8	0.136
Hydroxyacetone	$\text{C}_3\text{H}_6\text{O}_2\text{NH}_4^+$	92.0706	18,300	14	35.8	0.126
Furanone	$\text{C}_4\text{H}_4\text{O}_2\text{NH}_4^+$	102.055	63,400	57	40.3	0.149

Table 2.4.1 (continued): Sensitivities and detection limits of NH_4^+ CIMS for various VOC species, voltage (V_{50}), and corresponding kinetic energy ($\text{KE}_{cm\ 50}$) at which half of the ions have dissociated.

Species	Ion formula	m/z	Sensitivity (dcps/ppb)	3σ – LOD (pptv) (1s)	V_{50} (V)	$\text{KE}_{cm\ 50}$ (eV)
Biacetyl	$\text{C}_4\text{H}_6\text{O}_2\text{NH}_4^+$	104.0706	3,420	35	36.6	0.130
Pyruvic acid	$\text{C}_3\text{H}_4\text{O}_3\text{NH}_4^+$	106.0499	1,600	53	34.8	0.122
Angelica lactone	$\text{C}_5\text{H}_6\text{O}_2\text{NH}_4^+$	116.0706	60,800	0.86	39.6	0.145
Hexanone	$\text{C}_6\text{H}_{12}\text{ONH}_4^+$	118.1226	54,300	8	41.5	0.155
Benzaldehyde	$\text{C}_7\text{H}_6\text{ONH}_4^+$	124.0757	38,800	2	36.7	0.130
Heptanol	$\text{C}_7\text{H}_{16}\text{ONH}_4^+$	134.1539	10,500	2.3	39.5	0.144
Decanone	$\text{C}_{10}\text{H}_{20}\text{ONH}_4^+$	174.1852	67,800	2.5	47.1	0.189

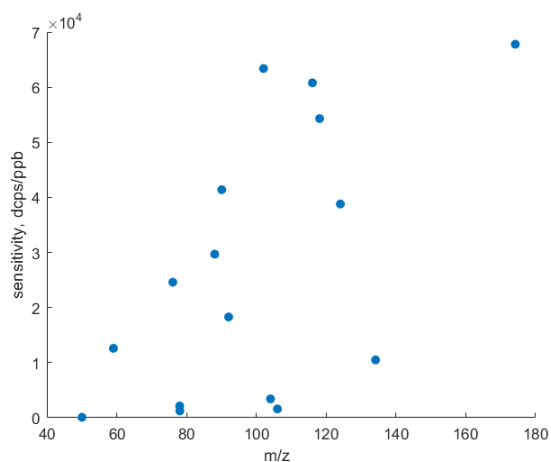


Figure 2.4.1: The relationship between NH_4^+ CIMS sensitivity to calibrated compounds and their molecular weights.

Signals of NH_4^+ ·VOC clusters decrease as humidity of the sampled air increases, as shown in Fig. 2.4.2. Increased reaction time (3 ms) and elevated pressure (60 mbar) in the reaction chamber, compared to the conventional PTR-MS instruments (0.1 ms and 2.3 mbar, respectively), promote equilibrium between the forward and backward ligand-switching Reaction R4. Hence, under humid conditions, excess water vapor favors formation of ammonium–water clusters, which in turn reduces the abundance of ammonium–organic clusters NH_4^+ ·VOC and hence the overall instrument sensitivity to oxygenated VOCs (OVOCs). Humidity dependence of sensitivity does not show a strong correlation to cluster stability, as quantified by $\text{KE}_{50 \text{ cm}}$ ($R^2 = 0.29$, Fig. 2.4.3). In addition, correlation between humidity dependence of sensitivity and polarity of analyte

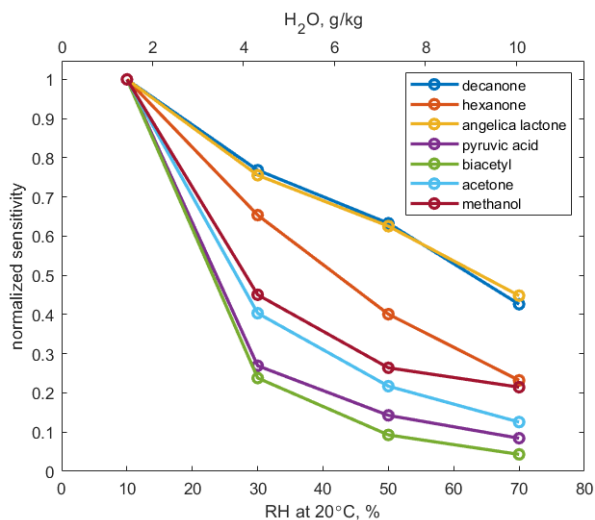


Figure 2.4.2: Humidity dependence curves for the normalized signals relative to the dryer conditions.

molecules is relatively weak ($R^2 = 0.31$).

2.5 COLLISION-INDUCED DISSOCIATION TECHNIQUES FOR CONSTRAIN- ING SENSITIVITY OF THE NH_4^+ CIMS

When the instrument operates in the NH_4^+ mode, organic molecules are detected almost entirely as ammonium–organic clusters. However, kinetic rate constants of ligand switching reaction R4 from ammonium–water ions to an organic molecule have only been measured for very few analyte molecules. In addition, enhanced reaction time in the reaction chamber relative to conventional PTR-MS instruments increases probability of reverse ligand-switching reactions. Therefore, effective rate constants for both for-

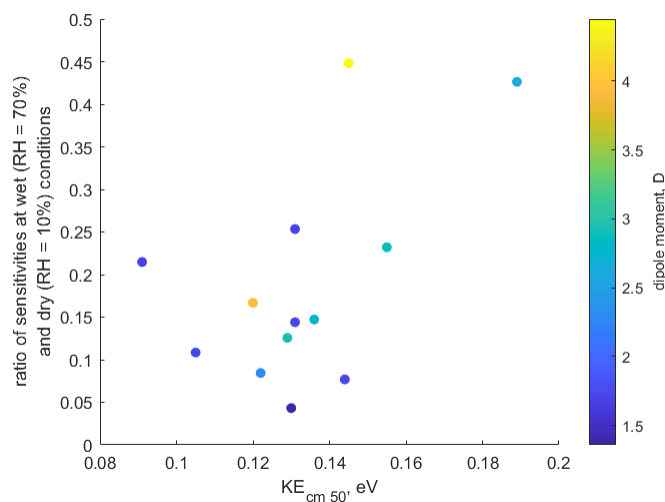


Figure 2.4.3: The relationship between the NH_4^+ CIMS sensitivity dependence on RH and $\text{KE}_{\text{cm } 50}$. Data points are color-coded using the permanent dipole moment of the species.

ward and backward reaction R4 are required for analytical estimation of the compound sensitivities. To avoid these complications, we constrain the instrument sensitivities to the detected compounds through an empirically based collision-induced dissociation (CID) technique similar to the one used by Lopez-Hilfiker et al.³³ for constraining sensitivity of iodide adduct CIMS. This is accomplished by varying the voltage between the ionization region and vacuum region of the mass spectrometer (Fig. 2.3.1), which increases the electric field, while measuring intensities of detected peaks in the mass spectrum.

The increase in the collisional kinetic energy of the ammonium–organic clusters and air molecules leads to collision-induced dissociation of the clusters. For each analyte

ion we determine the voltage value (V_{50}) at which the peak intensity drops by 50% relative to the intensity at the operational voltage value and calculate the ion kinetic energy corresponding to this voltage (KE_{50}). Therefore, we can experimentally determine the electric field strength necessary to break each ammonium–organic cluster, which defines the stability of these clusters and hence the sensitivity of our instrument to analyte molecules. The value of E/N (E is the electric field strength and N is the sample gas number density) is a suitable metric to characterize the motion of ions in the reaction chamber and kinematics of a chemical ionization reaction³⁰. The electric field strength E in a particular region of the reaction chamber depends on the voltage V applied in that region and the effective distance between electrodes d :

$$E = V/d \quad (2.1)$$

Drift velocity of ions in the reaction chamber v_d is determined by the electric field strength E and the ion mobility μ :

$$v_d = E \mu \quad (2.2)$$

The ion mobility μ depends on reaction pressure and temperature:

$$\mu = \mu_o \frac{1013 \text{ mbar}}{p_r} \frac{T_r}{273 \text{ K}} \quad (2.3)$$

where μ_o is the reduced mobility, which is estimated for each ion using its mass³⁴, p_r is pressure in the reaction chamber (mbar), and T_r is temperature in the reaction chamber (K). Further, we calculate mean kinetic energy of drifting ions KE_{ion} in the laboratory frame²⁰:

$$KE_{ion} = \frac{3}{2}k_B T + \frac{M_{buffer}v_d^2}{2} + \frac{M_{ion}v_d^2}{2} \quad (2.4)$$

where k_B is the Boltzmann constant, and M_{buffer} and M_{ion} are the masses of the buffer molecule in the air and reagent ion, respectively. Finally, the kinetic energy of analyte ions in the centre of mass for ion–molecule collisions is given by³⁵:

$$KE_{cm} = \frac{M_{buffer}}{M_{buffer} + M_{ion}} \left(KE_{ion} - \frac{3}{2}k_B T \right) + \frac{3}{2}k_B T \quad (2.5)$$

For each ammonium–organic cluster we measure V_{50} and from this calculate the corresponding kinetic energy at which half of the ions have dissociated ($KE_{cm\ 50}$) using eqs. 2.1–2.5. We show a set of de-clustering scans for eight organic molecules with different functional groups in Fig. 2.5.1. Intensities of all clusters follow similar sigmoidal shapes when the voltage is increased. Some clusters (i.e. small alcohols and heterocyclic compounds) are less stable and are dissociated at lower voltages while other clusters (i.e. large ketones) show higher stability. These scans can be obtained within 4 minutes by steadily increasing the voltage between the ionization region and vacuum region of the

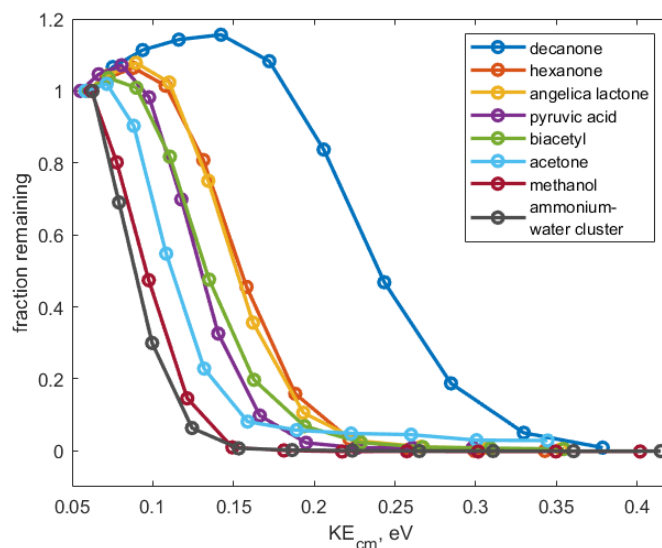


Figure 2.5.1: De-clustering scans of ammonium–organic clusters $\text{NH}_4^+(\text{VOC})$ for calibrated components and $\text{NH}_4^+(\text{H}_2\text{O})$ reagent ions.

mass spectrometer (Fig. 2.3.1).

Figure 2.5.2 shows the relationship between the calculated kinetic energy $\text{KE}_{\text{cm } 50}$ and measured sensitivity for 16 calibrated compounds at 10% RH and 20°C. We observe a linear relationship ($R^2 = 0.61$) between calculated $\text{KE}_{\text{cm } 50}$ and measured sensitivity for calibrated VOCs. This linear relationship is observed for molecules with $\text{KE}_{\text{cm } 50}$ in the range between 0.10 and 0.19 eV (region B in Fig. 2.5.2). Molecules characterized by collisional kinetic energies $\text{KE}_{\text{cm } 50}$ smaller than that of the ammonium–water cluster (0.09 eV, region A in Fig. 2.5.2) will show no significant reaction rate since ligand-switching reactions between such molecules and $\text{NH}_4^+(\text{H}_2\text{O})_n$ are endothermic. Conversely, the ligand ion–molecule switching reaction rate cannot exceed the kinetic limit for ion–

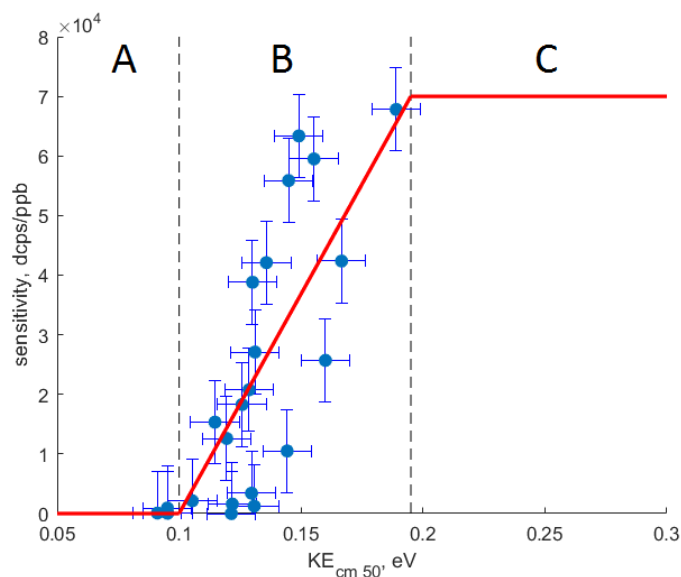


Figure 2.5.2: The relationship between calculated kinetic energy of the ammonium–organic clusters $KE_{cm\ 50}$ and measured sensitivity for calibrated compounds. Molecules characterized by $KE_{cm\ 50}$ smaller than 0.10 eV (region A) cannot be detected by NH_4^+ CIMS; for molecules characterized by $KE_{cm\ 50}$ between 0.10 and 0.19 eV (region B) a linear relationship between $KE_{cm\ 50}$ and measured sensitivity is observed; molecules characterized by $KE_{cm\ 50}$ greater than 0.19 eV (region C) are detected at the “kinetic sensitivity”.

molecule collisions, and therefore there is also an upper limit of observed sensitivities.

We calculate this limit by using experimentally determined pressure and reaction time in the reaction chamber and kinetic limit of ion–molecule reaction rate. We estimate the reaction time in the reaction chamber using the instrument sensitivity to specific compounds in the H_3O^+ mode. For polar compounds with proton affinity much higher than water (i.e. acetone), we can assume that reverse proton transfer reactions do not occur. In this case, the instrument sensitivity to those compounds is given by Lindinger et al.²⁰:

$$\frac{i[\text{RH}^+]}{[\text{R}]} = i_{\text{primary}} k t_{\text{react}} \frac{p_{\text{react}}}{1013 \text{ mbar}} \quad (2.6)$$

where $\frac{i[\text{RH}^+]}{[\text{R}]}$ is the component sensitivity, i_{primary} is the primary ion current, k is the rate constant for the proton-transfer reaction (e.g., $k = 3.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for acetone³⁶), and t_{react} and p_{react} are the reaction time and pressure in the reaction chamber, respectively. By measuring the instrument sensitivity to acetone in the H_3O^+ mode, we estimate t_{react} to be 3 ms. In our case, the instrument sensitivity cannot exceed 70,000 dcps ppb⁻¹, which is in agreement with the highest sensitivity measured for calibrated compounds. Therefore, we assume that all components with $\text{KE}_{\text{cm } 50}$ greater than 0.19 eV (region C in Fig. 2.5.2) will be detected at this “kinetic sensitivity”. As shown in Fig. 2.4.2, the sensitivity of NH_4^+ CIMS to many calibrated compounds is RH dependent; thus we observe that the relationship between the calibrated kinetic energy $\text{KE}_{\text{cm } 50}$ and the measured sensitivity also depends on the humidity of the sampled air

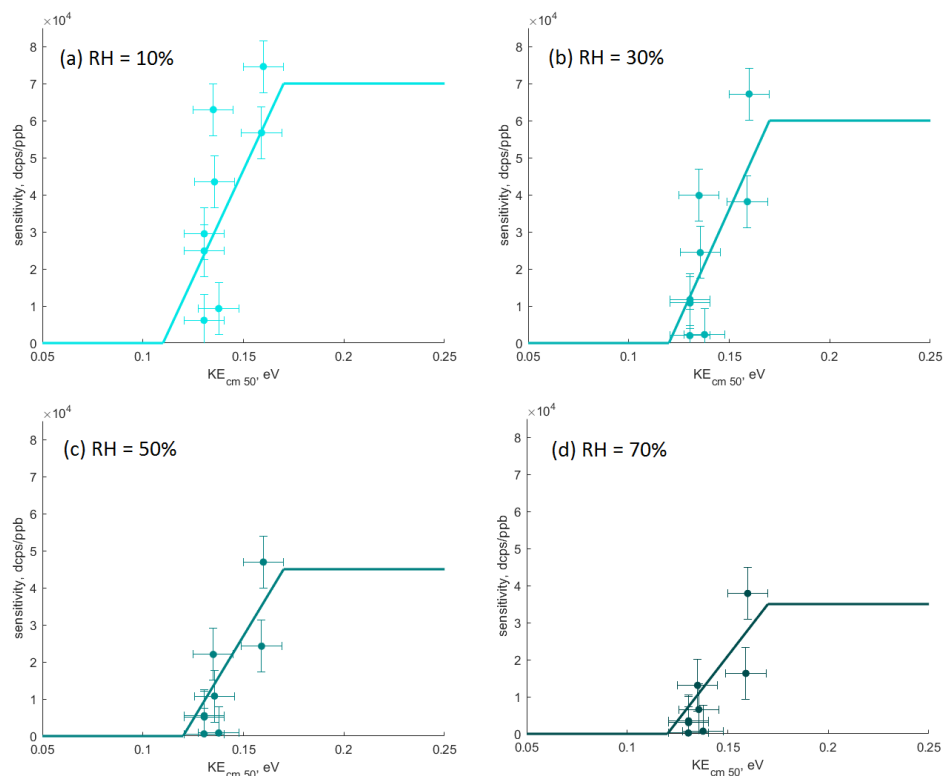


Figure 2.5.3: The relationship between calculated kinetic energy of the ammonium-organic clusters $KE_{cm\ 50^\circ}$ and measured sensitivity to calibrated compounds obtained at different RH of the sampled air.

(Fig. 2.5.3). Therefore, the values of the collisional limit and other calculated sensitivities reported herein are unique to the instrument setup (i.e. pressures and voltages in the reaction chamber) and vary with the humidity of the sampled air.

2.6 APPLICATION TO SECONDARY ORGANIC AEROSOL

To demonstrate the application of the procedure described above, we performed a series of laboratory chamber experiments. A complex mixture of organic compounds in both gas and particle phases was generated by the oxidation of 3-methylcatechol ($C_7H_8O_2$), a second-generation oxidation product of toluene and other anthropogenic aromatics, by hydroxyl (OH) radicals in an environmental chamber. Details of the chamber operations are given by Hunter et al.³⁷, so we include only a brief description here. Photochemical oxidation occurred in a 7.5 m³ temperature-controlled Teflon chamber by OH radicals generated through the photolysis of nitrous acid (HONO). In the experiment described here, 65 ppbv of 3-methylcatechol (Sigma-Aldrich, 98% purity) was injected in the chamber and further oxidized in the presence of ammonium nitrate seed aerosol at 20°C and low humidity (3% RH). Secondary organic aerosol particles produced in this experiment were detected using an Aerodyne aerosol mass spectrometer (AMS³⁸) and the described CIMS instrument operating in both the H_3O^+ and NH_4^+ modes, equipped with the thermal desorption unit described above. High-resolution mass spectra of 3-methylcatechol oxidation products derived in the NH_4^+ mode in the gas and particle phases are given in Fig. 2.6.1. In this experiment, we identified 202 peaks in the NH_4^+ mode mass spectrum and grouped them based on the calculated $KE_{cm\ 50}$ as shown in Fig. 2.6.2. Among those 202 $OC \cdot NH_4^+$ peaks, 125 analyte formulas were also detected as $OC \cdot H^+$ in the H_3O^+ mode. We plot the relationship between the detected

signals in both modes of our instrument in Fig. 2.6.3. We use the de-clustering technique described above to calculate volume mixing ratios of organic molecules detected as ammonium–organic clusters in the NH_4^+ mode. In the H_3O^+ mode, we apply the calibrated acetone sensitivity to calculate volume mixing ratios of OVOCs. Breitenlechner et al.²² showed that due to the enhanced reaction time and the increased pressure in the reaction chamber the equilibrium between the forward and reverse proton reactions can be achieved. Hence, many compounds require careful calibration over a broad humidity range. Since PTR3 has the highest detected sensitivity to ketones, we use the acetone sensitivity to calculate the lower-limit concentration of OVOCs. Volume mixing ratios of organic compounds detected by both modes are in excellent agreement with a slope of 0.94 as shown in Fig. 6 ($R^2 = 0.78$). In addition to 125 peaks measured by both modes, there are peaks that are detected solely by either the H_3O^+ or NH_4^+ mode. In Fig. 2.6.4, we plot 34 identified $\text{C}_x\text{H}_y\text{O}_z \cdot \text{H}^+$ peaks detected by the H_3O^+ mode and 17 identified $\text{C}_x\text{H}_y\text{O}_z \cdot \text{NH}_4^+$ peaks detected by the NH_4^+ mode on the carbon number-oxidation state diagram. Two modes cover different areas on this diagram: while the NH_4^+ CIMS is able to detect larger and more functionalized molecules, PTR-MS is better at detection of smaller organic compounds (some of them can be formed as a result of fragmentation during ionization). Hence, the two modes complement each other and allow for the detection and quantification of a broader range of oxidized organic molecules. Similar observations about the selectivity of NH_4^+ CIMS and PTR-MS have been reported in the previous studies. Aljawhary et al.³⁹ showed that $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ primary ions are more

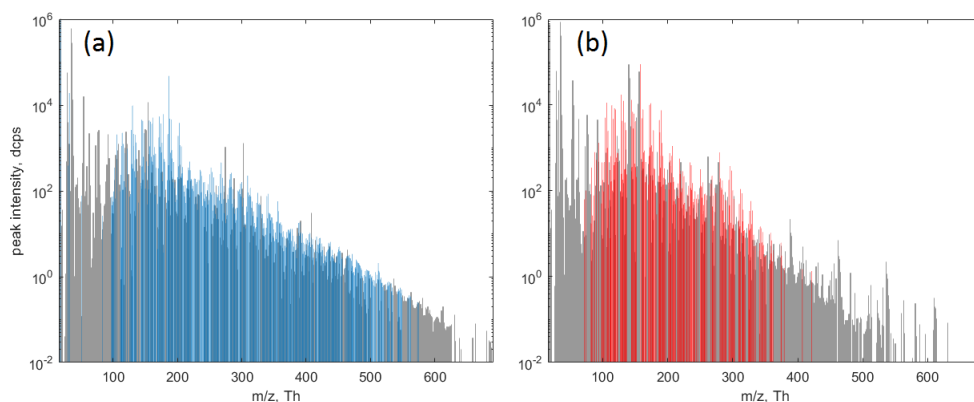


Figure 2.6.1: High-resolution mass-spectra obtained by NH_4^+ CIMS during photooxidation of 3-methylcatechol in (a) gas and (b) particle phases. High-lighted peaks are the ones that are enhanced during the experiment.

selective to the detection of less oxidized water-soluble organic compounds (WSOCs) extracted from alpha-pinene SOA comparing to acetate $\text{CH}_3\text{C}(\text{O})\text{O}^-$ and iodide water clusters $\text{I}^- \cdot (\text{H}_2\text{O})_n$ used as primary ions. Zhao et al.⁴⁰ demonstrated that multiple positive reagent ions (NH_4^+ , Li^+ , Na^+ , K^+) have higher selectivity for a wide range of highly oxygenated organics with higher molecular weights formed from ozonolysis of alpha-pinene, while negative reagent ions (I^- and NO_3^-) are more selective towards smaller species (e.g. CH_2O_2 , CH_2O_3 , $\text{C}_2\text{H}_2\text{O}_3$, and $\text{C}_2\text{H}_4\text{O}_3$).

Figure 2.6.5 shows a comparison between the total mass loading of all organic components measured by the AMS with the sum of masses of all organic compounds measured by our instrument in both H_3O^+ and NH_4^+ modes. The sum of signals of all compo-

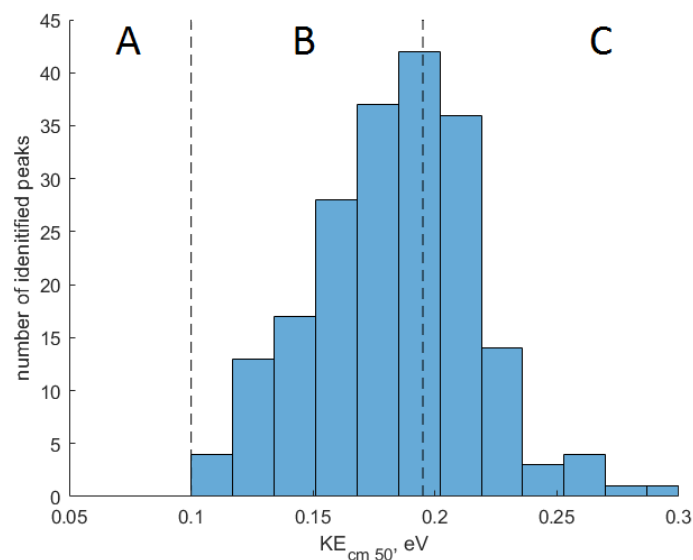


Figure 2.6.2: Application of the collision-induced dissociation techniques for measurement of SOA composition produced during photooxidation of 3-methylcatechol in a laboratory experiment. A total of 202 peaks are detected in NH_4^+ mode and binned based on their $\text{KE}_{\text{cm } 50}$. Molecules with $\text{KE}_{\text{cm } 50}$ smaller than 0.10 eV cannot be detected by NH_4^+ CIMS (region A); sensitivities of molecules characterized by $\text{KE}_{\text{cm } 50}$ between 0.10 and 0.19 eV (region B) can be calculated using the linear fit presented in Fig. 2.5.2; molecules with $\text{KE}_{\text{cm } 50}$ greater than 0.19 eV are detected at the “kinetic sensitivity” (region C).

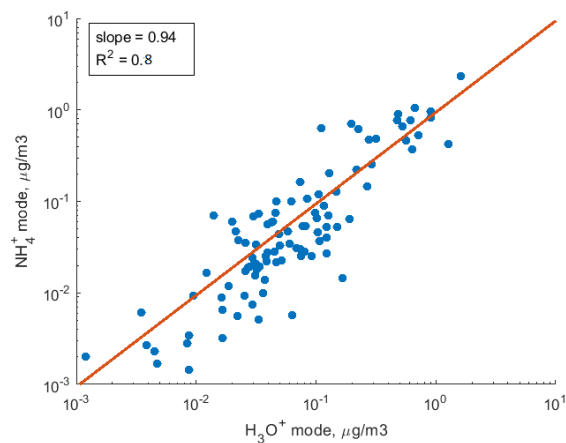


Figure 2.6.3: Comparison of volume mixing ratios of SOA components detected by the CIMS instrument in both H_3O^+ and NH_4^+ modes in the photooxidation experiment of 3-methylcatechol.

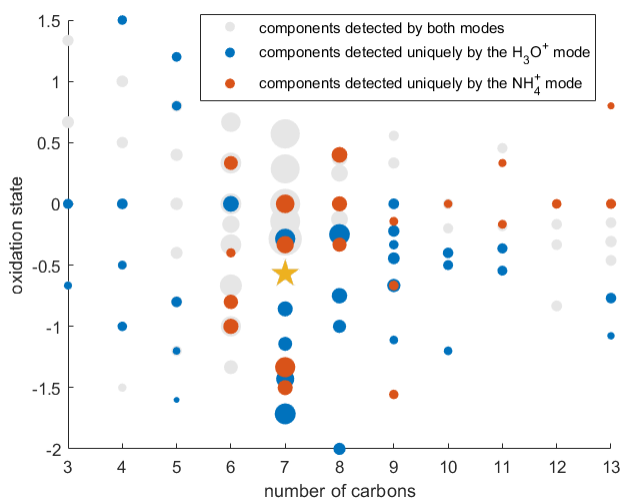


Figure 2.6.4: Identified SOA components detected in both H_3O^+ and NH_4^+ modes (125 peaks), uniquely in the H_3O^+ mode (34 peaks), and uniquely in NH_4^+ mode (17 peaks) plotted on the $n_{\text{C}}\text{-OS}_{\text{C}}$ diagram. The gold star corresponds to the precursor of the photooxidation experiment, 3-methylcatechol. The size of the dots is proportional to the logarithm of the volume mixing ratio of each compound produced at the end of the experiment.

nents detected in the NH_4^+ mode account for 65% of the total aerosol organic mass measured by the AMS as shown in Fig. 2.6.5. This discrepancy can be explained by a combination of the following factors: (1) uncertainties in the sensitivities obtained using the presented technique and in the AMS measurements; (2) thermal fragmentation of organic molecules in the thermal desorption unit, which leads to lower observed masses in the mass spectrum; (3) low NH_4^+ CIMS sensitivity to certain compounds of organic aerosols if ligand-switching reactions between these molecules and ammonium–water clusters are endothermic (e.g., small organic acids); and (4) wall losses of less volatile organic molecules in the NH_4^+ CIMS inlet. Although the NH_4^+ CIMS does not detect all organic compounds to explain the total organic mass measured by the AMS, it gives valuable insight into the composition of SOA as shown in Fig. 2.6.5.

2.7 CONCLUSIONS

In this study, a new CIMS instrument is described based on the recently introduced PTR₃. The instrument can be operated in both NH_4^+ and H_3O^+ modes as NH_4^+ CIMS and PTR-MS, respectively, while switching between the two modes can be done within 2 minutes. Compared to the H_3O^+ mode, the NH_4^+ mode is able to detect more functionalized and larger organic molecules. In the NH_4^+ mode, the instrument has sensitivities in the range of 80–65,000 dcps ppbv⁻¹ and detection limits in the range of 1.5–60 pptv for a 1 second integration time (3σ). We present a procedure based on collision-

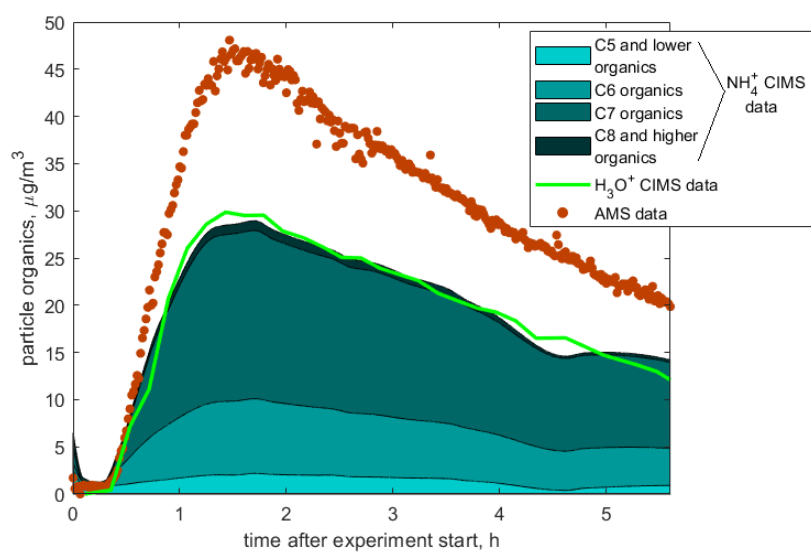


Figure 2.6.5: SOA produced during photooxidation of 3-methylcatechol in a laboratory experiment. The total organic aerosol mass is measured by an AMS and H_3O^+ CIMS. OVOCs detected by NH_4^+ CIMS are binned in four groups based on the carbon number.

induced dissociation that allows us to estimate the stability of detected ammonium-organic clusters and therefore to constrain the sensitivities of hundreds of compounds detected by the NH_4^+ mode of the new instrument without their direct calibration within several minutes.

2.8 ADDITIONAL INFORMATION

2.8.1 DETECTION OF PARTICLE PHASE ORGANICS USING GAS PHASE DENUDER AND THERMAL DESORPTION UNIT

In order to find the optimal temperature for the thermal desorption unit (TDU), we conduct a series of experiments with ammonia sulfate seeds coated with alpha-pinene ozonolysis products. We monitor the particle concentration after the thermal desorption unit using Scanning Mobility Particle Sizer Spectrometer (SMPS, TSI Incorporated) while increasing the temperature of TDU. The results are presented in Fig. 2.8.1. The majority of particles is evaporated at temperatures above 140°C .

We study thermal decomposition of OVOCs extracted from alpha-pinene SOA by measuring their peak intensities using NH_4^+ CIMS. Signals of many species increase at moderate temperatures ($T < 160^\circ\text{C}$) and level out or decrease at higher temperatures ($T > 180^\circ\text{C}$), as shown in Fig. 2.8.2. Therefore, we choose the TDU temperature to be 180°C , as at this temperature all particles are evaporated while thermal decomposition

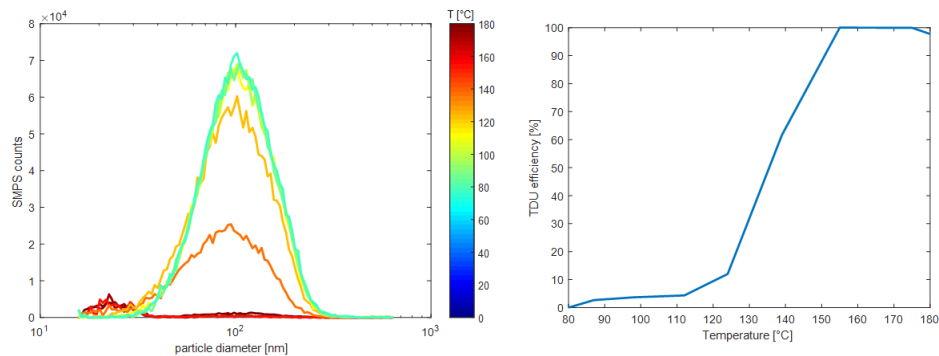


Figure 2.8.1: (a) Particle distribution measured by SMPS as a function of temperature of the thermal desorption unit of the NH_4^+ CIMS; (b) Percentage of particles evaporated in the thermal desorption unit as a function of temperature of the unit.

of labile species is relatively small.

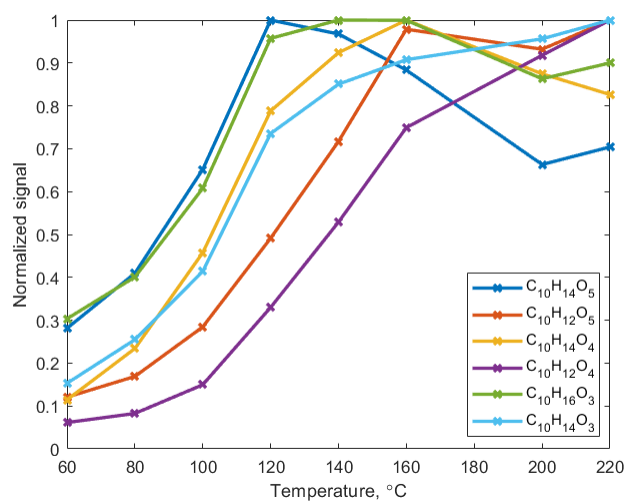


Figure 2.8.2: Thermograms of selected α -pinene ozonolysis SOA.

3

Mechanistic study of the formation of
ring-retaining and ring-opening products
from the oxidation of aromatic
compounds under urban atmospheric
conditions

This chapter originally published as A. Zaytsev et al. (2019). “Mechanistic study of the formation of ring-retaining and ring-opening products from the oxidation of aromatic compounds under urban atmospheric conditions”. *Atmospheric Chemistry and Physics* 19.23, pp. 15117-15129. This material is based upon work supported by the Harvard Global Institute, an NSF award (AGS-1638672), and a Core Center grant (grant no. P30-ES002109) from the National Institute of Environmental Health Sciences, National Institutes of Health.

3.1 ABSTRACT

AROMATIC HYDROCARBONS make up a large fraction of anthropogenic volatile organic compounds and contribute significantly to the production of tropospheric ozone and secondary organic aerosol (SOA). Four toluene and four 1,2,4-trimethylbenzene (1,2,4-TMB) photooxidation experiments were performed in an environmental chamber under relevant polluted conditions ($\text{NO}_x \sim 10$ ppb). An extensive suite of instrumentation including two proton-transfer reaction mass spectrometers (PTR-MS) and two chemical ionisation mass spectrometers (NH_4^+ CIMS and I^- CIMS) allowed for quantification of reactive carbon in multiple generations of hydroxyl radical (OH)-initiated oxidation. Oxidation of both species produces ring-retaining products such as cresols, benzaldehydes, and bicyclic intermediate compounds, as well as ring-scission products such as epoxides and dicarbonyls. We show that the oxidation of bicyclic intermediate products leads to the formation of compounds with high oxygen content (an O:C ratio of up to 1.1). These compounds, previously identified as highly oxygenated molecules (HOMs), are produced by more than one pathway with differing numbers of reaction steps with OH, including both auto-oxidation and phenolic pathways. We report the elemental composition of these compounds formed under relevant urban high-NO conditions. We show that ring-retaining products for these two precursors are more diverse and abundant than predicted by current mechanisms. We present the speciated elemental

composition of SOA for both precursors and confirm that highly oxygenated products make up a significant fraction of SOA. Ring-scission products are also detected in both the gas and particle phases, and their yields and speciation generally agree with the kinetic model prediction.

3.2 INTRODUCTION

Aromatic compounds represent a significant fraction of volatile organic compounds (VOCs) in the urban atmosphere and play a substantial role in the formation of tropospheric ozone and secondary organic aerosol (SOA)⁴². Typical anthropogenic sources include vehicle exhaust, solvent use, and evaporation of gasoline and diesel fuels. Toluene, the most abundant alkylbenzene in the atmosphere, is primarily emitted by the aforementioned anthropogenic processes⁴³. Toluene-derived SOA is estimated to contribute approximately 17%–29% of the total SOA produced in urban areas⁴⁴. More highly substituted aromatic compounds make up another important group of aromatic compounds as they tend to have high SOA yields⁴⁵ and account for a significant fraction of non-methane hydrocarbons in the industrialised regions of China^{46,47}. 1,2,4-Trimethylbenzene (1,2,4-TMB) is chosen as a model molecule to study the oxidation of more substituted aromatic compounds (i.e. trimethylbenzenes).

In the atmosphere, oxidation of aromatic hydrocarbons is primarily initiated by their reactions with hydroxyl radicals (OH) via H abstraction from the alkyl groups or OH

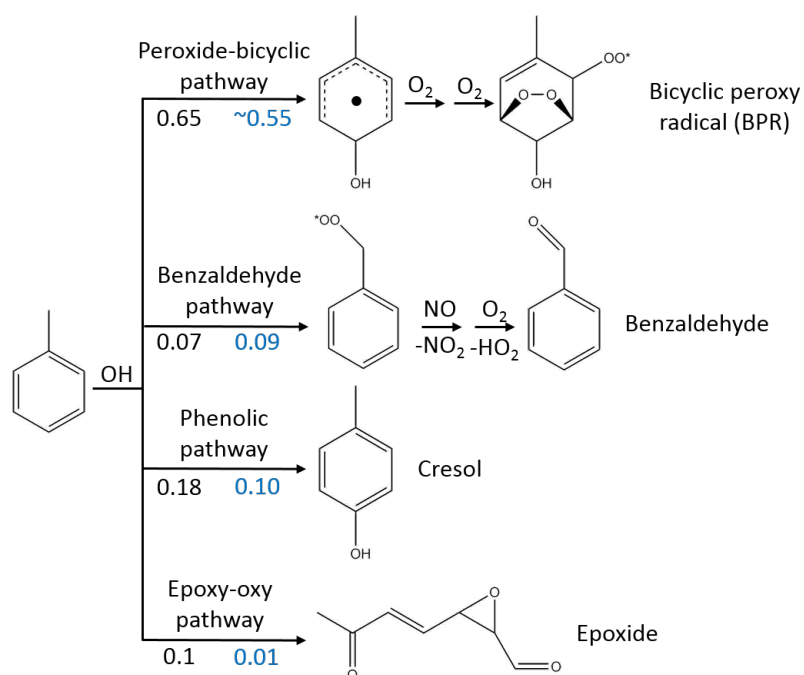


Figure 3.2.1: Major gas-phase oxidation pathways for aromatic hydrocarbons, using toluene as an example. Reaction yields for the oxidation pathways of toluene recommended by MCM v3.3.1 are shown in black⁴⁸. The proposed yields from the present study are shown in blue. The yield of the peroxide-bicyclic pathway is calculated based on the yields of ring-scission products.

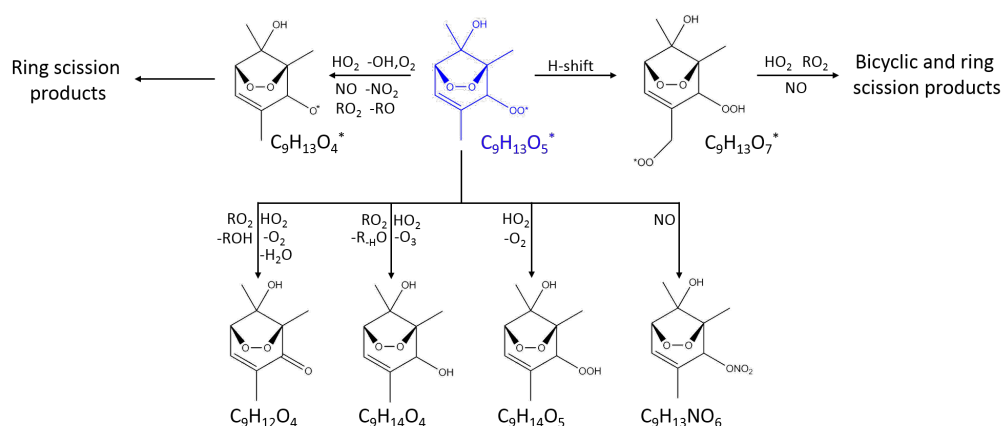


Figure 3.2.2: Oxidation pathways of bicyclic peroxy radicals in the OH-initiated oxidation of 1,2,4-trimethylbenzene. The starting radical is shown in blue. Bimolecular reactions are from MCM v3.3.1⁴⁸ and Birdsall and Elrod⁵⁵.

addition to the aromatic ring⁴² (Fig. 3.2.1). The abstraction channels are relatively minor, leading to the formation of benzyl radicals and benzaldehyde with yields of 0.07 in the case of toluene⁴³ and 0.06 in the case of 1,2,4-TMB⁴⁹. The OH adducts can react with atmospheric O_2 via H abstraction to form ring-retaining phenolic compounds (i.e. cresols and trimethylphenols)^{50,51}. The phenol formation yield decreases for the more substituted aromatics: in case of toluene, the cresol yield is 0.18^{52,53}, whereas for 1,2,4-TMB, the trimethylphenol yield is 0.03^{54,48}. Both abstraction and phenolic channels lead to the formation of products retaining the aromatic ring.

The OH adducts can also react with O_2 through recombination. In this case they lose aromaticity and form non-aromatic ring-retaining bicyclic peroxy radicals (BPRs). Under urban-relevant high-NO conditions BPRs react with NO to form bicyclic oxy

radicals that decompose to ring-scission carbonylic products such as (methyl) glyoxal and biacetyl. Recent theoretical studies have predicted new epoxy-dicarbonyl products that have not been reported in previous studies^{49,43}. Reaction of BPRs with NO can also result in the formation of bicyclic organonitrates. In addition, BPRs react with HO₂ and RO₂, forming bicyclic hydroperoxides and bicyclic carbonyls respectively (Fig. 3.2.2). Finally, BPRs can undergo unimolecular H migration followed by O₂ addition (auto-oxidation), leading to the formation of non-aromatic ring-retaining highly oxygenated organic molecules (HOMs)². Molteni et al.⁵⁶ reported the elemental composition of the HOMs from a series of aromatic compounds produced under low-NO conditions. The autooxidation pathway might be more important for the substituted aromatics because of the higher yield of BPR formation and the larger number of relatively weak C–H bonds⁵⁷. Both ring-retaining and ring-scission compounds are expected to be low in volatility and contribute significantly to SOA⁵⁸. A number of major uncertainties remains in the model representation of the oxidation of aromatic compounds, including the overprediction of ozone concentration, the underprediction of OH production and the lack of detailed description of SOA formation^{55,59}.

In the present work, we investigate detailed mechanisms of hydroxyl radical multi-generational oxidation chemistry of two aromatic hydrocarbons – toluene and 1,2,4-trimethylbenzene – under moderately high, urban-relevant NO_x levels (~ 10 ppbv). Laboratory experiments were conducted in an environmental chamber over approximately 1 day of atmospheric-equivalent oxidation. We use three chemical ionization

mass spectrometry (CIMS) techniques (I^- reagent ion, NH_4^+ reagent ion, and H_3O^+ reagent ion) to characterize and quantify gas-phase oxidation products. In addition, NH_4^+ CIMS and I^- CIMS were used to detect particle-phase products. The goal of this work is to identify gas-phase pathways leading to the production of low-volatility compounds, which are important for SOA formation and support these identifications with CIMS data and a method to characterise the kinetics of an oxidation system.

3.3 METHODS

3.3.1 EXPERIMENTAL DESIGN

All experiments were performed in a 7.5 m³ Teflon environmental chamber³⁷. Prior to experiments, the chamber was flushed and filled with purified air. During experiments the environmental chamber was operated in the constant-volume (“semi-batch”) mode, in which clean air (11–14 L min^{−1}) was constantly added to make up for instrument sample flow. The temperature of the chamber was controlled at 292 ± 1 K. All experiments were carried out under dry conditions (relative humidity, RH $2\% \pm 1\%$) to simplify gas- and particle-phase measurements. Higher RH can potentially shorten the lifetime of particle-phase hydroperoxides, epoxides, and organonitrates⁶⁰ as well as affect gas-particle partitioning kinetics and thermodynamics⁶¹.

Table 3.3.1: Description of toluene and 1,2,4-TMB photooxidation experiments. ^aThe following format is used: HONO injection in ppbv (time since the beginning of the experiment in min). ^bParticle loading was measured before the chamber lights were turned on. ^cNo seed was injected in the two experiments.

		Particle loading						
Expt.		Initial VOC	Initial HONO	Additional	after seed	Temp.	RH	Total
no	VOC	concentration	injection	HONO	injection ^b	(K)	(%)	dilution
		(ppbv)	(ppbv)	injections ^a (ppbv)	(cm ⁻³)			
1	Toluene	89	28	16(124); 28(220)	2.6×10^4	292	2%	0.44
2	Toluene	89	30	17(140); 6(180);	4.2×10^4	292	2%	0.62
				12(290)				
3	Toluene	89	31	21(125); 18	3.2×10^4	292	2%	0.65
				(290)				
4	Toluene	89	28	23(180)	100 ^c	292	3%	0.45
5	1,2,4-TMB	69	30	5(155); 10(300)	3.6×10^4	292	2%	0.56

Table 3.3.1 (continued): Description of toluene and 1,2,4-TMB photooxidation experiments.

		Particle loading						
Expt.		Initial VOC	Initial HONO	Additional	after seed	Temp.	RH	Total
no	VOC	concentration	injection	HONO	injection ^b	(K)	(%)	dilution
		(ppbv)	(ppbv)	injections ^a (ppbv)	(cm ⁻³)			
				13 (145); 10				
6	1,2,4-TMB	69	31	(245); 5 (345)	3.8×10^4	292	2%	0.72
7	1,2,4-TMB	69	34	18 (150); 6 (265);	5.7×10^4	292	2%	0.74
				13 (390)				
8	1,2,4-TMB	69	60	-	100 ^c	292	2%	0.27

We performed a series of photochemical experiments, in which toluene and 1,2,4-TMB were oxidized by OH (Table 3.3.1). The experiments were carried out under high-NO conditions such that the fate of peroxy radicals was primarily determined by their reaction with NO⁶². First, dry ammonium sulfate particles, used as condensation nuclei, were injected in the chamber to reach a number concentration of $2.5\text{--}5.7 \times 10^4 \text{ cm}^{-3}$. Seed particles were not injected into the chamber in two experiments. Hexafluorobenzene (C_6F_6 , which serves as a dilution tracer) was then added to the chamber. Next, nitrous acid (HONO) was injected as an OH precursor. HONO was generated in a bubbler containing a solution of sodium nitrite by adding 2–4 μL of sulfuric acid via a syringe pump. Purified air that was subsequently injected at 15 L min^{-1} carried HONO into the chamber, which resulted in a mixing ratio of 28–35 ppbv (except for experiment 8 in which the initial HONO mixing ratio was 60 ppbv). After the addition of the oxidant, the aromatic precursor (toluene or 1,2,4-TMB, Sigma-Aldrich) was added to the chamber by injecting 3 μL of the precursor into a heated inlet. The initial mixing ratio of the precursor was 89 ppbv in toluene experiments and 69 ppbv in 1,2,4-TMB experiments. The reagents were allowed to mix for several minutes, after which the ultraviolet (UV) lights, centred at approximately 340 nm, were turned on to start photolysis of HONO (resulting in the production of hydroxyl radicals and nitric oxide) and photooxidation of the precursor. During experiments, additional injections of HONO were added to the chamber in order to roughly maintain the OH levels. As a result, the mixing ratio of NO in the chamber during experiments was estimated to be ~ 0.3 ppbv, whereas

the NO_2 mixing ratio was approximately 10 ppbv (Fig. 3.3.1). Measurements were conducted within several hours, corresponding to 14–16 h of atmospheric-equivalent exposure (assuming an average OH concentration of $1.5 \times 10^6 \text{ molec cm}^{-3}$). Concentrations of O_3 and $\text{HONO} + \text{NO}_x$ for a typical run are shown in Fig. 3.3.1.

3.3.2 CHAMBER INSTRUMENTATION

The concentration of ozone (2B Technologies), relative humidity, and temperature were measured in the chamber. A 42i NO_x monitor (Thermo Fischer Scientific) was used to measure the sum of concentrations of HONO and nitrogen oxides (NO_x). Aromatic precursors as well as gas-phase oxygenated volatile organic compounds (OVOCs) were detected by chemical ionisation high-resolution time-of-flight mass spectrometry (CIMS) techniques: I^- CIMS, NH_4^+ CIMS and H_3O^+ CIMS. The I^- CIMS instrument (Aerodyne Research Inc.) is described by Lee et al.¹⁷ NH_4^+ CIMS and H_3O^+ CIMS were carried out using a mass spectrometer (PTR3, IONICON Analytik) which was operated in two ionization modes: $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n, n = 0, 1$ (as PTR3 H_3O^+ CIMS²²) and $\text{NH}_4^+ \cdot (\text{H}_2\text{O})_n, n = 0, 1, 2$ (as PTR3 NH_4^+ CIMS^{32,27}). Switching between ion modes occurred every 5 minutes. H_3O^+ CIMS was also conducted by a proton-transfer-reaction mass spectrometer (Vocus 2R PTR-TOF²³, Aerodyne Research Inc.). Each CIMS instrument used a $3/16''$ PFA Teflon sampling line of 1 m in length with a flow of 2 SLPM (standard litres per minute). The PTR3 and Vocus 2R PTR-TOF

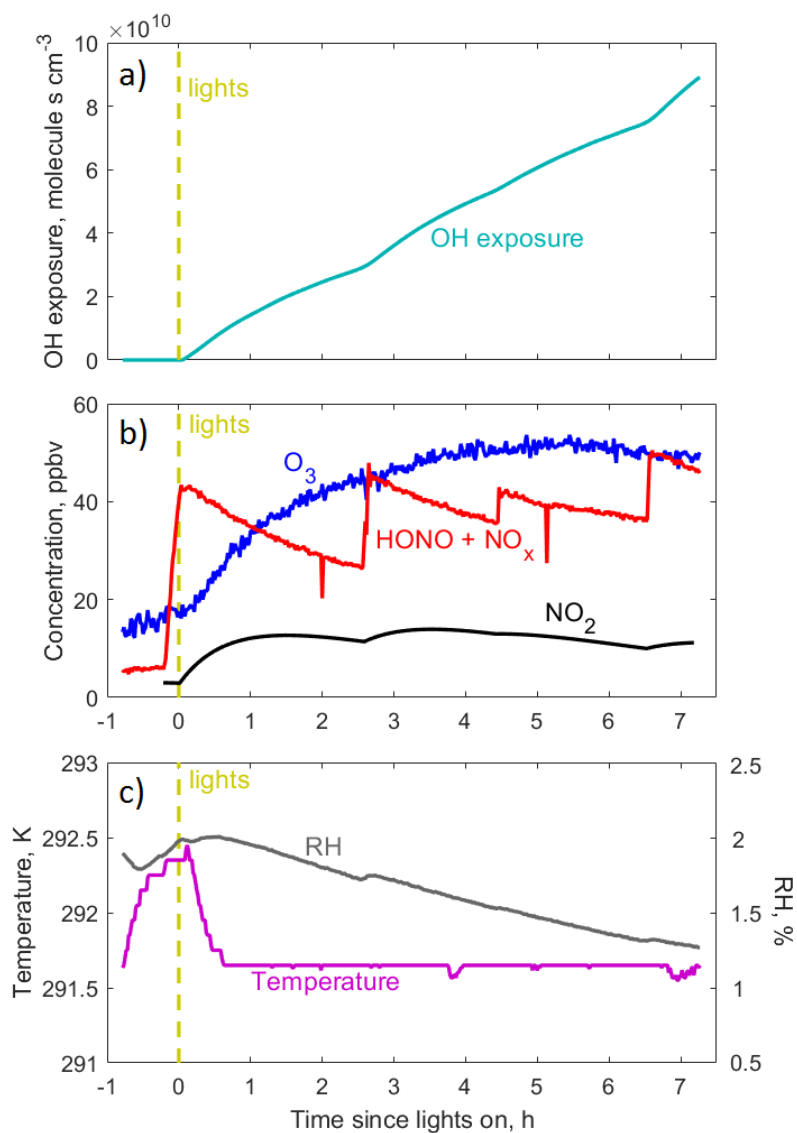


Figure 3.3.1: (a) OH exposure, (b) concentrations of O₃, NO₂, HONO+NO_x, and (c) temperature and RH for a typical photooxidation experiment. NO₂ concentration was estimated using F0AM⁶³ based on MCM v3.3.1⁴⁸.

are designed to minimize inlet losses of sampled compounds^{23,22}; for more details see Section 3.6.1. Detection efficiency and sensitivity of CIMS instruments depend critically on both the reagent ion and the measured sample molecule. The concentrations of aromatic precursors were measured by the Vocus 2R PTR-TOF, which was directly calibrated for the two compounds. Smaller, less oxidized molecules were primarily quantified by PTR-MS (PTR₃ H₃O⁺ CIMS and Vocus 2R PTR-TOF), whereas PTR₃ NH₄⁺ CIMS and I[−] CIMS were mainly used for the detection of larger and more functionalized molecules. The PTR₃ and I[−] CIMS instruments were directly calibrated for 10 VOCs with various functional groups (Tables 3.3.2, 3.3.3 and 3.3.4). An average calibration factor was applied to other species detected by PTR-MS instruments, while collision–dissociation methods were implemented to constrain sensitivities of I[−] CIMS and NH₄⁺ CIMS^{33,27}. Use of these methods and average calibration factors leads to uncertainties in estimated concentrations of detected compounds within a factor of 10. NH₄⁺ CIMS uncertainties are within a factor of 3, whereas I[−] CIMS is less certain. The majority of the analysis in this work relies on NH₄⁺ CIMS and PTR-MS data, while I[−] CIMS data are used as supporting measurements. Glyoxal was detected by laser-induced phosphorescence⁶⁴ (Madison LIP).

Table 3.3.2: Sensitivities of I^- CIMS for calibrated species.

Species	Ion formula	m/z	Sensitivity
			(ndcps/ppbv)
Formic acid	$\text{CH}_2\text{O}_2\text{I}^-$	172.91	3,000
Acetic acid	$\text{CH}_4\text{O}_2\text{I}^-$	186.93	130
Acrylic acid	$\text{C}_3\text{H}_4\text{O}_2\text{I}^-$	198.93	63
Glycolic acid	$\text{C}_2\text{H}_4\text{O}_3\text{I}^-$	202.92	880
cis-2-butene-1,4-diol	$\text{C}_4\text{H}_8\text{O}_2\text{I}^-$	172.91	3,000
1,2-butanediol	$\text{C}_4\text{H}_{10}\text{O}_2\text{I}^-$	216.97	110
1,2-butanediol	$\text{C}_4\text{H}_{10}\text{O}_2\text{I}^-$	216.97	110
Phenol	$\text{C}_6\text{H}_6\text{OI}^-$	220.95	180
o-cresol	$\text{C}_7\text{H}_8\text{OI}^-$	234.96	65
Nitrophenol	$\text{C}_6\text{H}_5\text{NO}_3\text{I}^-$	265.93	38,500

Table 3.3.3: Sensitivities of H_3O^+ CIMS for calibrated species

Species	Ion formula	m/z	Sensitivity
			(ndcps/ppbv)
Acetone	$\text{C}_3\text{H}_6\text{OH}^+$	59.05	12,900
Acetic acid	$\text{C}_2\text{H}_4\text{O}_2\text{H}^+$	61.03	9,600
Methacrolein	$\text{C}_4\text{H}_6\text{OH}^+$	71.05	15,300

Table 3.3.3 (continued): Sensitivities of H_3O^+ CIMS for calibrated species.

Species	Ion formula	m/z	Sensitivity
			(ndcps/ppbv)
2-furanone	$\text{C}_4\text{H}_4\text{O}_2\text{H}^+$	85.03	20,700
Diacetyl	$\text{C}_4\text{H}_6\text{O}_2\text{H}^+$	87.04	5,000
Angelica lactone	$\text{C}_5\text{H}_6\text{O}_2\text{H}^+$	99.04	19,400
Benzaldehyde	$\text{C}_7\text{H}_6\text{OH}^+$	107.05	16,200
o-cresol	$\text{C}_7\text{H}_8\text{OH}^+$	109.07	6,900
1,2,4-TMB	$\text{C}_9\text{H}_{12}\text{H}^+$	121.10	1,640
3-decanone	$\text{C}_{10}\text{H}_{20}\text{OH}^+$	157.16	13,600

Table 3.3.4: Sensitivities of NH_4^+ CIMS for calibrated species

Species	Ion formula	m/z	Sensitivity
			(ndcps/ppbv)
Acetone	$\text{C}_3\text{H}_6\text{ONH}_4^+$	76.08	10,600
Acetic acid	$\text{C}_2\text{H}_4\text{O}_2\text{NH}_4^+$	78.06	840
Methacrolein	$\text{C}_4\text{H}_6\text{ONH}_4^+$	88.08	4,900
2-furanone	$\text{C}_4\text{H}_4\text{O}_2\text{NH}_4^+$	102.06	10,300
Diacetyl	$\text{C}_4\text{H}_6\text{O}_2\text{NH}_4^+$	104.07	5,200
Angelica lactone	$\text{C}_5\text{H}_6\text{O}_2\text{NH}_4^+$	116.07	20,800

Table 3.3.4 (continued): Sensitivities of NH_4^+ CIMS for calibrated species.

Species	Ion formula	m/z	Sensitivity
			(ndcps/ppbv)
Benzaldehyde	$\text{C}_7\text{H}_6\text{ONH}_4^+$	124.07	14,500
o-cresol	$\text{C}_7\text{H}_8\text{ONH}_4^+$	126.09	370
1,2,4-TMB	$\text{C}_9\text{H}_{12}\text{NH}_4^+$	138.13	800
3-decanone	$\text{C}_{10}\text{H}_{20}\text{ONH}_4^+$	174.19	23,200

Total organic aerosol mass was measured using an Aerodyne aerosol mass spectrometer³⁸ (AMS), calibrated with ammonium nitrate particles and assuming a collection efficiency of 1. Particle-phase compounds were quantified using the FIGAERO-HRToF-I[−] CIMS²⁶ and a second PTR₃ that could be operated in two positive modes as described above, which was equipped with an aerosol inlet comprising a gas-phase denuder and a thermal desorption unit heated to 180 °C (TD- NH_4^+ CIMS and TD- H_3O^+ CIMS). At this temperature, all particles were evaporated while thermal decomposition of labile oxygenated compounds was relatively small²⁷. Uncertainties of the particle-phase CIMS measurements are similar to the corresponding uncertainties of the gas-phase CIMS instruments.

3.3.3 KINETIC MODEL

The Framework for o-D Atmospheric Modelling v3.1⁶³ (FoAM) containing reactions from the Master Chemical Mechanism^{65,48} (MCM v3.3.1) was used to simulate the photooxidation of 1,2,4-TMB and toluene in the environmental chamber and to compare the modelled products with the measurements. Model calculations were constrained to physical parameters of the environmental chamber (pressure, temperature, photolysis frequencies, and dilution rate). The dilution term for volatile compounds was estimated based on the concentration of the dilution tracer, hexafluorobenzene. Injections of aromatic compounds and HONO were modeled as sources during the time of injection, and the chamber lights' intensity was tuned to match the measured time-dependent concentration of aromatic precursors with the modelled values. As for semi- and low-volatile compounds, the wall deposition rate was estimated to be $5 \times 10^{-4} \text{ s}^{-1}$ using the "rapid burst" method described in detail by Krechmer et al.⁶⁶

3.3.4 CALCULATION OF OH EXPOSURE AND PRODUCT YIELDS

The OH concentration was determined using the decay of the aromatic precursor, accounting for losses from dilution. The mixing ratio of the aromatic VOC (ArVOC: toluene or 1,2,4-TMB) is given by the following kinetics equation:

$$[\text{ArVOC}]_t = [\text{ArVOC}]_o \exp \left(-k_{\text{ArVOC}} + \text{OH}[\text{OH}_{\text{exposure}}]_t - k_{\text{dilution}} t \right) \quad (3.1)$$

where $[\text{ArVOC}]$ is the time-dependent mixing ratio of the aromatic precursor, $k_{\text{ArVOC} + \text{OH}}$ is the second-order rate constant for the $\text{ArVOC} + \text{OH}$ reaction ($k_{\text{toluene} + \text{OH}} = 5.63 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and $k_{1,2,4\text{-TMB} + \text{OH}} = 3.25 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 293 K⁴²), $[\text{OH}_{\text{exposure}}] = \int_0^t [\text{OH}] d\tau$ is the integrated OH exposure, k_{dilution} is the unimolecular rate constant determining dilution, and t is the time since the beginning of irradiation by the UV lights.

Yields of first-generation products were determined based on the decay of the aromatic precursor, the rise of the product, and accounting for physical (dilution and chamber wall deposition) and chemical (reaction with OH, NO₃, O₃ and photolysis) losses. A correction procedure described in detail by Galloway et al.⁶⁷ is applied to calculate product yields. This correction takes physical and chemical losses of products in the environmental chamber into account:

$$[\text{X}]_i^{\text{corr}} = [\text{X}]_{i-1}^{\text{corr}} + \Delta[\text{X}]_i + [\text{X}]_{i-1}t (k_{\text{chemical loss}} + k_{\text{physical loss}}) \quad (3.2)$$

where $[\text{X}]_i^{\text{corr}}$ is the corrected mixing ratio of the compound at measurement time i , t is time between measurements i and $i-1$, $[\text{X}]_{i-1}$ is the measured product mixing ratio of measurement $i-1$, $\Delta[\text{X}]_i$ is the observed net change in $[\text{X}]$ that occurs over Δt , and $k_{\text{chemical loss}}$ and $k_{\text{physical loss}}$ are the rate constants describing chemical and physical losses of the product respectively.

Yields of first-generation products were determined from the linear relationship be-

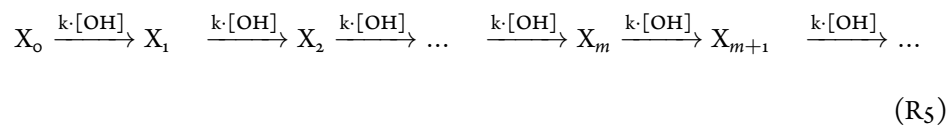
tween the amount of the corrected product formed and the amount of the primary ArVOC reacted:

$$[X]^{\text{corr}} = Y[\text{ArVOC}]^{\text{reacted}} \quad (3.3)$$

where $[X]^{\text{corr}}$ is the amount of the corrected product formed, $[\text{ArVOC}]^{\text{reacted}}$ is the amount of the primary ArVOC reacted, and Y is the first-generation yield of the product.

3.3.5 GAMMA KINETICS PARAMETERIZATION

Photooxidation products can be characterized not only by their concentration and yield, but also by their time series behavior. In a laboratory experiment, the time series behavior of a product is dependent on the kinetic parameters of the molecule: the relative rates of formation and reactive loss, and the number of reactions to create the product. We characterize time series behavior of products using the gamma kinetics parameterization (GKP), which describes kinetics of an oxidation system in terms of multigenerational chemistry. The detailed description of this parameterization technique is given by Koss et al.⁶⁸, so we include only a brief description here. A multigenerational hydroxyl radical oxidation system can be represented as a linear system of reactions:



where k is the second-order rate constant and m is the number of reactions needed to produce species X_m .

In laboratory experiments, oxidation reactions can be parameterized as a linear system of first-order reactions if reaction time t is replaced by OH exposure $[\text{OH}_{\text{exposure}}] = \int_0^t [\text{OH}] d\tau$. In this case, the time-dependent concentration of a compound X_m can be parameterized by⁶⁸:

$$X_m(t) = a \left(k[\text{OH}_{\text{exposure}}]_t \right)^m e^{-k[\text{OH}_{\text{exposure}}]_t} \quad (3.4)$$

where a is a scaling factor, k is the effective second-order rate constant ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$), m is the generation number, and $[\text{OH}_{\text{exposure}}]_t$ is the integrated OH exposure (molec s cm^{-3}).

Equation 3.4 can be used to fit the observed concentration of a compound to return its parameters a , k , and m . The parameter m determines the number of reactions with OH needed to produce the compound, whereas the parameter k gives an approximate measure of the compound reactivity. We define “generation” here as the number of reactions with OH. At low generations ($m = 1-2$), the standard deviation of the fit is 0.1, while it can be higher (up to 0.8) at higher ($3+$) generations⁶⁸. Examples of fitted chamber measurements are shown in Fig. 3.3.2.

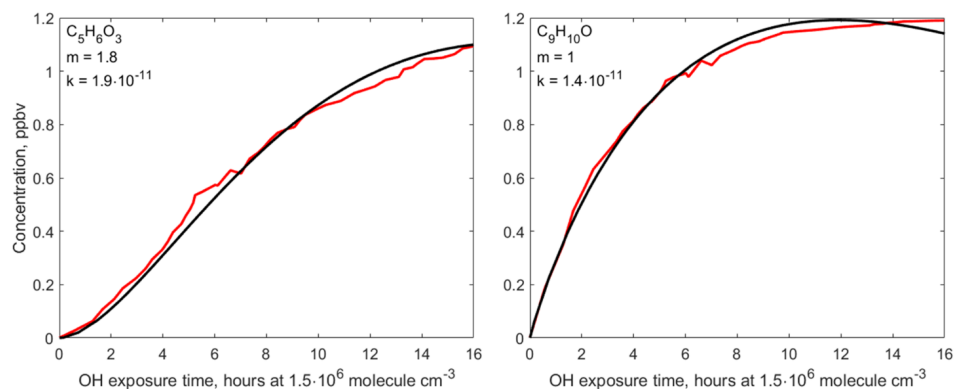


Figure 3.3.2: Species detected by NH_4^+ CIMS in 1,2,4-TMB photooxidation experiment (red) and kinetic best fit (black).

3.4 RESULTS AND DISCUSSION

Toluene and 1,2,4-TMB react with OH to form both ring-retaining (via benzaldehyde, phenolic, and bicyclic channels) and ring-scission (via bicyclic and epoxide channels) products. (These four channels are illustrated using the example of toluene in Fig. 3.2.1)

First- and later-generation gas- and particle-phase oxidation products are detected and quantified for both systems. In the following sections we compare products suggested by MCM and previous studies to corresponding molecular formulas detected by CIMS. In some cases, the ion identity is well established from previous research or because there are a limited number of reasonable structures (e.g. phenols, benzaldehydes, and ring-scission dicarbonyl products); in other cases, multiple isomers are possible, which could contribute to some differences between modeled and observed behavior.

3.4.1 PRODUCTS FROM BENZALDEHYDE, PHENOLIC, AND EPOXIDE CHANNELS

In the toluene experiments, the approximate yields of benzaldehyde and cresol (0.10 and 0.16 respectively) were calculated based on the decay of toluene measured by the Vocus 2R PTR-TOF, the rise of the two products measured by PTR₃ H₃O⁺ CIMS and NH₄⁺ CIMS (cresol was measured by H₃O⁺ CIMS while NH₄⁺ CIMS was used for detecting benzaldehyde), and accounting for losses of cresol and benzaldehyde from wall deposition and reaction with OH and NO₃. MCM v3.3.1 recommends a 0.07 yield of benzaldehyde and a 0.18 yield of cresol (total of all isomers) from OH-initiated oxidation of toluene. Benzaldehyde and cresol concentrations predicted by MCM agree within uncertainties with the PTR₃ H₃O⁺ CIMS and NH₄⁺ CIMS measurements, and the time series behavior of measurements and kinetic model predictions is similar (Fig. 3.4.1a). In general, MCM predicts that phenolic and benzaldehyde channels are less important for more substituted aromatics⁴⁸. Hence, the MCM-based kinetic model recommends a 0.06 yield of dimethylbenzaldehyde and a 0.03 yield of trimethylphenol from the OH-initiated oxidation of 1,2,4-TMB. The kinetic model predictions for the two products agree within uncertainties with the H₃O⁺ CIMS measurements, and the time series behavior is again similar (Fig. 3.4.1b). Phenols and benzaldehydes can further react within the MCM v3.3.1 scheme to form highly oxidized second-generation compounds. The importance of this pathway is discussed further in Sect. 3.4.2.

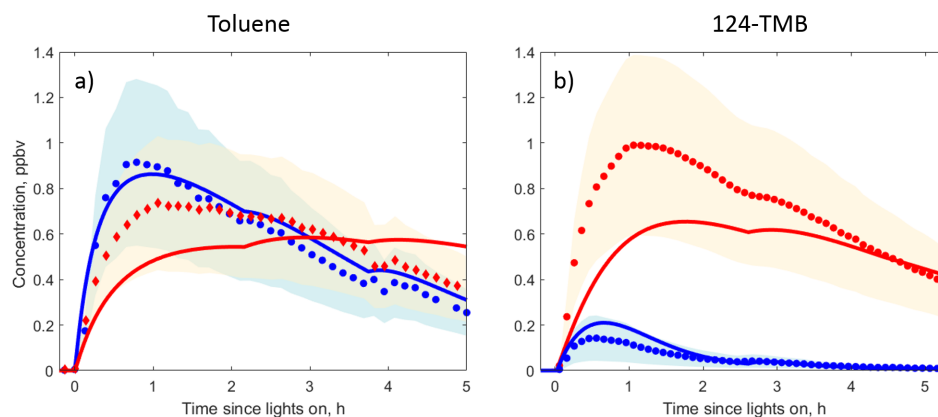


Figure 3.4.1: MCM v3.3.1 predictions (solid lines) compared to H_3O^+ CIMS (circles) and NH_4^+ CIMS (diamonds) measurements under high-NO oxidation of (a) toluene and (b) 1,2,4-TMB for phenols (red) and benzaldehydes (blue). The uncertainty in the H_3O^+ CIMS and NH_4^+ CIMS measurements is shown using blue and red shading.

MCM v3.3.1 also includes an epoxy-oxy channel in which it predicts formation of non-fragmented linear epoxide-containing products (Fig. 3.2.1). The MCM-predicted yields of these species are 0.10 and 0.30 for toluene and 1,2,4-TMB systems respectively. The yields of these products observed with NH_4^+ CIMS are significantly smaller (0.01 in both systems). However, the observations are consistent with theoretical studies^{49,43} in which it has been shown that only a negligible fraction of the bicyclic radicals would break the O–O bond to form epoxide-containing products.

3.4.2 PRODUCTS FROM BICYCLIC PATHWAY

NON-FRAGMENTED, RING-RETAINING PRODUCTS

Bicyclic peroxy radicals are formed through the addition of O_2 to the OH adducts (Fig. 3.2.1). Starting from a generic aromatic compound C_xH_y , we expect the formation of BPRs with the formula $C_xH_{y+1}O_5$. BPRs likely react with RO_2 , HO_2 , or NO , leading to the following products⁵⁵ (Fig. 3.2.2): bicyclic carbonyls ($C_xH_yO_4$), bicyclic alcohols ($C_xH_{y+2}O_4$), bicyclic hydroperoxides ($C_xH_{y+2}O_5$), and bicyclic organonitrates ($C_xH_{y+1}NO_6$), as well as alkoxy radicals (discussed later). A number of oxygenated products are detected by NH_4^+ CIMS including $C_7H_8O_4$, $C_7H_{10}O_5$, and $C_7H_9NO_6$ in the toluene experiments, and $C_9H_{12}O_4$, $C_9H_{14}O_4$, and $C_9H_{13}NO_6$ in the 1,2,4-TMB experiments (Table 3.4.1). As authentic standards are not available, these compounds were quantified using a voltage scanning procedure based on collision-induced dissociation. The majority of OVOCs with high carbon numbers were detected at the maximum sensitivity, which was experimentally determined in each photooxidation experiment and depends on operational conditions of the NH_4^+ CIMS instrument²⁷ (Fig. 3.4.2, Tables 3.4.2 and 3.4.3). A number of products with the same molecular formulas corresponding to bicyclic carbonyls ($C_7H_8O_4$ and $C_9H_{12}O_4$) and alcohols ($C_7H_{10}O_4$ and $C_9H_{14}O_4$) were also detected by I^- CIMS and PTR-MS. In MCM v3.3.1, the bicyclic peroxy radical undergoes analogous reactions: (1) it can react with HO_2 to produce a hydroperoxide; (2) it can react with RO_2 to produce an alkoxy radical, an alcohol, or

a carbonyl; and (3) it can react with NO to produce an alkoxy radical or a nitrate. According to MCM, under relevant urban conditions BPRs nearly exclusively react with NO and HO₂ and dominantly form alkoxy radicals which further decompose to smaller ring-scission compounds (Figs. 3.2.2, 3.4.5 and 3.4.6). In this study, the approximate lifetime of BPRs, calculated as inverse reactivity, is estimated to be 5 seconds for toluene and 7 seconds for 1,2,4-TMB. MCM v3.3.1 does not include the formation of the bicyclic carbonyl, C₉H₁₂O₄ in the 1,2,4-TMB oxidation scheme, whereas in the case of toluene it predicts that a major fraction of bicyclic carbonyl C₇H₈O₄ is produced as a second-generation product from the reaction of bicyclic hydroperoxide and organonitrate with OH. In contrast, the GKP fit based on the NH₄⁺ CIMS measurements implies that a significant fraction of the detected compounds is formed in the first generation in both systems (Fig. 3.4.3, Table 3.4.1). These first-generation bicyclic carbonyls can be produced by the reaction of BPR with HO₂ or RO₂. In addition, MCM predicts a higher than observed concentration of bicyclic alcohol (C₉H₁₄O₄ for the 1,2,4-TMB system) as the only channel present in the MCM-based kinetic model is a reaction of BPR with RO₂, although it can also be produced via the BPR+HO₂ pathway (Fig. 3.2.2). Finally, MCM v3.3.1 predicts that a notable fraction of BPR reacts with HO₂ to form bicyclic hydroperoxide. NH₄⁺ CIMS measurements of C₉H₁₄O₅ and C₇H₁₀O₅ are less than the kinetic model prediction for each chemical system but agree within measurement uncertainties. The generation number *m* of C₇H₁₀O₅ and C₉H₁₄O₅ is approximately between 1.7 and 1.8 which suggests that a compound with the same molecular formula can be

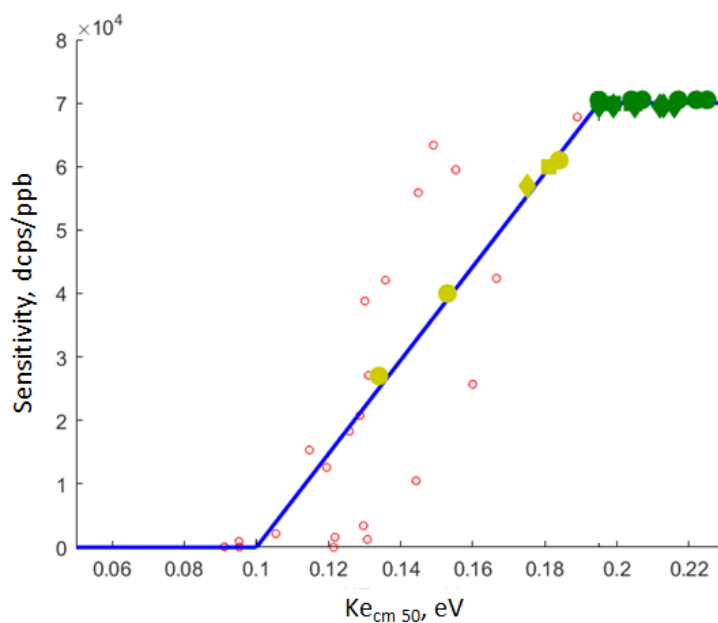


Figure 3.4.2: Estimated sensitivities for highly oxygenated C_9 (circles), C_8 (diamonds), and C_7 (squares) compounds detected in 1,2,4-TMB experiments based on their $KE_{cm\ 50}$. Red circles are the calibration points. The majority of observed compounds was observed at the maximum sensitivity (green symbols), while a few compounds were observed at lower sensitivities (yellow symbols).

produced by more than one pathway with a different number of reaction steps. Bird-sall and Elrod⁵⁵ proposed that the BPR from several aromatic precursors reacting with HO_2 can form an alkoxy radical and OH. Similarly, recent studies have shown that numerous peroxy radicals do not form a hydroperoxide in unity yield while reacting with HO_2 ^{69,1}. Hence, we observe the formation of numerous highly oxygenated compounds with molecular formulas corresponding to bicyclic carbonyls, alcohols, organonitrates,

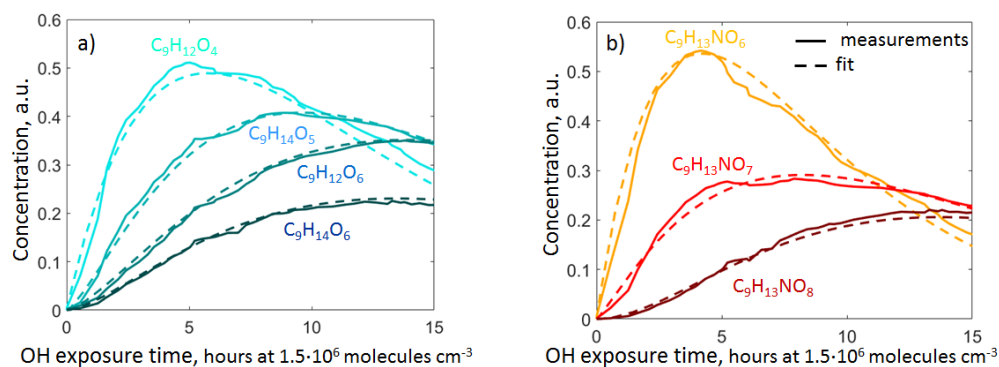


Figure 3.4.3: Measured highly oxygenated non-nitrogen containing (a) and nitrogen-containing (b) C_9 compounds from 1,2,4-TMB experiment and GKP best fit..

and hydroperoxides via the peroxide-bicyclic channel under high-NO conditions.

Table 3.4.1: Kinetics fit of gas-phase highly oxygenated compounds detected in toluene (top five rows) and 1,2,4-TMB (bottom seven rows) oxidation experiments.

Product formula	Generation	Kinetic parameter k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
	parameter m	
$C_7H_8O_4$	1.5	1.0×10^{-11}
$C_7H_{10}O_5$	1.5	1.0×10^{-11}
$C_7H_8O_6$	1.6	1.1×10^{-11}
$C_7H_9NO_6$	2.1	0.8×10^{-11}
$C_7H_9NO_8$	2.0	0.9×10^{-11}
$C_9H_{12}O_4$	1.5	1.8×10^{-11}

Table 3.4.1: Kinetics fit of gas-phase highly oxygenated compounds detected in toluene (top five rows) and 1,2,4-TMB (bottom seven rows) oxidation experiments.

Product formula	Generation	Kinetic parameter k
	parameter m	($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
$\text{C}_9\text{H}_{14}\text{O}_4$	1.6	1.7×10^{-11}
$\text{C}_9\text{H}_{14}\text{O}_5$	1.8	1.9×10^{-11}
$\text{C}_9\text{H}_{12}\text{O}_6$	1.8	1.4×10^{-11}
$\text{C}_9\text{H}_{13}\text{NO}_6$	1.4	1.7×10^{-11}
$\text{C}_9\text{H}_{13}\text{NO}_7$	2.1	2.3×10^{-11}
$\text{C}_9\text{H}_{13}\text{NO}_8$	2.3	1.8×10^{-11}

Table 3.4.2: Estimated NH_4^+ CIMS sensitivity factors for species detected in toluene experiments.

Species	m/z	$\text{KE}_{\text{cm } 50} \text{ (eV)}$	Sensitivity
			factor
$\text{C}_7\text{H}_7\text{NO}_3$	171.077	0.166	0.69
$\text{C}_7\text{H}_8\text{O}_4$	174.077	0.185	0.89
$\text{C}_7\text{H}_5\text{NO}_4$	185.056	0.166	0.69
$\text{C}_7\text{H}_7\text{NO}_4$	187.072	0.293	1
$\text{C}_7\text{H}_6\text{O}_5$	188.056	0.192	0.97
$\text{C}_7\text{H}_8\text{O}_5$	190.072	0.208	1

Table 3.4.2 (continued): Estimated NH_4^+ CIMS sensitivity factors for species detected in toluene experiments.

Species	m/z	$\text{KE}_{\text{cm } 50}$ (eV)	Sensitivity
			factor
$\text{C}_7\text{H}_{10}\text{O}_5$	192.087	0.192	0.97
$\text{C}_7\text{H}_5\text{NO}_5$	201.051	0.175	0.79
$\text{C}_7\text{H}_6\text{O}_6$	204.051	0.198	1
$\text{C}_7\text{H}_9\text{NO}_5$	205.083	0.183	0.87
$\text{C}_7\text{H}_8\text{O}_6$	206.067	0.197	1
$\text{C}_7\text{H}_{10}\text{O}_6$	208.082	0.193	0.98
$\text{C}_7\text{H}_7\text{NO}_6$	219.062	0.188	0.93
$\text{C}_7\text{H}_9\text{NO}_6$	221.077	0.187	0.92

Table 3.4.3: Estimated NH_4^+ CIMS sensitivity factors for species detected in 1,2,4-TMB experiments.

Species	m/z	$\text{KE}_{\text{cm } 50}$ (eV)	Sensitivity
			factor
$\text{C}_9\text{H}_{10}\text{O}_4$	200.092	0.236	1
$\text{C}_9\text{H}_{12}\text{O}_4$	202.108	0.204	1
$\text{C}_9\text{H}_{14}\text{O}_4$	204.124	0.184	0.89
$\text{C}_9\text{H}_{11}\text{NO}_4$	215.103	0.217	1

Table 3.4.3 (continued): Estimated NH_4^+ CIMS sensitivity factors for species detected in 1,2,4-TMB experiments.

Species	m/z	$\text{KE}_{\text{cm } 50}$ (eV)	Sensitivity
			factor
$\text{C}_9\text{H}_{10}\text{O}_5$	216.087	0.222	1
$\text{C}_9\text{H}_{12}\text{O}_5$	218.103	0.225	1
$\text{C}_9\text{H}_{14}\text{O}_5$	220.119	0.195	1
$\text{C}_9\text{H}_9\text{NO}_5$	229.083	0.134	0.36
$\text{C}_9\text{H}_{11}\text{NO}_5$	231.098	0.199	1
$\text{C}_9\text{H}_{12}\text{O}_6$	234.098	0.207	1
$\text{C}_9\text{H}_{14}\text{O}_6$	236.114	0.225	1
$\text{C}_9\text{H}_{13}\text{NO}_6$	249.109	0.153	0.56
$\text{C}_9\text{H}_{11}\text{NO}_7$	263.088	0.207	1
$\text{C}_9\text{H}_{13}\text{NO}_8$	281.099	0.207	1

In addition to the formation of closed-shell products, bicyclic peroxy radicals can undergo isomerization reactions to form more oxidized peroxy radicals^{57,56} (Fig. 3.2.2). These reactions are not included in MCM v3.3.1. These radicals can subsequently react with RO_2 , HO_2 , or NO leading to a series of more oxidised bicyclic products, so-called highly oxygenated molecules (HOMs): carbonyl ($\text{C}_x\text{H}_y\text{O}_6$), alcohol ($\text{C}_x\text{H}_{y+2}\text{O}_6$),

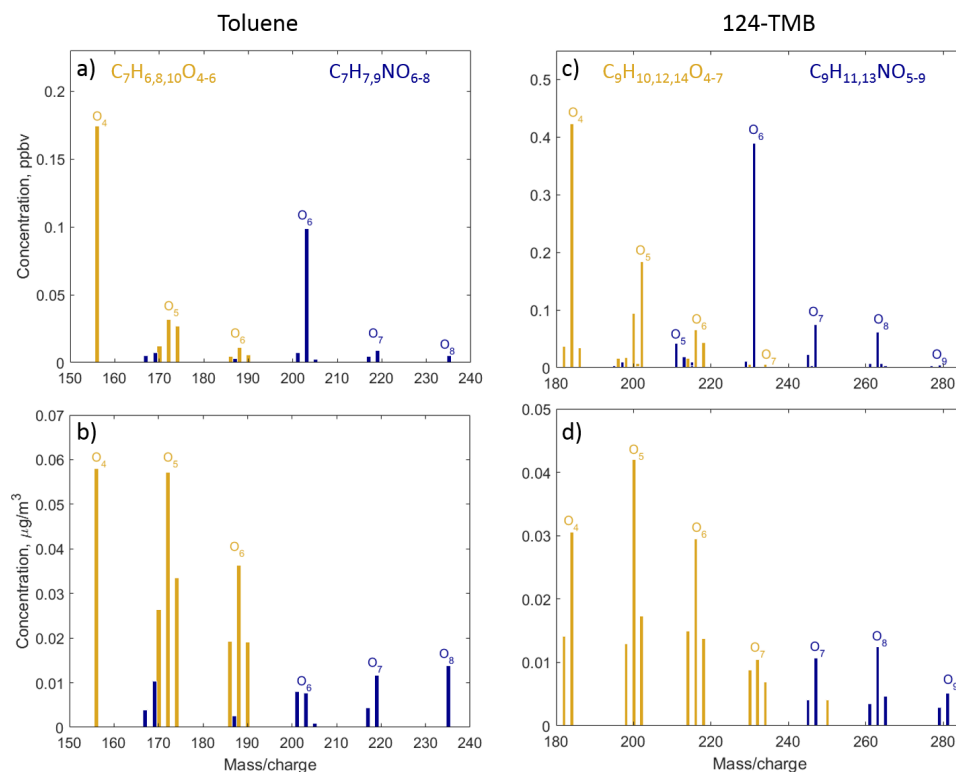


Figure 3.4.4: Mass spectra of compounds with high oxygen content ($O:C > 0.44$) from toluene (a, b) and 1,2,4-trimethylbenzene (c, d) detected by NH_4^+ CIMS. Gas-phase mass spectra are shown in (a, c), and particle-phase mass spectra are shown in (b, d). Non-nitrogen-containing compounds are shown using yellow, and nitrogen-containing compounds are shown using blue.

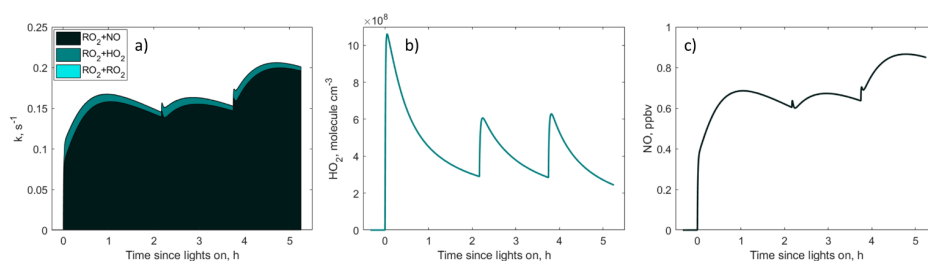


Figure 3.4.5: (a) Calculated chemical loss of bicyclic peroxy radicals calculated from the modelled concentrations of NO , HO_2 , and RO_2 ; (b) and (c) modelled concentrations of NO and HO_2 during photooxidation of toluene.

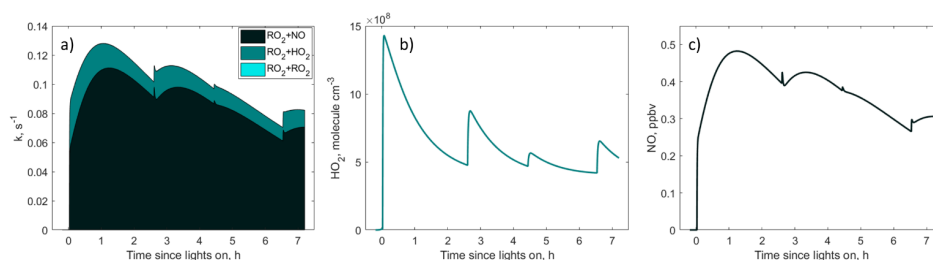


Figure 3.4.6: (a) Calculated chemical loss of bicyclic peroxy radicals calculated from the modelled concentrations of NO, HO₂, and RO₂; (b) and (c) modelled concentrations of NO and HO₂ during photooxidation of 1,2,4-TMB.

hydroperoxide ($C_xH_{y+2}O_7$), and nitrate ($C_xH_{y+1}NO_8$). Several products with the aforementioned molecular formulas are detected by NH_4^+ CIMS (Fig. 3.4.4). In the toluene experiments, $C_7H_8O_6$, $C_7H_{10}O_6$ and $C_7H_9NO_8$ were detected by NH_4^+ CIMS as $(NH_4^+) \cdot OVOCs$. In the 1,2,4-TMB experiments, $C_9H_{14}O_6$ and $C_9H_{13}NO_8$ were detected as $(NH_4^+) \cdot OVOC$, while $C_9H_{12}O_6$ was detected as both $(NH_4^+) \cdot C_9H_{12}O_6$ (m/z 234.098) and as $[(NH_4) \cdot (H_2O) \cdot C_9H_{12}O_6]^+$ (m/z 252.108). The yield of molecules with a high O:C (greater than 0.44) ratio is larger in the case of 1,2,4-TMB compared with toluene. However, the gamma kinetics parameterization suggests that none of these compounds are solely first-generation products (Table 3.4.1) which implies that there are multiple chemical pathways in which products with the same molecular formula (but potentially different structure) are formed. Some of the products can be produced in the bicyclic oxidation pathway of cresol or trimethylphenol resulting in the formation of alcohols ($C_xH_{y+2}O_5$), hydroperoxides ($C_xH_{y+2}O_6$) and nitrates ($C_xH_{y+1}NO_7$).

Formation of bicyclic alcohols and hydroperoxides from the phenolic channel is included in MCM v3.3.1. We conclude that although a plethora of compounds with a high O:C ratio was observed, only some of them are formed via first-generation isomerization/autooxidation pathways. These findings underline the importance of phenolic and benzaldehyde channels for producing highly oxygenated compounds, especially for the less substituted aromatics given the high yields of phenols and benzaldehydes and their high reactivity.

FRAGMENTED RING-RETAINING PRODUCTS

In addition to non-fragmented functionalized C₉ and C₇ products possibly formed via the bicyclic channel, a variety of lower-carbon-containing (C₈ and C₆) products were also detected in both chemical systems. The total concentration of C₈ components predicted by MCM v3.3.1 for 1,2,4-TMB is in good agreement with the NH₄⁺ CIMS and H₃O⁺ CIMS measurements (less oxidized compounds, O:C < 0.25, were detected using H₃O⁺ CIMS, whereas NH₄⁺ CIMS was used for more oxidized species), although the observed composition is distinctly different from the MCM prediction (Fig. 3.4.7). According to MCM, there are only four C₈ products with mixing ratios at or above the parts per trillion (ppt) level. The most abundant predicted compound, bicyclic carbonyl (C₈H₁₀O₄, MXYOBPEROH in MCM), is produced via the reaction of bicyclic nitrate C₉H₁₃NO₆ with OH, whereas the second most abundant compound, dimethylnitrophenol (C₈H₉NO₃, DM124OHNO₂ in MCM), is formed in the benzaldehyde pathway.

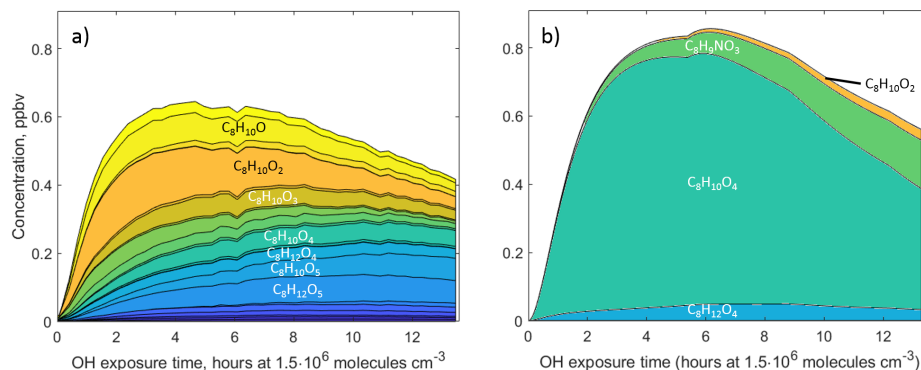


Figure 3.4.7: The C_8 gas-phase products (a) detected by H_3O^+ CIMS and NH_4^+ CIMS and (b) predicted by MCM v3.3.1 during oxidation of 1,2,4-trimethylbenzene.

While all of the predicted products have been observed, NH_4^+ CIMS and H_3O^+ CIMS also detect a plethora of C_8 compounds not included in MCM. Furthermore, MCM only predicts a total of 0.16 ppb for all C_6 compounds in the toluene experiments, while the combined measured mixing ratio of 15 C_6 compounds is ~ 0.5 ppb (Fig. 3.4.8). The two most prominent C_6 products recommended by MCM, $C_6H_5NO_3$ and $C_6H_6O_2$, are predicted to be formed in the benzaldehyde channel.

There are several pathways that may lead to the formation of the fragmented ring-retaining C_8 and C_6 products. One of them is ipso addition followed by dealkylation⁷⁰. In their study of the dealkylation pathway in the OH-initiated oxidation of several aromatic compounds, Noda et al.⁷¹ showed the importance of this pathway and reported dealkylation yields of 0.054 for toluene. Similarly, Birdsall and Elrod⁵⁵ determined a

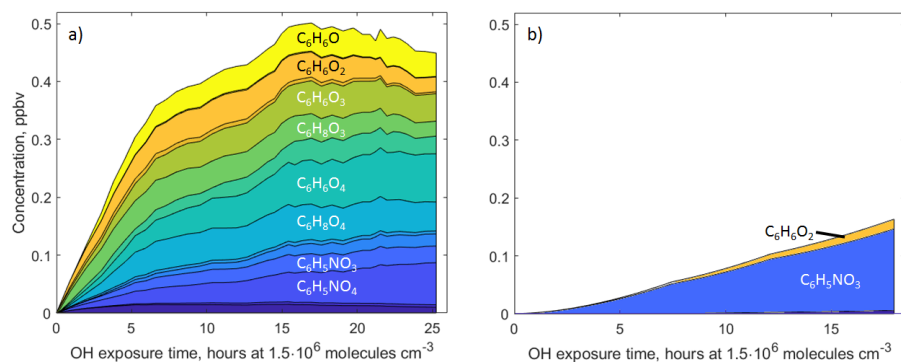


Figure 3.4.8: The C_6 gas-phase products (a) detected by H_3O^+ CIMS and NH_4^+ and (b) predicted by MCM v3.3.1 during oxidation of toluene

0.047 yield of dealkylation products for toluene. Loison et al.⁷⁰ reported a 0.02 yield of dealkylation pathway products from the hexamethylbenzene+OH reaction. However, in some studies, yields of dealkylation products have been found below 0.01⁷². While we cannot determine exact yields of observed dealkylation compounds as many of them are later-generation products, we estimate an overall amount of carbon of ~ 3 and ~ 5 ppbC stored in C_6 and C_8 compounds for toluene and 1,2,4-TMB respectively, compared with 600 ppbC in the system as a whole. Although observed concentrations of these products are not very high, a significant fraction ($> 40\%$) of them are highly oxygenated products with an O:C ratio greater than 0.5. These products can effectively partition to the particle phase and contribute to SOA formation.

PRODUCTS FROM THE RING-SCISSION PATHWAY

Recent theoretical studies suggest that the ring-scission pathway leads to a series of two ring-scission products such that the total number of carbon atoms present in the original aromatic compound is conserved in the two products^{43,49}. In particular, a toluene study by Wu et al.⁴³ predicted significant yields of 1,2-dicarbonyls and a range of C₄ and C₅ products. Those larger compounds include dicarbonyls (butenedial C₄H₄O₂ and methylbutenedial C₅H₆O₂), which had already been detected in previous experimental studies⁴², and newly proposed epoxy-dicarbonyl products (epoxybutenedial C₄H₄O₃ and methylepoxybutenedial C₅H₆O₃). As for 1,2,4-TMB, Li and Wang⁴⁹ also predict two groups of ring-scission products: (1) smaller 1,2-dicarbonyls such as glyoxal, methylglyoxal and biacetyl and (2) larger C₅, C₆ and C₇ products. Similar to the toluene system, those larger compounds include dicarbonyls (C₅H₆O₂, C₆H₈O₂, and C₇H₁₀O₂), which had previously been reported in numerous studies, and new epoxy-dicarbonyl products (C₅H₆O₂ and C₆H₈O₃). Some experimental studies reported that larger ring-scission products were found at systematically lower yields than the corresponding 1,2-dicarbonyl products⁷³. This result suggests that either the product pair carbon conservation rule is not followed or that the larger products undergo further photochemical or heterogeneous degradation in the environmental chamber.

Table 3.4.4: Major toluene oxidation products measured by H_3O^+ CIMS and NH_4^+ CIMS.

Product Name	Product formula	Generation	Kinetic parameter k	
		parameter m	($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Yield (%)
Glyoxal	$\text{C}_2\text{H}_2\text{O}_2$	1.2	1.3×10^{-11}	8%
Methylglyoxal	$\text{C}_3\text{H}_4\text{O}_2$	1.3	1.1×10^{-11}	15%
Butenedial	$\text{C}_4\text{H}_4\text{O}_2$	0.8	2.0×10^{-11}	8%
Methylbutenedial	$\text{C}_5\text{H}_6\text{O}_2$	0.7	2.0×10^{-11}	37%
Epoxybutanedial	$\text{C}_4\text{H}_4\text{O}_3$	1.3	1.0×10^{-11}	5%
Methylepoxybutanedial	$\text{C}_5\text{H}_6\text{O}_3$	1.3	1.0×10^{-11}	5%
Benzaldehyde	$\text{C}_7\text{H}_6\text{O}$	1.0	1.0×10^{-11}	9%
Cresol	$\text{C}_7\text{H}_8\text{O}$	1.0	2.3×10^{-11}	10%
Dicarbonyl epoxide	$\text{C}_7\text{H}_8\text{O}_3$	0.9	2.2×10^{-11}	1%

Table 3.4.5: Major 1,2,4-TMB oxidation products measured by H_3O^+ CIMS and NH_4^+ CIMS.

Product Name	Product formula	Generation	Kinetic parameter k	
		parameter m	($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Yield (%)
Methylglyoxal	$\text{C}_3\text{H}_3\text{O}_3$	1.3	1.8×10^{-11}	25%
Biacetyl	$\text{C}_4\text{H}_6\text{O}_2$	1.3	2.2×10^{-11}	10%
Methylbutenedial	$\text{C}_5\text{H}_6\text{O}_2$	0.7	3.5×10^{-11}	5%
Dimethylbutenedial	$\text{C}_6\text{H}_8\text{O}_2$	0.9	4.1×10^{-11}	40%
Trimethylbutenedial	$\text{C}_7\text{H}_{10}\text{O}_2$	1.0	5.1×10^{-11}	2%
Methylepoxybutanedial	$\text{C}_5\text{H}_6\text{O}_3$	1.8	1.9×10^{-11}	N/A
Dimethylepoxybutanedial	$\text{C}_6\text{H}_8\text{O}_3$	1.1	2.4×10^{-11}	2%
Dimethylbenzaldehyde	$\text{C}_9\text{H}_{10}\text{O}$	1.0	1.4×10^{-11}	3%
Trimethylphenol	$\text{C}_9\text{H}_{12}\text{O}$	1.0	3.5×10^{-11}	2%
Dicarbonylepoxide	$\text{C}_9\text{H}_{12}\text{O}_3$	1.0	4.0×10^{-11}	1%

A series of dicarbonyls were experimentally detected including glyoxal and methylglyoxal in the toluene experiments, and methylglyoxal and biacetyl in the 1,2,4-TMB experiments (Tables 3.4.4 and 3.4.5). Although a relatively small amount of glyoxal (2.5 ppb) is predicted to be formed from the 1,2,4-TMB+OH pathway, observed amounts of glyoxal were below the limit of detection of the Madison LIP instrument (1 ppb) suggesting that the glyoxal yield does not exceed 0.03 in this system. Measured glyoxal and methylglyoxal formation yields, combined with the biacetyl yield from the 1,2,4-TMB oxidation, indicate that under high-NO conditions the first-generation yield of all 1,2-dicarbonyls is ~ 0.43 and ~ 0.35 for toluene and 1,2,4-TMB respectively (Tables 3.4.4 and 3.4.5). For all 1,2-dicarbonyls the observed generation number m is greater than 1 and is consistent between the two systems, which suggests that these compounds are produced by more than one pathway with different numbers of reaction steps. In addition to the aforementioned 1,2-dicarbonyls, a series of dicarbonyls with a higher carbon number was observed in both systems (Tables 3.4.4 and 3.4.5). For all of these species (except trimethylbutenedial) the generation number m is slightly smaller than 1. Finally, ions corresponding to newly proposed epoxy-dicarbonyl products were also observed (Tables 3.4.4 and 3.4.5). However, the generation number m for these compounds is between 1 and 2, suggesting that there are multiple pathways resulting in compounds with those molecular formulas. Overall, we observed ~ 0.45 and ~ 0.47 yields of larger carbonyls in the toluene and 1,2,4-TMB experiments respectively.

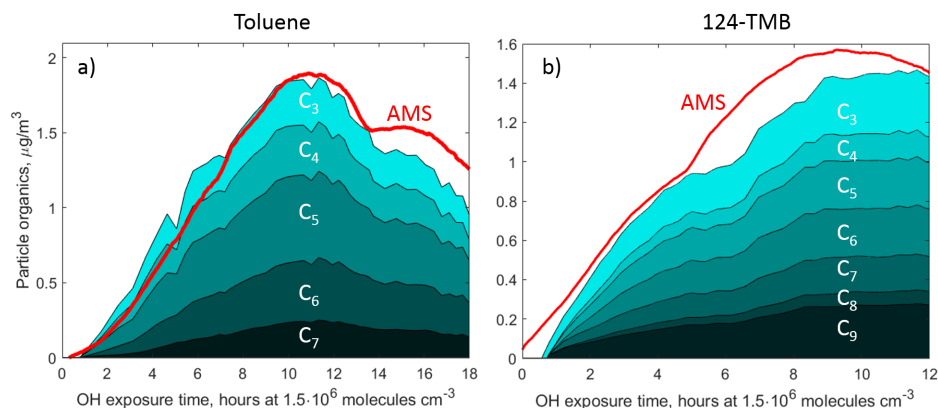


Figure 3.4.9: Total organics measured in the particle phase by NH_4^+ CIMS and binned by the carbon atom number in (a) the toluene photooxidation experiment and (b) the 1,2,4-TMB photooxidation experiment. Total carbon measured by AMS is in red.

3.4.3 SOA ANALYSIS

The peak SOA concentration measured by TD- NH_4^+ CIMS was $1.8 \mu\text{g m}^{-3}$ for the toluene oxidation experiment and $1.4 \mu\text{g m}^{-3}$ for 1,2,4-TMB which is in good agreement with the AMS measurements (1.9 and $1.6 \mu\text{g m}^{-3}$ respectively). Figure 3.4.9 depicts the relative distribution of carbon in the particle phase according to the carbon atom number n_C for 1,2,4-TMB and toluene SOA respectively. The O:C ratios calculated from individual species measured from thermally desorbed SOA using NH_4^+ CIMS were ~ 0.95 for toluene SOA and ~ 0.7 for 1,2,4-TMB SOA. These ratios are in good agreement with the atomic O:C ratios measured by AMS⁷⁴ (0.85 and 0.65 for toluene and 1,2,4-TMB SOA respectively).

Products observed in the gas phase are compared to those detected in the particle phase to further understand the mechanism of SOA formation from aromatics precursors. A variety of ring-retaining products were observed in the particle phase for oxidation of 1,2,4-TMB and toluene: non-fragmented products (e.g., $C_9H_{12}O_{4-6}$ for 1,2,4-TMB and $C_7H_8O_{4-6}$ for toluene) and fragmentary products (e.g., $C_8H_{10}O_{4-5}$ and $C_7H_8O_{4-5}$ for 1,2,4-TMB and $C_6H_6O_{4-5}$ for toluene). The same non-fragmentary ring-retaining oxioxidation products, detected by NH_4^+ CIMS in the gas phase and expected to be low in volatility, are observed in the particle phase (Fig. 3.4.4). Overall, ring-retaining products make up a significant fraction of the total 1,2,4-TMB SOA mass ($\sim 25\%$ for 1,2,4-TMB SOA and $\sim 30\%$ for toluene SOA) (Fig. 3.4.9), even though the total concentration of these products in the gas phase is relatively small (~ 2 ppb for 1,2,4-TMB and ~ 1 ppb for toluene). Furthermore, numerous species corresponding to those of the ring-scission products were detected including $C_5H_8O_3$, $C_4H_6O_3$, and $C_3H_4O_2$. It is likely that the concentration of larger ring-retaining products in the particle phase is underestimated due to their thermal fragmentation in the desorption unit inlet of the NH_4^+ CIMS instrument²⁷, although it should be noted that many highly oxygenated compounds were detected, e.g., $C_7H_6O_6$ and $C_9H_{10}O_7$. These findings underscore the importance of bicyclic, phenolic, and benzaldehyde channels for producing ring-retaining highly oxygenated compounds that comprise a significant fraction of SOA (more than 25%).

3.5 CONCLUSIONS AND IMPLICATIONS FOR THE AROMATIC OXIDATION

MECHANISM

In the present work, we studied the multigenerational photooxidation of two aromatic compounds (toluene and 1,2,4-trimethylbenzene) in an environmental chamber under relevant urban high-NO conditions. We identified a number of oxidation products based on their molecular formula and determined yields for certain first-generation products. We provided kinetic and mechanistic information on numerous products using a gamma kinetics parameterization fit.

We compare and contrast observed products with predictions from the Master Chemical Mechanism (MCM v3.3.1), which provides explicit representation of chemical reactions that constitute the overall aromatic oxidation mechanism on the basis of the extensive body of existing experimental work. Laboratory studies are a vital support for the mechanism, and the agreement between these studies and the MCM output is one of the important criteria demonstrating the accuracy of the kinetic model prediction. MCM accurately predicts the overall presence and importance of the three major channels for the primary OH-initiated oxidation of aromatic compounds (peroxide-bicyclic, benzaldehyde, and phenolic). However, the epoxy-oxy channel appears to be overpredicted by the MCM-based kinetic model. In both systems we observed a variety of stable bicyclic products which underlines the importance of the bicyclic channel in

the oxidation of aromatic compounds (Fig. 3.2.1). MCM correctly predicts the greater importance of the bicyclic pathway for the more substituted aromatics, although the speculated fate of BPRs is not entirely consistent with observations. In addition to bicyclic organonitrates, carbonyls and alcohols, we detect numerous compounds with molecular formulas corresponding to bicyclic hydroperoxides, which suggests that this class of products may be formed in the oxidation of aromatic molecules even under high-NO conditions. Recent studies^{56,57} suggest that bicyclic peroxy radicals can undergo isomerization and autooxidation reactions, leading to the formation of HOMs. Furthermore, Molteni et al.⁵⁶ report that the HOM yields from various aromatics are relatively uniform and are not linked to bicyclic peroxy radical or phenol formation yields. Here, we observe the formation of highly oxygenated compounds with a high O:C ratio (of up to 1.1) in both systems. However, the abundance of these compounds is greater in the case of 1,2,4-TMB for which the yield of the bicyclic peroxy radicals is higher (Fig. 3.4.4). Moreover, the observed kinetics of these compounds suggests that they might be produced by more than one pathway, including both the isomerization/autooxidation reactions and further oxidation of phenols and benzaldehydes. Many of these compounds are low in volatility and comprise a significant fraction (more than 25%) of SOA mass, which was measured using AMS and TD-NH₄⁺ CIMS and the two measurements are in good agreement. These findings emphasise the significance of ring-retaining highly oxygenated products for SOA formation and provide further evidence that isomerization and autooxidation reactions can be fast enough to compete with bimolecular reactions

with NO and HO₂ even under high-NO conditions (in this study the total BPR loss rate is estimated to be $\sim 0.1\text{--}0.2\text{ s}^{-1}$; Figs. 3.4.5 and 3.4.6). A plethora of fragmentary ring-retaining products is observed in the gas phase in both systems, many of which are not present in the MCM, which underlines the importance of the fragmentation pathway in the oxidation of aromatic compounds. Numerous ring-scission products are detected, including C₂–C₇ dicarbonyls and C_{4–6}H_{4–8}O₃ products, possibly epoxydicarbonyls. The kinetics of the ring-scission products (e.g., generation number *m*) is consistent between the two systems, which suggests that many of those carbonyls are produced in more than one pathway with a differing number of reaction steps with OH, and those pathways are similar between different aromatic systems.

3.6 ADDITIONAL INFORMATION

3.6.1 INLET LOSSES IN CIMS INSTRUMENTS

Concentrations of gaseous analytes can be perturbed by gas-wall interactions occurring in the tubing used for sampling gases from the environmental chamber or inside the instruments. In order to estimate the response timescale of CIMS instruments (PTR₃, VOCUS 2R PTR-TOF, and I[−] CIMS), we follow the procedure described in detail by Pagonis et al.⁷⁵. At the beginning of the procedure, the instruments sampled air from the environmental chamber containing decane photooxidation products. Later, the instruments sampling lines were abruptly reconnected to zero air resulting in step-function

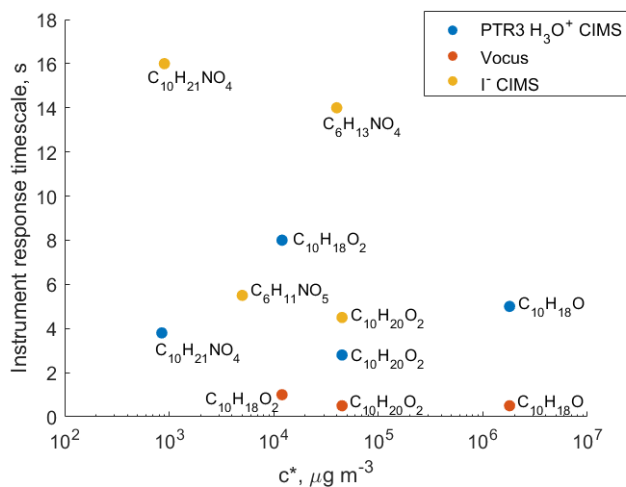


Figure 3.6.1: Measured instrument delay times as a function of SIMPOL c^* for CIMS instruments.

decrease in the concentrations of the oxidation products. PTR₃, VOCUS 2R PTR-TOF and I^- CIMS time responding profiles measured in response to this step-function decrease were used to calculate delay times for the three instruments. Inlet delay times for all measured compounds did not exceed 20 seconds (Fig. 3.6.1).

4

Application of spin trapping and chemical derivatization techniques combined with chemical ionization mass spectrometry to detect Criegee intermediates and peroxy radicals in the gas phase

4.1 ABSTRACT

SHORT-LIVED HIGHLY REACTIVE ATMOSPHERIC SPECIES, such as organic peroxy radicals (RO_2) and Criegee intermediates (CIs), play an important role in controlling the oxidative removal of many natural and anthropogenic trace gases in the atmosphere. Direct speciated measurements of these components are required for understanding their atmospheric fate and impact. We describe the development of an online field-deployable

method for integrated production measurements of CIs and RO₂ in laboratory experiments using chemical derivatization and spin trapping techniques combined with H₃O⁺ and NH₄⁺ chemical ionization mass spectrometry (CIMS). Using chemical derivatization agents with low proton affinity, we scavenge all CIs produced from a wide range of alkenes without depleting CIMS reagent ions. Comparison between our measurements and results from numeric modelling, using the Master Chemical Mechanism, shows that the method can be used for quantification of CIs in laboratory experiments. We show that spin traps are highly reactive with atmospheric radicals by studying the kinetics of their reaction with hydroxyl radical (OH) and efficiently form stable adducts with them in the gas phase. We also demonstrate that spin trap adducts with CIs and RO₂ can be simultaneously probed and quantified with detection limits of $\sim 6 \times 10^6$ molecules cm⁻³ for a 1 s integration time. Spin trapping allows for preventing radical secondary reactions and cycling, which ensures that measurements are not biased by chemical interferences, and can be implemented for detecting CIs and RO₂ species in the ambient atmosphere.

4.2 INTRODUCTION

The Earth's atmosphere is an oxidizing environment. The initial oxidation step of volatile organic compounds (VOCs) involves reaction of a parent hydrocarbon with an oxidant. The hydroxyl radical (OH) is the most important oxidation compound in the atmosphere, although oxidation can be also initiated by O₃, NO₃ and Cl- or Br-atoms. Gen-

erally, reaction of VOCs with OH, NO₃ and Cl-atoms occurs via H-abstraction or via addition to unsaturated carbon double bonds leading to formation of alkyl radicals. This reaction is quickly followed by O₂ addition resulting in production of organic peroxy radicals (RO₂). In an NO-rich environment, peroxy radicals predominantly react with NO, while at lower NO concentrations reactions with HO₂, potentially other RO₂, and unimolecular reactions become more important. The common tendency is formation of closed-shell, more oxidized VOCs (OVOCs). OVOCs may have lower volatilities than the parent hydrocarbons and may partition to the particle phase, thereby contributing to secondary organic aerosol (SOA) formation. OH, HO₂ and RO₂ radicals can form a catalytic reaction cycle, which is connected to the photochemically driven equilibrium between NO₂ and NO, leading to the production of tropospheric ozone. This cycle is terminated by the formation of organic hydroperoxides and nitrates, which can be viewed as reservoirs of the corresponding radicals. Overall, atmospheric radicals, especially their cycling, play an important role in formation of SOA and tropospheric ozone, as well as in controlling atmospheric oxidation capacity.

Organic peroxy radicals can also be formed via ozonolysis of unsaturated organic compounds. Ozonolysis of alkenes results in the formation of primary ozonides that promptly decompose to a stable carbonyl and a vibrationally excited carbonyl oxide, also known as a Criegee intermediate (CI), some of which are thermally stabilized (sCI). CI can further react with water vapor and other trace gases and are believed to play an important role in oxidation of SO₂ to form H₂SO₄⁴. *cis*-CI can also undergo a unimolecular

reaction and form a vinyl hydroperoxide, which rapidly decomposes to an OH radical and a vinyl radical. This radical is in resonance with an acetonyl-type radical, which can combine with molecular oxygen to form an RO₂ species⁵.

Measurements of atmospheric radicals and reactive intermediates, such as RO₂ and CIs, are challenging because of their high reactivity towards trace gases and surfaces and rapid cycling, which may lead to potential interferences. Highly sensitive detection systems are required to determine the minute concentrations of these species, which are typically on the order of 10⁸ molecules cm⁻³ for organic peroxy radicals⁷⁶ and are expected to be less than 10⁵ molecules cm⁻³ for CIs⁴. The concentrations of individual RO₂ species can be much lower due to the large number of different RO₂. With respect to organic peroxy radicals, there are several direct measurement techniques available. Matrix Isolation Electron Spin Resonance Spectroscopy (MIESR) is an established, but rarely used, method for field measurements⁷⁷. MIESR is an offline technique with a low time resolution (~30 min), however, its main advantage is that it does not require instrument calibration. Besides MIESR, chemical amplification and conversion systems represent another class of instruments for field studies^{78, 79, 80, 81}. A detection limit of 10⁷ cm⁻³ can be achieved at a temporal resolution of 15 s, however discrimination of different RO₂ is not possible⁷⁸. Finally, laser-induced fluorescence (LIF) technique was also applied for field measurements of peroxy radicals⁷⁶. This technique is characterized by an excellent limit of detection of $(2 - 7) \times 10^7$ cm⁻³ for an integration time of 30 s. LIF and chemical amplification techniques are indirect methods that are based

on chemical conversion of RO_2 to other radicals or closed-shell molecules (e.g., OH , NO_2 , or H_2SO_4). The sensitivity of these methods depends on the RO_2 conversion efficiency, which may vary for different RO_2 species. In addition, secondary chemistry, that is, additional sources of radical production and destruction, has to be considered, and care needs to be taken to ensure that measurements are not biased by any chemical interferences^{82,83}. Recently, novel mass spectrometric techniques using different ionization schemes to directly detect individual RO_2 species were developed^{32, 84, 85}.

As for CIs, indirect measurement techniques were widely used in the past. In these techniques CIs are chemically converted to other species^{86, 87, 88} (e.g., H_2SO_4 or hydroxymethyl hydroperoxide, HMHP). In 2008, the simplest CI, CH_2OO , was directly detected for the first time⁸⁹. Later synchrotron photoionization mass spectrometry was combined with the CI generation technique using diiodoalkane photolysis⁹⁰, which spurred several studies to examine kinetics of bimolecular and unimolecular CI reactions^{91, 92, 93}. Recently two new techniques for direct measurements of CIs using spin trapping and chemical ionization mass spectrometry (CIMS) were introduced^{94, 95}.

Despite the abundance of different analytical methods used for detection of atmospheric radicals and reactive intermediates, there is still a need for an online, direct, field-deployable technique for measuring these short-lived highly reactive compounds in a speciated way. Free radicals have been conventionally detected by chemical derivatization techniques including spin trapping in biological and chemical systems^{96, 97}. However, there are only few studies in which these techniques were applied for probing

atmospheric radicals and intermediates. Watanabe et al.⁹⁸ presented an offline method to quantify hydroxyl radicals using the spin trap 4-POBN where stable adducts were detected by electron spin resonance. Recently, Giorio et al.⁹⁴ used the spin trap DMPO to characterize CIs by detecting spin trap adducts with online mass spectrometry. Here we describe how chemical derivatization and spin trapping agents could be implemented for detection and quantification of several atmospheric radicals and reactive intermediates. By combining chemical derivatization and spin trapping techniques with CIMS, we can obtain online integrated production measurements of organic peroxy radicals and Criegee intermediates formed from ozonolysis of a wide range of parent hydrocarbons. Effective stabilization and scavenging of CIs and RO₂ species using spin traps and chemical derivatization agents leads to suppression of the radical secondary chemistry within the experimental setup, which helps to reduce potential measurement interferences. We show that by implementing chemical derivatization agents, which are reactive towards CIs only, have low proton affinity and high vapor pressure, we can react away all CIs without depleting CIMS reagent ions. Next, we demonstrate that spin traps are highly reactive towards radicals in the gas phase, by studying kinetics of their reaction with OH, and therefore can effectively scavenge atmospheric radicals and intermediates. We also show that CIs and RO₂ species from the same precursor can be simultaneously detected as adducts with the spin trap using NH₄⁺ and H₃O⁺ CIMS. The analytical methods presented here can be used for quantification of CIs and RO₂ formed in laboratory experiments as well as for field measurements.

4.3 METHODS

4.3.1 OZONOLYSIS EXPERIMENTS WITH CHEMICAL DERIVATIZATION AGENT HFA

The ozonolysis experiments of multiple hydrocarbons including tetramethylethylene (TME), isoprene, pentene, hexene, α -pinene and limonene were conducted in a flow tube setup at ambient pressure and temperature (293 K) and dry conditions (relative humidity < 2%). The experimental setup comprised of a flow tube with a residence time of ~ 10 s. The parent hydrocarbon was mixed with ozone and the chemical derivatization agent hexafluoroacetone (HFA, C_3F_6O) in the flow tube leading to formation of CIs and their further stabilization as CI-HFA adducts. CIs are known to be highly reactive towards ketones, especially electron poor ones such as HFA⁹¹. The other advantage of employing this chemical derivatization agent is its relatively low proton affinity (PA 670.4 kJ/mol^(ref 99)). Since the PA of HFA is lower than that of water, HFA cannot be protonated in H_3O^+ CIMS. Hence, one can introduce significant amount of HFA to the system to make sure that all CIs are reacted away very rapidly without any concern that H_3O^+ reagent ions would be depleted. The hydrocarbon was vaporized from a flask filled with pure substance by passing a constant flow of zero air regulated via a 0.1-10 cm³ min⁻¹ mass flow controller (Bronkhorst). HFA flow was regulated by another mass flow controller (Bronkhorst). Ozone was produced by passing zero air through an ozone generator using a low-pressure mercury ultraviolet lamp. Ozone concentration

was measured using an ozone monitor (2B Technologies).

A proton-transfer-reaction mass spectrometer (PTR-8000, IONICON Analytik) was used to observe formed HFA·CI adducts as well as parent hydrocarbons and their oxidation products. This instrument was operated using H_3O^+ reagent ions (H_3O^+ CIMS) and was directly calibrated to 10 VOCs with different functional groups using LCU.

4.3.2 EXPERIMENTS WITH SPIN TRAPS

KINETICS EXPERIMENTS WITH SPIN TRAP TEMPO

A set of experiments, in which the reaction rate coefficient between the spin trap (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO, $\text{C}_9\text{H}_{18}\text{NO}$) and OH was measured, was conducted at Forschungszentrum Jülich. TEMPO is commonly used to detect carbon-centered radicals in chemical and biological systems¹⁰⁰ and is known to be highly reactive towards OH in the aqueous phase¹⁰¹. The experimental setup comprised of a flow tube flushed with purified zero air with the total flow set to 3 l SLPM. TEMPO was introduced in the flow tube using a liquid calibration unit (LCU, IONICON Analytik). One part of the outflow was drawn to a laser photolysis – laser-induced fluorescence (LP-LIF) instrument¹⁰², with which OH reactivity of TEMPO was measured. Laser flash photolysis of ozone was used to produce OH in the experimental setup, and LIF was applied to monitor the time dependent OH decay. Another part of the outflow was

drawn to a CIMS instrument PTR₃ (IONICON Analytik) to monitor concentrations of TEMPO and its oxidation products. This instrument was operated in two ionization modes: using $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$, $n = 0, 1$ (as H_3O^+ CIMS²²) and $\text{NH}_4^+ \cdot (\text{H}_2\text{O})_n$, $n = 0, 1, 2$ (as NH_4^+ CIMS²⁷) reagent ions. The PTR₃ is designed to minimize inlet losses of sampled compounds. It was directly calibrated to 10 VOCs using with different functional groups using LCU. Collision-dissociation methods were used to constrain sensitivities of NH_4^+ CIMS²⁷.

OZONOLYSIS EXPERIMENTS WITH SPIN TRAP DMPO

An additional set of ozonolysis experiments of several hydrocarbons including TME and α -pinene were conducted in a double flow tube setup (Fig. 4.3.1). The goal of these experiments was to demonstrate how spin traps can be used for simultaneous detection of Criegee intermediates and peroxy radicals. The parent hydrocarbon was mixed with ozone in the first flow tube, while the spin trap 5,5-Dimethyl-1-pyrroline N-oxide (DMPO, $\text{C}_6\text{H}_{11}\text{NO}$) was introduced in the second flow tube using an LCU. DMPO was widely used to detect oxygen-centered radicals, such as OH, HO_2 and RO_2 , in chemical and biological systems^{103, 104}. Recently, DMPO was also employed to detect CIs in the gas phase⁹⁴. Similar to the previous ozonolysis experiments described in Section 4.3.1, the parent hydrocarbon was vaporized from a flask filled with pure substance by passing zero air regulated by a mass flow controller, and ozone was generated using a low-pressure mercury ultraviolet lamp. The PTR₃ was implemented to detect spin trap

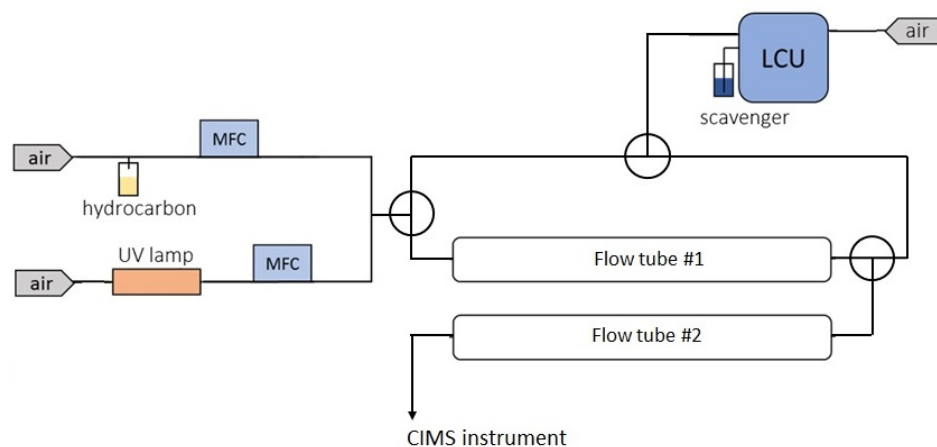


Figure 4.3.1: Schematic of experimental setup.

adducts with CIs and RO₂ species, while ozone levels were observed using an ozone monitor (2B Technologies).

4.3.3 KINETIC MODEL AND QUANTUM-CHEMICAL CALCULATIONS

The Framework for o-D Atmospheric Modelling v3.1 (FoAM⁶³) containing reactions from the Master Chemical Mechanism^{105,106} (MCM v3.3.1) was used to simulate the photooxidation of studied alkenes in experimental setups and to compare mixing ratios of modelled products with the measurements. Model calculations were constrained to physical parameters of the experimental setup (pressure and temperature) as well as to observed mixing ratios of the parent hydrocarbon, ozone and the chemical derivatization agent.

Geometry optimization and proton affinity calculations were performed with the

Gaussian 09 package¹⁰⁷ using the B3LYP functional¹⁰⁸ and TZVP basis set.

4.4 RESULTS AND DISCUSSION

4.4.1 DETECTION OF CRIEGEE INTERMEDIATES USING CHEMICAL DERIVATIZATION TECHNIQUES

Starting with $(\text{CH}_3)_2\text{COO}$, a CI produced from the ozonolysis of TME, the primary goal was detection of Criegee intermediates as adducts with the chemical derivatization agent HFA to prevent secondary reactions within the detection setup. We observed the formation of CI·HFA adducts when TME, ozone and HFA were present in the system (Fig. 4.4.1). $(\text{CH}_3)_2\text{COO}\cdot\text{HFA}$ ($\text{C}_6\text{F}_6\text{H}_6\text{O}_3\cdot\text{H}^+$, m/z 241.03) can be easily identified in the mass-spectrum due to its unique mass defect associated with six F-atoms. Since the reaction rate constant of CI·HFA with H_3O^+ ions is unknown, we assumed that all CI·HFA adducts performed proton transfer from hydronium ions and therefore used the sensitivity we obtained from acetone calibration to quantify detected CI·HFA species. In addition, we did not take into account possible fragmentation of CI·HFA adducts which may impede detection of larger CIs (e.g., C_{10} CIs formed via ozonolysis of monoterpenes). These assumptions may lead to measurement uncertainties as discussed later in this section.

We measured the $(\text{CH}_3)_2\text{COO}\cdot\text{HFA}$ adduct signal as a function of different reactant

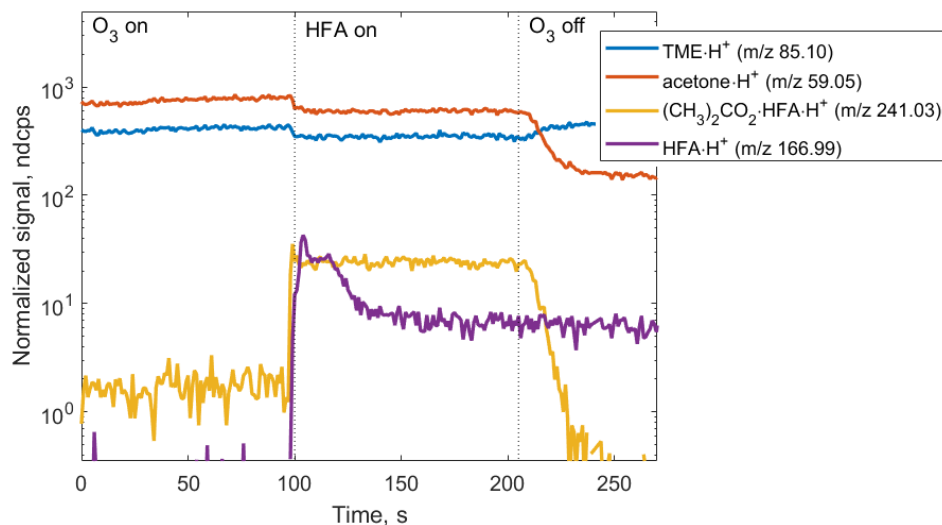
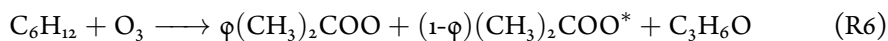


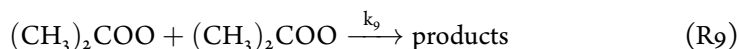
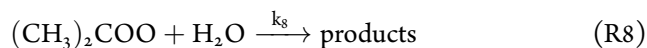
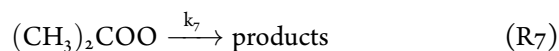
Figure 4.4.1: Ion tracers observed in a TME ozonolysis experiment as a function of different reactant conditions. Reactant concentrations are $[TME] = 1.85 \times 10^{12}$; $[O_3] = 1.67 \times 10^{13}$; $[HFA] = 6.09 \times 10^{15}$ molecules cm^{-3} .

conditions: initial TME concentration were in the range of $(1.48 - 1.85) \times 10^{11}$ molecule cm^{-3} , ozone, $(6.77 - 108.2) \times 10^{12}$ molecule cm^{-3} , HFA $(1.17 - 6.13) \times 10^{15}$ molecule cm^{-3} . Concentration of $(CH_3)_2COO \cdot HFA$ adducts were calculated using MCM with updated kinetics data from the literature^{109,93,110}. Acetone oxide $(CH_3)_2COO$ and acetone are formed via ozonolysis of TME, while only a certain fraction of CIs is thermally stabilized:



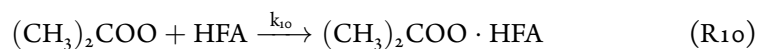
where $\varphi = 0.32$ is the yield of sCIs for this reaction¹⁰⁹.

Stabilized CI can in turn undergo unimolecular and bimolecular reactions with trace gases:



where $k_7 = 305 \text{ s}^{-1}$ (ref⁹³), $k_8 = 1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (ref¹¹⁰), $k_9 = 6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (ref⁹³).

Stabilized CI can also react with HFA and form stable adducts:



The reaction rate coefficient k_{10} was not measured experimentally, so we used the k -value for $\text{CH}_2\text{OO} + \text{HFA}$ reaction: $k_{10} = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (ref⁹¹). It was suggested that the reaction between HFA and acetone oxide may be slower comparing to the one with CH_2OO ^{111,91}. However, the concentration of HFA was two orders of magnitude higher than concentrations of other chemical compounds, so even at lower k -values reaction with HFA remains the major chemical loss pathway for $(\text{CH}_3)_2\text{COO}$ (Fig. 4.4.2).

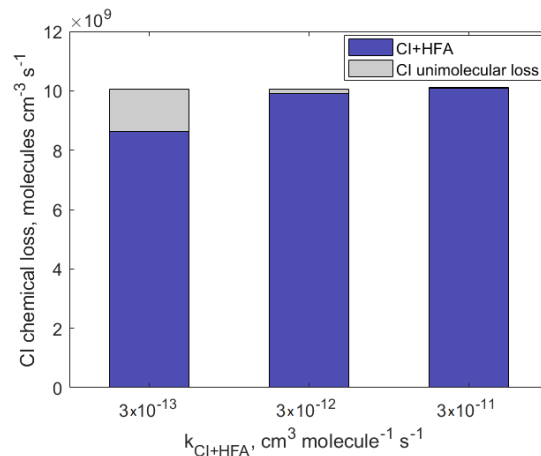


Figure 4.4.2: Chemical loss of Criegee intermediates $(\text{CH}_3)_2\text{COO}$ calculated assuming different $k_{\text{Cl+HFA}}$ reaction rates under experimental conditions. $k_{\text{Cl+HFA}} = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ corresponds to the rate constant for $\text{CH}_2\text{OO} + \text{HFA}$ reaction. Even at lower values of the reaction rate the major chemical loss pathway for CI is reaction with HFA.

The observed mixing ratio of $(\text{CH}_3)_2\text{COO} \cdot \text{HFA}$ is a factor of 3 lower than the mixing ratio predicted by the model (Fig. 4.4.3). This discrepancy can be explained by a combination of the following factors: (1) wall losses of $(\text{CH}_3)_2\text{COO} \cdot \text{HFA}$ in the PTR 8000 instrument; (2) uncertainty in the sensitivity at which the $\text{CI} \cdot \text{HFA}$ adducts were detected; (3) potential ionic fragmentation of protonated $\text{CI} \cdot \text{HFA}$ adducts and (4) potential chemical losses of CIs due to reactions with other trace gases.

Besides TME, we also observed formation of $\text{CI} \cdot \text{HFA}$ for a series of precursors including isoprene, pentene and hexene. (Figs. 4.4.4, 4.4.5 and 4.4.6). Proton affinities for

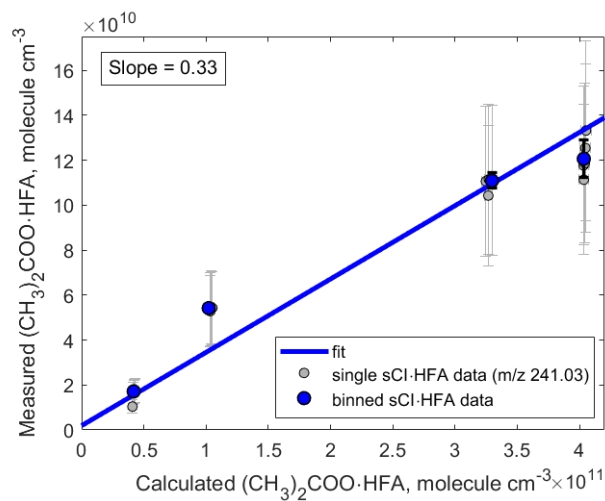


Figure 4.4.3: $(\text{CH}_3)_2\text{COO}\cdot\text{HFA}$ adduct signal, measured as $(\text{CH}_3)_2\text{COO}\cdot\text{HFA}\cdot\text{H}^+$ ion (m/z 241.03), as a function of calculated $(\text{CH}_3)_2\text{COO}\cdot\text{HFA}$ steady-state concentration.

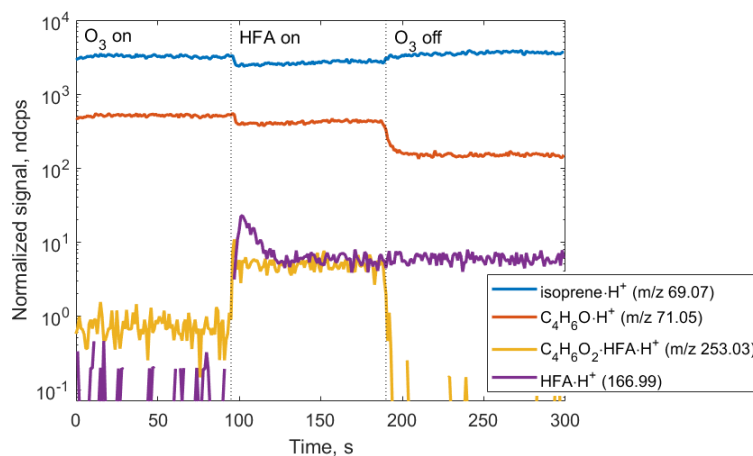


Figure 4.4.4: Ions observed in an isoprene ozonolysis experiment as a function of different reactant conditions. Reactant concentrations are $[\text{isoprene}] = 1.23 \times 10^{13}$; $[\text{O}_3] = 3.20 \times 10^{14}$; $[\text{HFA}] = 5.35 \times 10^{15} \text{ molecules cm}^{-3}$.

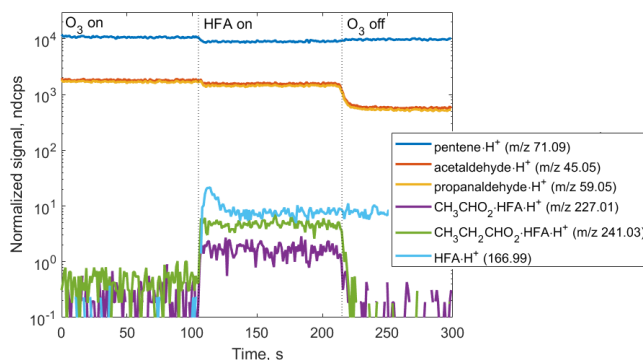


Figure 4.4.5: Ions observed in a pentene ozonolysis experiment as a function of different reactant conditions. Reactant concentrations are $[\text{pentene}] = 4.18 \times 10^{13}$; $[\text{O}_3] = 6.15 \times 10^{13}$; $[\text{HFA}] = 5.35 \times 10^{15}$ molecules cm^{-3} .

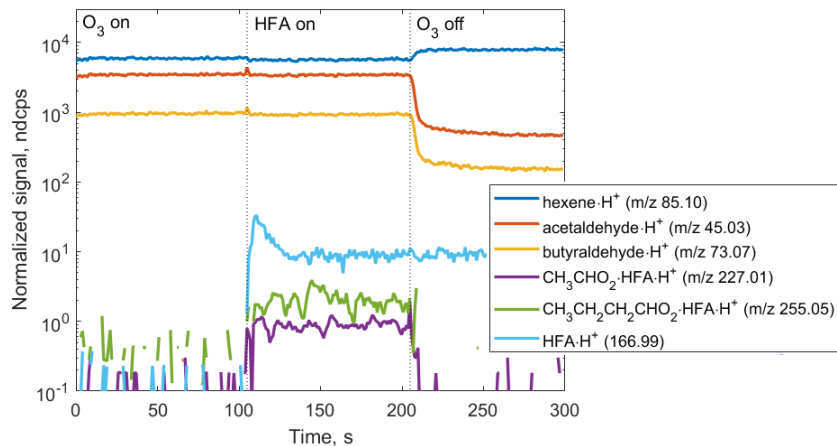


Figure 4.4.6: Ions observed in a hexene ozonolysis experiment as a function of different reactant conditions. Reactant concentrations are $[\text{hexene}] = 2.21 \times 10^{13}$; $[\text{O}_3] = 2.95 \times 10^{14}$; $[\text{HFA}] = 5.35 \times 10^{15}$ molecules cm^{-3} .

different CI·HFA adducts were calculated using DFT methods (Table 4.4.1). A variety of those adducts can be detected using H_3O^+ CIMS since their PAs are significantly higher than that of water which is in agreement with experimental data. $\text{CH}_2\text{OO}\cdot\text{HFA}$ cannot be detected because of its low PA (Table 4.4.1). We also did not observe CI·HFA adducts for larger C_{10} CIs produced via ozonolysis of α -pinene and limonene. This can be explained by lower reactivity of larger CIs with HFA or potential fragmentation of adducts during their ionization inside the PTR-8000 instrument.

Table 4.4.1: Proton affinities of acetone, HFA and secondary ozonides produced in reactions of sCIs with HFA. Species with PAs higher than that of water can be detected in H_3O^+ CIMS.

Species	Proton affinity	
	(kcal/mol)	Reference
$\text{CH}_2\text{OO}\cdot\text{HFA}$	662.9	This work
HFA	670.4	Hunter and Lias ⁹⁹
H_2O	691	Hunter and Lias ⁹⁹
$\text{CH}_3\text{CH}_3\text{CHOO}\cdot\text{HFA}$	720.7	This work
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHOO}\cdot\text{HFA}$	730.8	This work
$(\text{CH}_3)_2\text{COO}\cdot\text{HFA}$	747.2	This work
$(\text{CH}_2=\text{C}(\text{CH}_3))\text{CHOO}\cdot\text{HFA}$	779.6	This work

4.4.2 REACTIVITY OF SPIN TRAPS

Spin traps are shown to be highly reactive towards radicals and efficiently form adducts with them in the aqueous phase. However, their reactivity with atmospheric radicals and stability of formed adducts in the gas phase remain unknown. In order to address these questions, we conducted a set of experiments to estimate the reaction rate between the spin trap TEMPO and hydroxyl radical by measuring its OH reactivity.

OH reactivity of a specific reactant can be calculated as a product of the reactant concentration and its reaction rate with OH¹¹²:

$$k_{\text{OH}} = k_{\text{OH+TEMPO}}[\text{TEMPO}] \quad (4.1)$$

k_{OH} was measured as a function of TEMPO concentration by varying the amount of TEMPO introduced into the setup using an LCU (Fig. 4.4.7). The slope in Fig. 4.4.7 determines the reaction rate coefficient $k_{\text{OH+TEMPO}} = 9 \times 10^{-11} \text{ molecule s}^{-1} \text{ cm}^{-3}$. This k -value is close to the collisional limit of typical radical-molecule reactions in the atmosphere and is one order of magnitude greater than the rate constant for the same reaction in the aqueous phase ($k_{\text{aqueous}} = 7.5 \times 10^{-12} \text{ molecule cm}^{-3} \text{ s}^{-1}$ (ref¹⁰¹)). This experiment demonstrates that TEMPO is highly reactive towards OH in the gas phase, emphasizing the applicability of spin trapping and chemical derivatization techniques for atmospheric measurements. Furthermore, TEMPO + OH reaction leads to the pro-

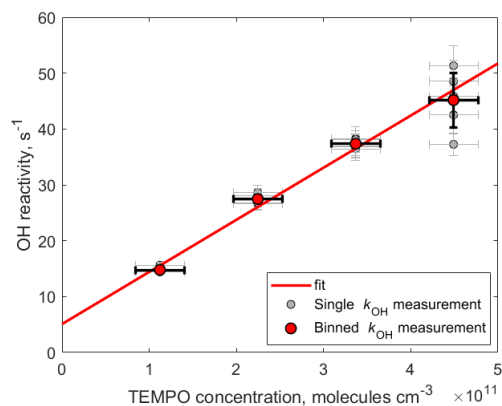


Figure 4.4.7: OH reactivity measured as a function of TEMPO concentration.

duction of TEMPO·OH adducts that can be detected by H_3O^+ CIMS ($C_9H_{18}NO \cdot H^+$, m/z 174.149) and therefore could be used for quantification of hydroxyl radicals in the atmosphere (Fig 4.4.8). Further tests are desired to compare the measurement capability of this method (e.g., sensitivity, wall losses, and potential interferences) with that of a well-established technique, such as LIF.

4.4.3 SIMULTANEOUS DETECTION OF CI AND RO_2 FROM THE OZONOLYSIS OF ALKENES USING SPIN TRAPPING TECHNIQUES

Next, we implemented spin trapping for detection of CIs and other short-lived species formed via the ozonolysis of larger cyclic alkenes, such as α -pinene. Decomposition of the α -pinene primary ozonide yields four different C_{10} CIs, all of which have the same

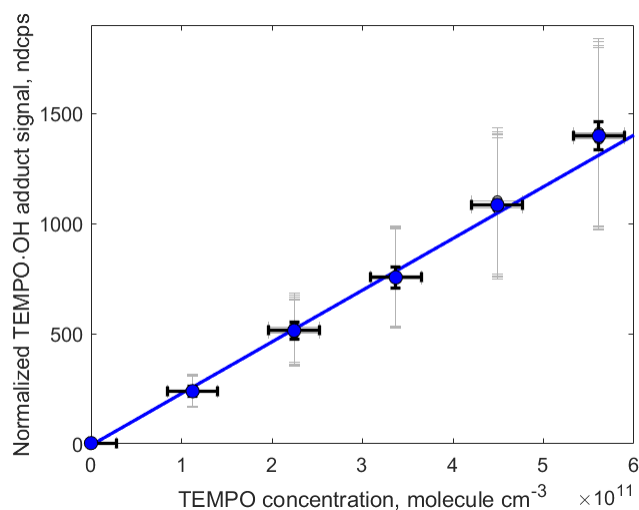


Figure 4.4.8: TEMPO·OH adduct signal ($\text{C}_9\text{H}_{18}\text{NO}\cdot\text{H}^+$, m/z 174.149), as a function of TEMPO concentration measured by H_3O^+ CIMS in the OH reactivity setup.

molecular formula $\text{C}_{10}\text{H}_{16}\text{O}_3$ ¹¹³. These CIs can further undergo a unimolecular reaction and decompose to peroxy radicals $\text{C}_{10}\text{H}_{15}\text{O}_4$ (Fig. 4.4.9).

In order to detect CIs and RO_2 radicals produced from the ozonolysis of α -pinene, we used a measurement method based on the stabilization of these species using the spin trap DMPO followed by detection by the means of NH_4^+ and H_3O^+ CIMS. Signals of $\text{C}_{10}\text{-CI}\cdot\text{DMPO}$ and $\text{C}_{10}\text{-RO}_2\cdot\text{DMPO}$ adducts were observed both in NH_4^+ CIMS ($\text{C}_{16}\text{H}_{27}\text{NO}_4\cdot\text{NH}_4^+$, m/z 315.228 and $\text{C}_{16}\text{H}_{26}\text{NO}_5\cdot\text{NH}_4^+$, m/z 330.216) and H_3O^+ CIMS ($\text{C}_{16}\text{H}_{27}\text{NO}_4\cdot\text{H}^+$, m/z 298.202 and $\text{C}_{16}\text{H}_{26}\text{NO}_5\cdot\text{H}^+$, m/z 313.189) (Figs. 4.4.10, 4.4.11). In addition, we observed formation of $\text{C}_3\text{-CI}\cdot\text{DMPO}$ ($\text{C}_9\text{H}_{17}\text{NO}_3$)

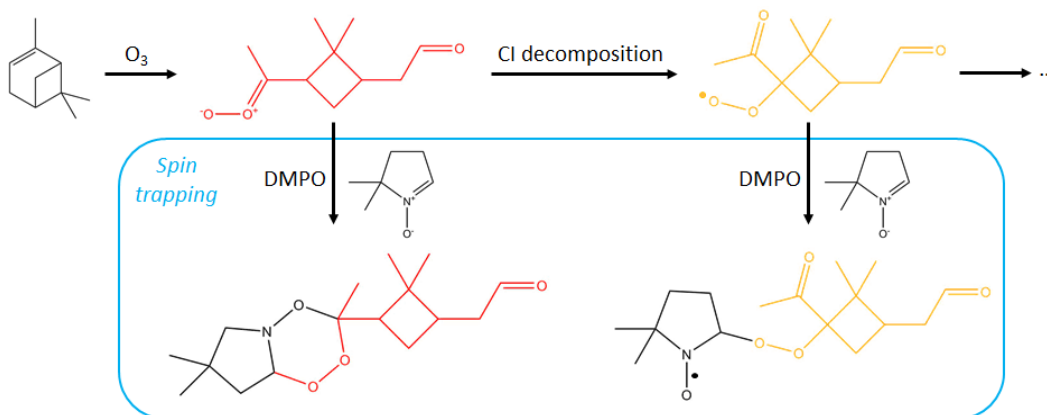


Figure 4.4.9: Mechanism of α -pinene ozonolysis. Criegee intermediates can either react with the spin trap DMPO or decompose to peroxy radicals. Those radicals can in turn react with DMPO. Reactions involving CI are from MCM v3.3.1¹⁰⁵ and Giorio et al.⁹⁴.

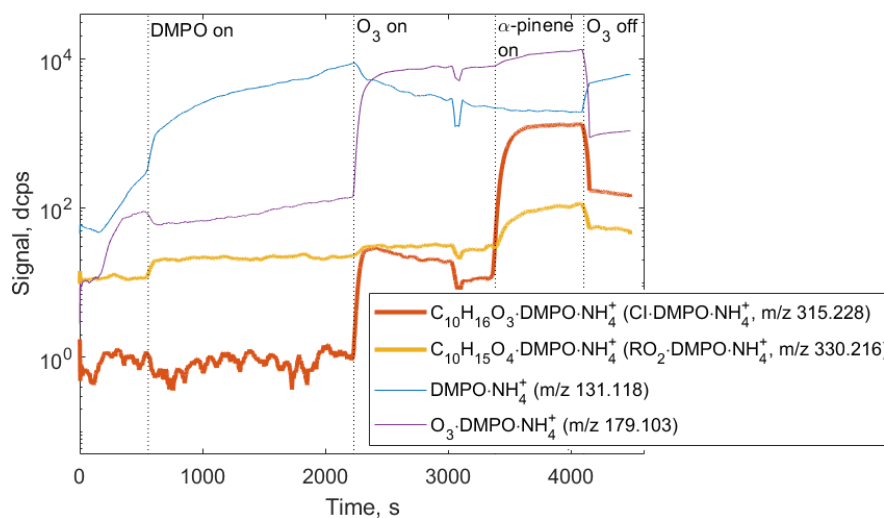


Figure 4.4.10: Ion tracers observed by NH_4^+ CIMS in an α -pinene ozonolysis experiment as a function of different reactant conditions. Reactant concentrations are $[\alpha\text{-pinene}] = 4.92 \times 10^{11}$; $[\text{O}_3] = 1.03 \times 10^{13}$; $[\text{DMPO}] = 1.10 \times 10^{13}$ molecules cm^{-3} .

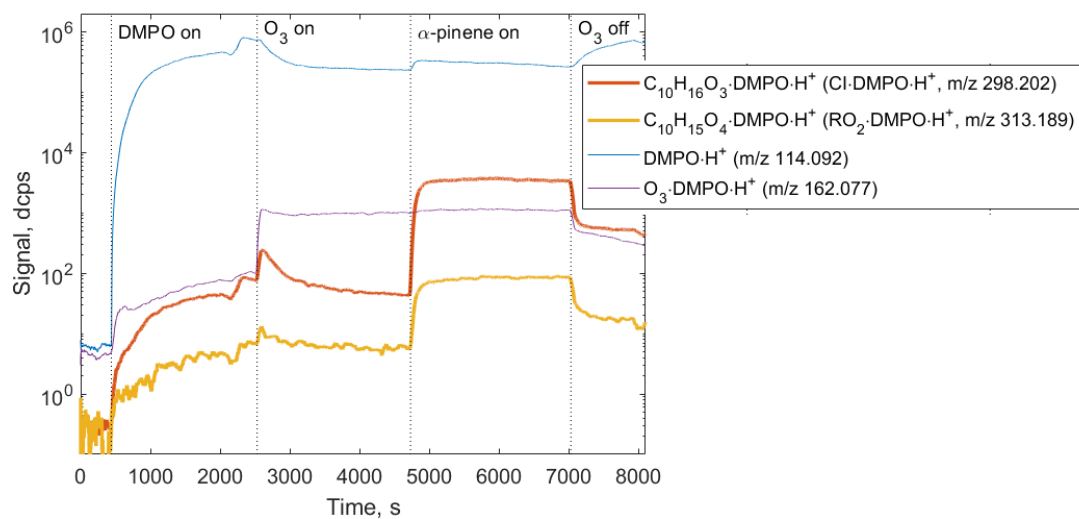


Figure 4.4.11: Ion tracers observed by H_3O^+ CIMS in an α -pinene ozonolysis experiment as a function of different reactant conditions. Reactant concentrations are $[\alpha\text{-pinene}] = 4.92 \times 10^{11}$; $[\text{O}_3] = 1.03 \times 10^{13}$; $[\text{DMPO}] = 1.10 \times 10^{13}$ molecules cm^{-3} .

and $C_3\text{-RO}_2\cdot\text{DMPO}$ ($C_9H_{16}NO_4$) adducts formed via the ozonolysis of TME (Figs 4.4.12, 4.4.13).

One of the benefits of NH_4^+ CIMS is the possibility to quantify compounds for which authentic standards are not available using a voltage scanning procedure based on collision-induced dissociation²⁷. DMPO as well as its adducts with CIs and RO_2 were detected at high sensitivities: 14,000 duty-cycle-corrected ion counts per second per part per billion by volume (dcps ppbv⁻¹) for CI·DMPO and 35,000 dcps ppbv⁻¹ for $RO_2\cdot\text{DMPO}$ (Table 4.4.2). Sensitivities were experimentally determined in each ozonolysis experiment and depend on operational conditions of the NH_4^+ CIMS instrument. Detection limits for CI·DMPO and $RO_2\cdot\text{DMPO}$ adducts were 5.7×10^6 and 5.8×10^6 molecule cm⁻³, respectively. These limits of detection are calculated for 1 s integration time as 3 standard deviations of measured background divided by derived sensitivity. The detection limits and high sensitivities that were measured for CIs and RO_2 species in the laboratory under close to atmospheric conditions show promise that this technique would also work when sampling ambient air.

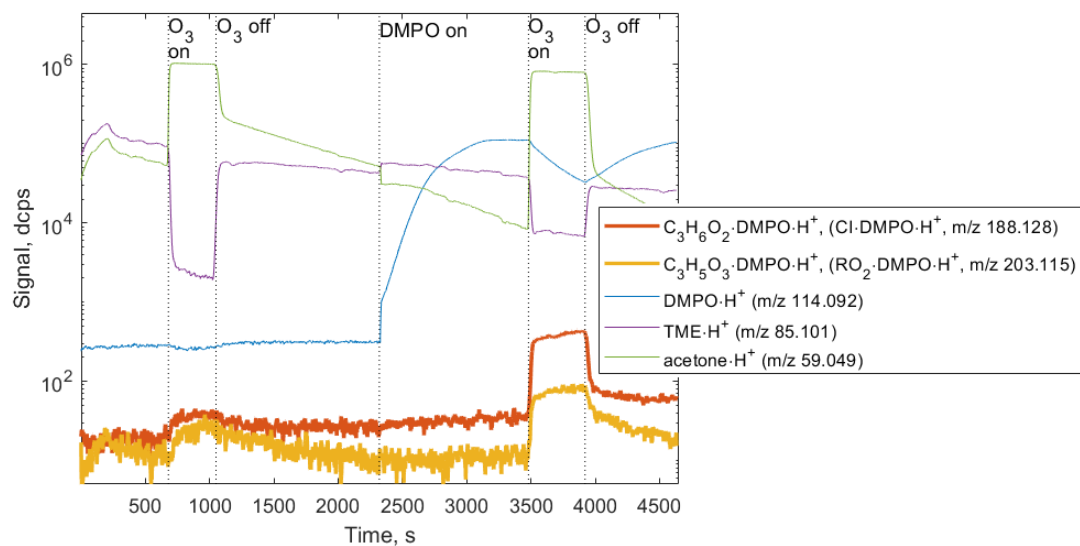


Figure 4.4.12: Ion tracers observed by H_3O^+ CIMS in a TME ozonolysis experiment as a function of different reactant conditions. Reactant concentrations are $[\text{TME}] = 4.92 \times 10^{11}$; $[\text{O}_3] = 1.89 \times 10^{13}$; $[\text{DMPO}] = 1.27 \times 10^{12}$ molecules cm^{-3} .

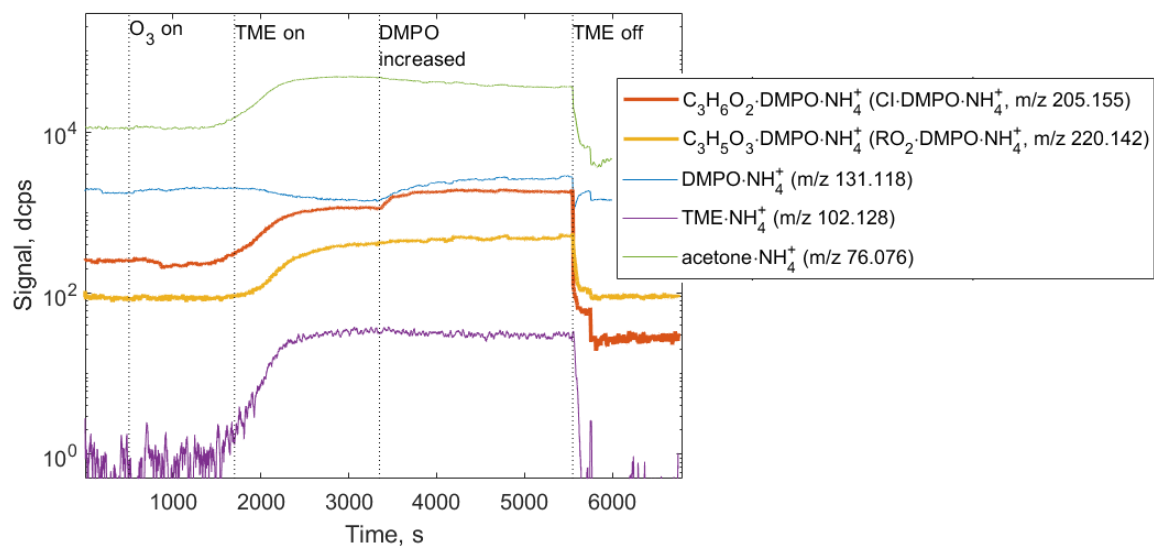


Figure 4.4.13: Ion tracers observed by NH_4^+ CIMS in a TME ozonolysis experiment as a function of different reactant conditions. Reactant concentrations are $[\text{TME}] = 3.69 \times 10^{11}$; $[\text{O}_3] = 7.87 \times 10^{12}$; $[\text{DMPO}] = 2.01 \times 10^{12}$ molecules cm^{-3} .

Table 4.4.2: Estimated NH_4^+ CIMS sensitivity factors for DMPO and its adducts with reactive intermediates detected in α -pinene ozonolysis experiments. The maximum sensitivity of NH_4^+ CIMS was experimentally determined in each experiment and depends on operational conditions. For typical operational conditions the maximum sensitivity is 70,000 dcps/ppb.

Species	Ion formula	m/z	Estimated
			sensitivity factor
DMPO	$\text{C}_6\text{H}_{11}\text{NONH}_4^+$	131.118	0.92
$\text{C}_{10}\text{-Cl}\cdot\text{DMPO}$	$\text{C}_{16}\text{H}_{27}\text{NO}_4\text{NH}_4^+$	315.228	0.20
$\text{C}_{10}\text{-RO}_2\cdot\text{DMPO}$	$\text{C}_{16}\text{H}_{26}\text{NO}_5\text{NH}_4^+$	330.216	0.50

4.5 CONCLUSIONS

In summary, we experimentally demonstrated the direct probing of short-lived highly reactive atmospheric species, such as Criegee intermediates and organic peroxy radicals, formed via ozonolysis of alkenes. The analysis was carried out using spin trapping and chemical derivatization techniques, while the detection of formed adducts was performed by the means of H_3O^+ and NH_4^+ CIMS. Detected adducts show little to no fragmentation, have unique mass defects, and can therefore be clearly separated from other observed compounds in the mass spectrum. Implementation of chemical derivatization agents with lower proton affinity allows for full scavenging of Criegee intermediates without depleting CIMS reagent ions. We show that spin traps can be also used

to effectively scavenge atmospheric radicals and reactive intermediates by demonstrating their high reactivity with radicals in the gas phase using the TEMPO+OH reaction as an example. Using the spin trap DMPO, CIs and RO₂ species can be simultaneously detected while quantification of observed adducts can be done without their direct calibration. Estimated detection limits of spin trap adducts of 5.7×10^6 molecules cm⁻³ for CIs and 5.8×10^6 molecules cm⁻³ for RO₂ for 1 s integration time are sufficient for integrated production measurements of studied species under atmospheric conditions. Since spin traps, such as DMPO, are reactive towards a plethora of atmospheric radicals and reactive intermediates, including OH, HO₂, RO₂, and CIs, implementation of such spin traps results in the effective suppression of the radical secondary chemistry and, thus, elimination of potential chemical interferences. The direct detection method of CIs and RO₂ provides a means to study the atmospheric chemistry of these compounds. For the future application of the method in field and laboratory experiments, various modifications of the experimental setup can be implemented to improve its measurement capability. We plan to synthesize and test new chemical derivatization agents optimized for the gas-phase measurements with respect to their vapor pressure, selective reactivity and by labelling with atomic isotopes to simplify mass spectrometric detection. With labeled spin traps, the identification of reactive intermediates may be greatly simplified and detection limits may be further improved, as the spin trap can provide a unique signature in the complex mass-spectrum and move the observed m/z to a region with very low background.

5

Conclusions

5.1 SUMMARY OF CURRENT WORK

RADICALS AND REACTIVE INTERMEDIATES determine the oxidative capacity of the atmosphere, which can also be seen as the atmosphere's self-cleaning mechanism. Oxidation chemistry governed by these species results in formation of secondary pollutants,

such as ozone and particulate matter, which have adverse effects on human health and climate. Since the molecular structure strongly affects the reactivity of these species, a key challenge in atmospheric science is to determine the fate of individual radicals and reactive intermediates. Detailed and reliable measurements of these short-lived components will assist climate and air quality modelers, and eventually policymakers, in evaluating steps required to further improve air quality and slow down climate change.

In this dissertation, I described the development and application of mass spectrometric tools to measure atmospheric radicals and reactive intermediates, as well as closed-shell oxidized volatile organic compounds. A new CIMS instrument for measuring a plethora of organic species in both the gas and particle phases was developed. This instrument can be operated in one of two ionization modes: using either ammonium ion ligand-switching reactions (as NH_4^+ CIMS) or proton transfer reactions from hydronium ions (as PTR-MS or H_3O^+ CIMS). The sensitivity of NH_4^+ CIMS to a wide range of oxidized volatile organic compounds can be effectively constrained using a mass spectrometric voltage scanning procedure based on collision-induced dissociation. The instrument was first used to quantify the composition of secondary organic aerosols in a series of laboratory experiments.

NH_4^+ CIMS along with other CIMS techniques were then applied to examine oxidation products formed via photooxidation of aromatic compounds, i.e., toluene and 1,2,4-trimethylbenzene. We show that even under urban conditions ($\text{NO}_x \sim 10$ ppbv) bicyclic peroxy radicals, produced via OH-oxidation of aromatic compounds, can re-

act with HO_2 or undergo unimolecular reactions resulting in the formation of highly oxygenated organic molecules. HOMs as well as other closed-shell products have significantly lower volatilities than the parent aromatic compound and can contribute to secondary organic aerosol formation. It was further observed that other oxidation pathways such as phenol and benzaldehyde can lead to the formation of oxidized compounds with a high O:C ratio.

Finally, CIMS was combined with spin trapping and chemical derivatization techniques to measure atmospheric radicals and reactive intermediates, such as organic peroxy radicals and Criegee intermediates in a series of laboratory experiments. Using chemical derivatization agents with low proton affinity, it is possible to scavenge all CIs formed via ozonolysis of several alkenes and therefore prevent CI and RO_2 secondary chemistry, which helps to eliminate chemical interferences. It was also demonstrated that spin trap adducts with CIs and RO_2 can be simultaneously detected and quantified. Measurements were complimented with numeric modeling to show that this analytic method can be used for quantification of radicals and reactive intermediates under close to atmospheric conditions.

5.2 FUTURE DIRECTIONS

5.2.1 FURTHER DEVELOPMENT OF SWITCHABLE REAGENT ION CIMS INSTRUMENTATION

One of the advantages of the CIMS instrument described in Chapter 2 is the possibility to switch between two ionization modes within 2 minutes. In fact, the instrument has three ionization sources, hence yet another ionization scheme could be implemented, which would further improve its measurement capability. Exothermic ligand switching reactions with alkali ions serving as the core reagent ion could be used to ionize analyte molecules:



where $X^+ \cdot H_2O$ is the reagent ion species with X^+ being the core reagent ion (e.g., Li^+ , Na^+ or K^+). Reaction R11 is exothermic if the binding energy of the $X^+ \cdot VOC$ cluster is higher than that of the reagent ion $X^+ \cdot H_2O$. Selectivity and ionization efficiency of this technique varies among different alkali ions. For instance, $Li^+ \cdot H_2O$ ions will ionize the broadest range of species as the binding energy of these reagent ions is the smallest among all alkali ions. In addition, it will prevent backward reactions from $Li^+ \cdot VOC$ to $Li^+ \cdot H_2O$ occurring when $Li^+ \cdot VOC$ collides with water and therefore will minimize

humidity dependence of the instrument sensitivity. On the other hand, $\text{Li}^+\cdot\text{VOC}$ ions have higher dissociation energy which may result in formation of ionic fragments other than Li^+ and VOC, which will complicate the interpretation of mass-spectra. Hence, the choice of the optimal alkali ion would be determined through future laboratory experiments.

5.2.2 MEASURING AMBIENT PEROXY RADICALS AND CRIEGEE INTERMEDIATES USING CIMS AND SPIN TRAPPING

The proof-of-concept experiments to measure integrated production of peroxy radicals and Criegee intermediates in the laboratory were described in Chapter 4. The overall sensitivity and detection limits presented here should be sufficient for ambient measurements of these short-lived species. However, further method optimization may be beneficial in order to make it more field-deployable. For instance, it is possible to synthesize and test new spin traps optimized for the gas-phase measurements with respect to their vapor pressure, reactivity, and by labeling with atoms that improve mass spectrometric detection. With isotopically-labelled spin traps, the identification of radicals and reactive intermediates can be facilitated, as the spin trap can provide a special signature in mass-spectrum. In addition, the current system can be upgraded to have better control of radical production, especially to suppress secondary reactions before addition of the spin trap.

The direct detection method presented here should also allow study of the reactiv-

ity of a wide range of atmospheric radicals and reactive intermediates. As it was shown in Chapter 3, autooxidation reactions make up an important class of reactions for RO_2 species, as they result in formation of more oxidized radicals and close-shell molecules, which can contribute significantly to formation of secondary particulate matter. To date, our knowledge of these reactions, including their kinetic parameters, is limited. Using CIMS combined with spin trapping, it will be possible to quantify the degree of oxidation of the radicals produced in autooxidation reactions and therefore deduce critical information on the kinetics of these reactions. These measurements can improve our understanding of oxidative capacity of the atmosphere and SOA formation.

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